PROPERTIES OF SOME ETHYLENEDIAMINE COBALT COMPLEXES COORDINATED WITH DICARBOXYLIC ACIDS AND RELATED COMPOUNDS

A Thesis submitted to the University of London

for the degree of Master of Philosophy

by

Irene Mary Keefe

October 1970

Bedford College

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I am also grateful to the D.S.I.R. for the award of a grant for postgraduate research.

A B S T R A C T

Coordination compounds of the type $[Coen_2AA]Y$ were prepared by known methods where AA = carbonate, Y = chloride, bromide, iodide, perchlorate, nitrate, thiocyanate, dithionate and sulphate; AA = oxalate, Y = bromide; AA = malonate, Y = bromide and malonate; AA = succinate, Y = bromide and perchlorate.

The infrared spectra of these complexes were measured and also of complexes of the type trans-$[Coen_2Cl_2]AA$ where AA = oxalate, malonate and succinate. The spectra of the cis-complexes were found to fall into two classes and possible reasons for this are discussed.

The visible and ultra-violet spectra of the complexes were measured and also the change in these spectra when alkali and acid were added to solutions of the complexes.

The base hydrolysis of the complex $[Coen_2CO_2CH_2CO_2]Br$ was studied at hydroxide concentrations of about 0.1M and 1M and at temperatures in the range 38°- 55° and was found to follow second-order kinetics with an activation energy of 29,000 cals $mole^{-1}$.

The malonato complex was optically resolved giving the dextro-rotatory iodide and the optical rotatory dispersion of this optical isomer was measured. This isomer was found to be stable in neutral solution but lost its optical activity in basic solution at the same rate as the base hydrolysis. The mechanism of the base hydrolysis and loss of optical activity is thought to be similar to that of the oxalato complex as suggested by Taube.

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GENERAL INTRODUCTION

The object of this work was to study bis(ethylenediamine) complexes of cobalt(III) containing the dicarboxylate groups, carbonate, oxalate, malonate and succinate as bidentate ligands.

The cobalt is six coordinated in all the complexes. The two ethylenediamine groups provide four coordinating nitrogen atoms and the carboxylate groups two coordinating oxygen atoms. Since the carbonato complex is used in the preparation of the other compounds, the ethylenediamine groups must be arranged in a cis formation relative to the cobalt ion and acid groups.

It is known[18] that the cobalt-ethylenediamine ring is in the gauche conformation and this can be achieved by the carbon-carbon bond bending in two different ways[25] designated k and k'. Two bidentate ethylenediamine molecules bound to the cobalt ion can either have the same conformation, kk or k'k', or different conformations kk'.

Molecular models of the complexes show that, with the exception of the oxalato complex, the cobalt-carboxylate rings are strained or distorted. In the case of the succinate group, this is a seven membered ring and as such would be considered to be so unstable that it might not exist in this form but rather as a unidentate ligand or as a polymer.

Since these complexes contain three bidentate ligands there is the possibility of optical isomerism, since the molecules contain no plane or centre of symmetry but only a three-fold axis of symmetry.

The methods of preparation of the complexes were obtained from the work of Werner and Price, and of Duff and Brazier.

Certain physical and chemical methods were used for studying structural and chemical properties of the complexes:-

1. Infrared Absorption Spectra. The infrared absorption spectra of the complexes in the solid state were measured to evaluate:-

(1) qualitatively the degree of covalency in the cobalt-oxygen bond and relate this to the strain and distortion in the ring,

(2) the effect of anions on the infrared spectra.

2. Visible and Ultra-violet Absorption Spectra. The visible and ultra-violet absorption spectra of the complexes were measured. The position and intensity of the ultra-violet absorption bands due to the carboxylate group are affected by strain and distortion in the ring. A coordination compound containing ligands arranged in a cis formation will give rise to a different d-d transition than one containing ligands arranged in a trans formation. This could assist in determining the arrangement of the succinate ligand.

3. Base Hydrolysis. In the present work reactions of the malonato complex were studied and compared with the results of the known work on the oxalato and malonato complexes and attempts were made to determine the mechanisms of the reactions of the malonato complex.

4. Optical Activity. The malonato complex was resolved and the optical rotatory dispersion curve of one of the optical isomers was measured so as to determine the absolute configuration of this isomer.

The rate of loss of optical activity of the resolved malonato complex in alkaline solution was measured and compared with the rate of its decomposition.[100] It is known that the rate of loss of optical activity and the rate of decomposition of the carbonato complex are different and that the reactions are quite dissimilar mechanistically.[85] In the case of the oxalato complex it has been found that the loss of optical activity, decomposition and oxalate exchange reactions in the presence of aqueous alkali all have identical second-order kinetics and therefore proceed by the same mechanism. By measuring the rate of loss of optical activity of the malonato isomer it can be seen whether this complex is similar in its reactions to the carbonato or oxalato complex which would help to determine the structure of the malonato complex and the mechanisms of its reactions.

INFRARED ABSORPTION SPECTRA

INTRODUCTION

Molecular Symmetry and the Symmetry Groups

It is known that polyatomic molecules have 3N-6 normal vibrations if they are non-linear and 3N-5 if they are linear. Now for any given molecule only those vibrations which are permitted by the selection rule for that molecule appear in the infrared and Raman spectra. This selection rule is governed by the symmetry of the molecule so obviously molecular symmetry is an important part of any infrared spectra studies.

Now the symmetry of a molecule is determined by the spatial geometrical arrangement of the nuclei constituting the molecule. The symmetry properties of a molecule are best described in terms of the symmetry operations which can be performed on the molecule. A symmetry operation is an operation which, when applied to an object, results in a new object which is indistinguishable from the original one and hence superimposable on it. A symmetry operation usually consists of rotation about an axis or plane, or reflection in a mirror, or a combination of both. Each symmetry operation implies the existence of an element of symmetry so that a symmetry element is defined as a geometrical entity such as a line, a plane, or a point, with respect to which one or more symmetry operations may be carried out. Thus the symmetry properties of an object may be indicated by specifying the symmetry elements which the object possesses. In fact there are five basic symmetry elements corresponding to symmetry operations which will now be briefly discussed.

1. A p-fold axis of symmetry, C_p.

If rotation of a molecule about an axis through an angle of $360^\circ/p$ produces a configuration indistinguishable from the original one, the axis is called a p-fold axis of symmetry, Cp, where C stands for cyclic. The case where p = 1 is trivial since this applies to any molecule.

2. A centre of symmetry, i.

If reflection at the centre, i.e. inversion, produces a configuration indistinguishable from the original one, the centre is called a centre of symmetry, i, where 'i' stands for inversion. This means that if a straight line is drawn from each atom through the centre of the molecule it always meets an equal atom at the same distance from the centre on the opposite side.

3. A plane of symmetry.

If reflection of a molecule with respect to some plane produces a configuration indistinguishable from the original one, the plane is called a plane of symmetry.

4. A p-fold rotation-reflection axis, Sp.

If rotation by $360^\circ/p$ about the axis followed by reflection at a plane perpendicular to the axis produces configuration, indistinguishable from the original one, the axis is called a p-fold rotation-reflection axis.

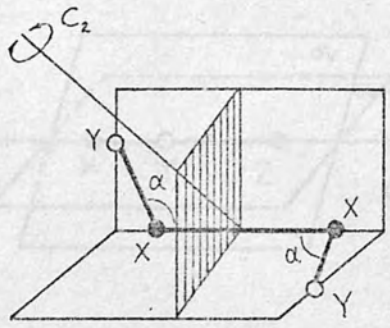
5. Identity, I.

This is a symmetry element possessed by every molecule no matter how unsymmetrical it is, the corresponding operation being to leave the molecule unchanged. This symmetry element is introduced for mathematical reasons.

A molecule may have more than one of these symmetry elements. Combination of more and more of these elements produces systems of higher and higher symmetry. A possible combination of symmetry operations whose axes intersect at a point is called a point group. In fact only a limited number of point groups can exist. The diagrams on pages 12 and 13 illustrate the symmetry elements of the point groups which appear in this section.

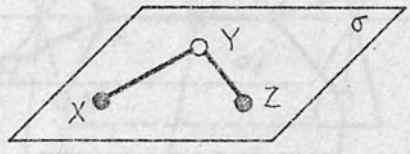
Symmetry Elements of Point Groups referred to in this study.

C_2



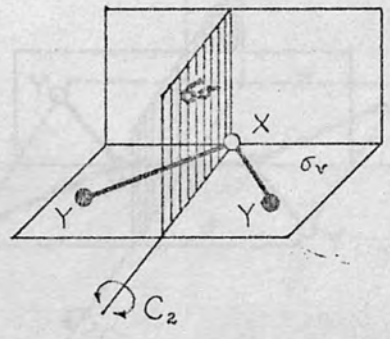
Ethylenediamine in gauche configuration.

C_s
(a plane of symmetry)



Unidentate carbonate ligand

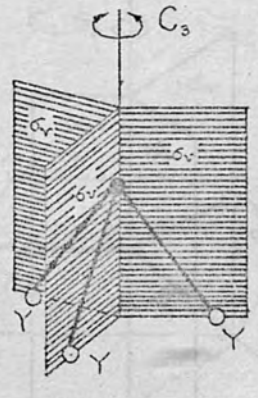
C_{2v}
$(C_2, 2\sigma v)$



Bidentate carbonate and oxalate ligands.

C_{3v}

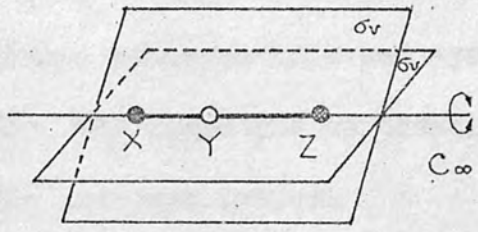
$(C_3, 3\sigma v)$



Ammonia

$C_{\infty v}$

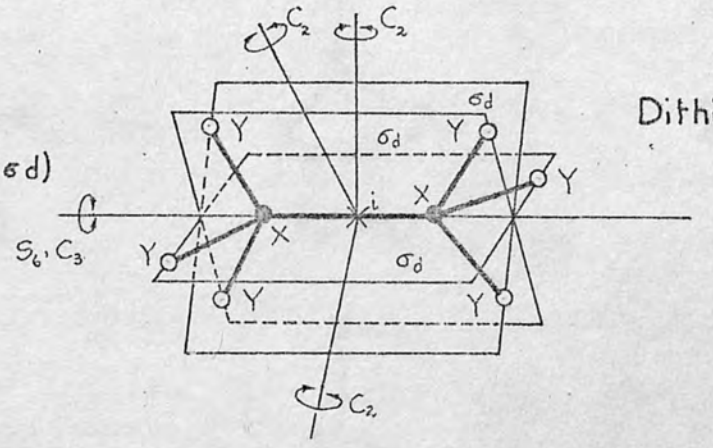
$(C_\infty \equiv C_p, \infty \sigma_v)$



Thiocyanate Ion

D_{3d}

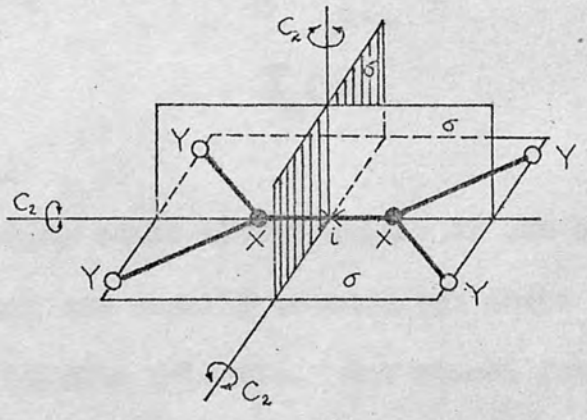
$(S_6 \approx C_3, 3C_2, i, 3\sigma_d)$



Dithionate Ion

$D_{2h} \equiv V_h$

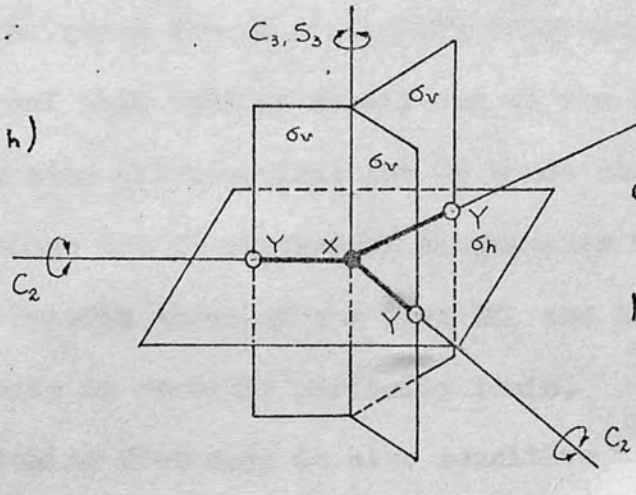
$(3C_2, 3\sigma i)$



Oxalate Ion

D_3h

$(C_3 \approx S_3, 3C_2, 3\sigma_v, \sigma_h)$

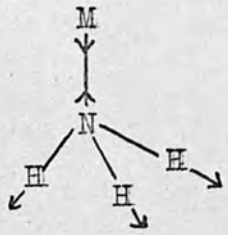


Carbonate Ion

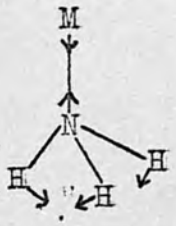
Nitrate Ion

Ammino Complexes

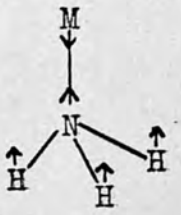
An ammonia molecule coordinated to a metal atom or ion forms a tetrahedral grouping, M-NH_3, which belongs to the point group C_{3v}. Thus there are six vibrations expected:- antisymmetric and symmetric NH stretching, NH_3 degenerate deformation, NH_3 symmetric deformation, NH_3 rocking and M-N stretching and all are infrared active.



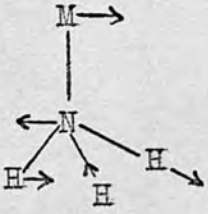
$\nu_s(NH_3)$



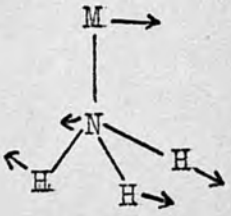
$\delta_s(NH_3)$



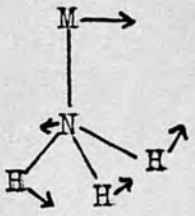
$\nu_s(M\text{-}N)$



$\nu_a(NH_3)$



$\delta_d(NH_3)$



$\rho_r(NH_3)$

NH stretching bands

The NH stretching bands always appear as one or more bands between 3400-3000 $cm.^{-1}$ They are usually broader and their frequencies lower than those of the free ammonia molecule. One reason for this is the effect of coordination which lowers the NH stretching frequency by 100-150 $cm.^{-1}$ [1, 2, 3, 4] It has been proposed that this is mainly due to the drainage of electrons from the nitrogen atom which weakens the NH bonds and hence decreases the NH bond order. Since the NH stretching frequencies of the ammine complexes are intermediate between those of the free NH_3 and NH_4^+ the M-N bond of the ammine complexes is probably partially ionic.

The NH stretching frequency is also sensitive to changes in the anion.

There is ample evidence of the presence of hydrogen bonding between the N-H of ammine complex ions and anions such as halogens.[5] Here the hydrogen bonding[3] weakens the N-H bond and shifts the band to a lower frequency.

In addition Svatos et al.[4] also cite hydration and configuration as being factors which affect the NH stretching frequency. In the case of hydration it was found that if the water of hydration absorbs in the 3500 $cm.^{-1}$ region then the NH stretching frequency is hardly affected; if the water absorbs at appreciably lower frequencies the NH vibration may be lowered considerably. The effect of configuration was that in some complexes e.g. a trans square-planar configuration, a coupling of the two trans NH vibrations would yield symmetric and antisymmetric vibrations, only the latter being infrared active. But in the cases of cis square-planar, tetrahedral and octahedral complexes both the symmetric and antisymmetric NH vibrations result in a change in dipole moment and so are infrared active.

NH_3 deformation and rocking bands

Mizushima et al.[6] assigned these bands by observing the shifts resulting on complete deuteration of $[Co(NH_3)_6]^{3+}$ to $[Co(ND_3)_6]^{3+}$. These conclusions have been further substantiated by others.[7, 8, 9] The asymmetric NH_3 deformation occurs at about 1600 $cm.^{-1}$ (usually one band, always quite broad), the symmetric NH_3 deformation occurs at about 1300 $cm.^{-1}$ (usually one band with shoulders, sharp) and the rocking band occurs at about 800-850 $cm.^{-1}$ (one band generally, fairly broad).

The effects of coordination and hydrogen bonding shift the three bending bands to higher frequencies.[10] Svatos et al. have found that the NH_3 rocking frequency is most sensitive and the degenerate deformation

frequency least sensitive to the metal. These results can be reasonably explained by the conclusions drawn from normal coordinate analysis.[6,11]

Recently Wilmshurst[12] has found a linear relation between the electronegativity of the metal and the square of either the symmetric deformation or the rocking frequency.

M-N stretching bands.

The M-N stretching frequency is of particular interest since it provides direct information about the coordinate bond. Because of the relatively heavy mass of the metal and the low bond order of the coordinate bond, the M-N stretching vibration is expected to appear in the lower frequency region. There has been some controversy as to the position of this band. Powell and Sheppard[9] attributed a very weak band at about 500 $cm.^{-1}$ in the $[Co(NH_3)_6]^{3+}$ ion to ν(Co-N). But Barrow et al.[7] missed this weak absorption and attributed a strong band at 330 $cm.^{-1}$ in $[Co(NH_3)_6]^{3+}$ to ν(Co-N). This assignment was followed by Bertin et al.[13] who also studied Co(II) compounds and found absorption near 320 $cm.^{-1}$ which they also assigned to ν(Co-N).

Shimanouchi and Nakagawa[14] seem to be the first to have found both bands. The weak band at about 500 $cm.^{-1}$ has been assigned to ν(Co-N) and the strong band at about 320 $cm.^{-1}$ to δ(N-Co-N) for a hexamine. This is in agreement with the work of Watt and Klett[15] who showed that whereas $[Co(NH_3)_6]$ chloride and bromide are monoclinic the iodide is cubic, the complex ion having O_h site-symmetry. The three weak bands observed near 500 $cm.^{-1}$ for the chloride and bromide are therefore components of ν_3; in the iodide a single band appears at about 464 $cm.^{-1}$ in agreement with the high site-symmetry.

These assignments have been further verified by the very complete

work done by Sacconi [16] et al and Griffith.[17]

However, for the hexammines of divalent metals it has been found that ν(M-N) is near 300 and δ(N-M-N) is near 200 cm^{-1} as found by Bertin [13] et al.

Effect of Metal-Ligand Bond Character on Vibrational Frequencies.

Several attempts have been made to correlate the variations in the frequencies of the stretching, bending and rocking modes of ammonia ligands with the strength of the metal-nitrogen bonds. Fujita, Nakamoto and Kobay-[3]-ashi have studied the chloride, bromide, iodide, nitrate and perchlorate salts of $[Co(NH_3)_6]^{3+}$ and observed variations in the absorption bands which can be correlated with the varying strength of hydrogen bonds to the anions. They found that the NH stretching frequencies increased and the rocking vibrations decreased in the above order. They also examined the hexammine perchlorates of Ni(II), Cr(III) and Co(III) in which extraneous variations due to varying strength of hydrogen bonding in the different lattices were minimised. They found that the stretching frequ-encies decreased, the symmetric deformation frequencies increased and the rocking frequencies markedly increased in the above order.

Svatos [10] et al have examined a wider variety of ammine complexes and found that the rocking frequency decreased in the order Pt(IV), Pt(II), Co(III), Pd(II), Cr(III), Cu(II), Ni(II), Co(II). These authors also showed from simple force field calculations that the rocking frequency is expected to depend strongly on metal-nitrogen bond strength, the symmetric deformation less so and the asymmetric deformation rather little and that the variations with increase of metal-nitrogen bond strength should be in the directions actually found.

Ethylendiamine Complexes

Ethylenediamine or 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$, may exist in the cis, trans or gauche conformation, depending on the angle of internal rotation. These forms are shown on page 20. The trans form is not suitable for coordination because the two nitrogen atoms are too far apart. The cis form will coordinate to give a planar ring and the gauche form gives a puckered ring.

Quagliano and Mizushima[18] indicated that the cobalt-ethylenediamine ring is in the gauche conformation. Their spectra for complexes containing ethylenediamine as a chelating group were very similar to those for compounds having a known gauche conformation. The X-ray crystallographic data on the compounds trans-$[Coen_2Cl_2]Cl,HCl,2H_2O$[19] and $[Coen_3]Cl_3$[20] support this conclusion. Since the infrared spectra of all the cobalt-ethylenediamine complexes measured show the same general band type, it seems reasonable to assume that all the chelate rings have the same gauche conformation.

Sheppard and Powell[21] compared the infrared spectra of a number of ethylenediamine complexes and found them to be of two types:- A type spectra which are found in octahedral Co(III), Cr(III) and Rh(III) and square-planar Pt(II) and Pd(II) complexes; and B type spectra which are seen in octahedral Ni(II) and square-planar Cu(II) complexes. These authors concluded that this difference can be attributed only to a difference of conformation of the chelate ring. Since the Co(III) complex is definitely gauche, the A type spectrum must result from the gauche conformation. Although Powell and Sheppard attributed the B type spectrum to the cis conformation, the chelate rings in the $[Cuen_2]^{2+}$[22] and $[Nien_3]^{2+}$[23] ions have been proved by X-ray analysis to be of the gauche type.

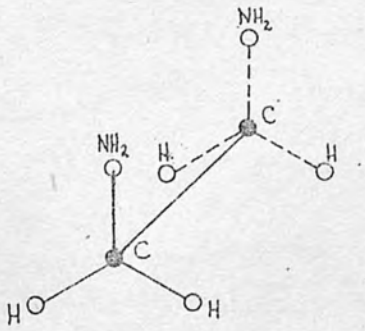
These authors have therefore abandoned their hypothesis and subsequently[24] suggested that the two different types of spectra are due in part to hydrogen bonding between NH_2 groups and the anion. In order to test this hypothesis they minimised the hydrogen bonding effects by choosing the large tetrachloroplatinate(II) ion. The infrared spectra of metal-ethylenediamine-tetrachloroplatinate(II) salts were measured in the solid state and there was seen to be a good correlation between features of the spectra and the general stability of the complexes. A series of bands, caused principally by NH_2 rocking vibrations, vary in position from about 800 $cm.^{-1}$ in the spectra of the most stable complexes (type A) to near 600 $cm.^{-1}$ in the spectrum of the least stable complex (type B). Another sequence of bands, due to the metal-nitrogen bond stretching, also show regular frequency changes from about 585 to 478 $cm.^{-1}$ The order of decreasing stability and decreasing frequency in both sets of bands was found to be:- Pt(II), Rh(II), Co(III), Pd(II), Cr(III), Hg(II), Cu(II), Ni(II), Co(II), Zn(II), Cd(II). The values for the $[Coen_3]^{3+}$ ion being:-

Log $k_{average}$	Log K_1	Spectrum type	NH_2 rock		M-N
16.3	18.7	A	782	770	585

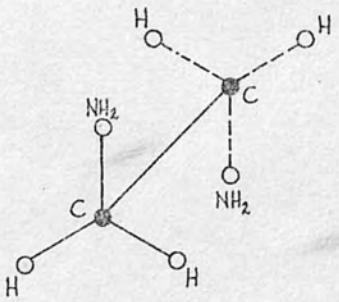
Log $k_{average}$ = log. of the overall stability constant ($\log\beta_n$) divided by the number (n) of groups bound to the metal ion. K_1 = the first successive stability constant.

It has been pointed out by Bailar and Corey[25] that an isolated metal-ethylenediamine ring in the <u>gauche</u> form can adopt either of two conformations (k and k') which are energetically and geometrically equivalent, but are enantiomeric (diagram on page). A compound having more than one ethylenediamine ring may then have rings with either the k or k' conformation.

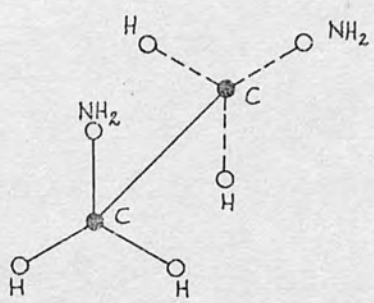
Conformations of the ethylenediamine molecule



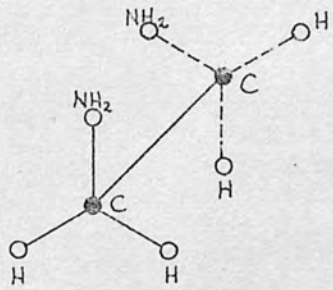
Cis C_{2v}



Trans C_{2h}

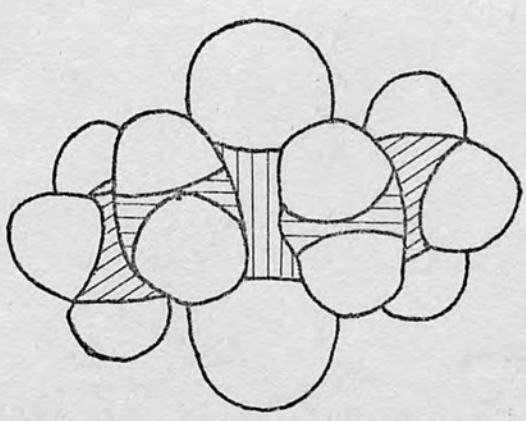


Gauche 1.

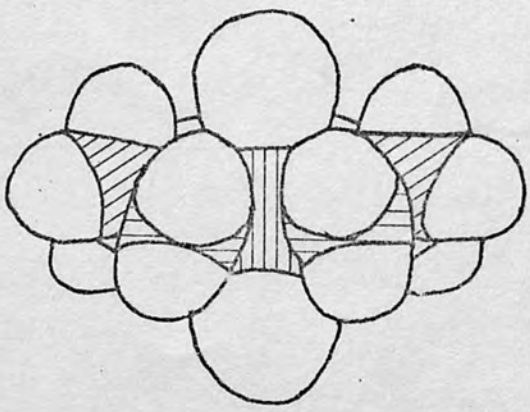


Gauche 2.

C_2.



kk form



kk' form

Relation of two coordinated bidentate ethylenediamine molecules in the gauche form

Although the energy of conversion is expected to be small, the compound containing different ring forms will differ slightly in thermodynamic stability. By considering the non-bonded interactions of donor nitrogen groups, Bailar and Corey estimated that for the trans-bis(ethylenediamine) arrangement, the kk form is more stable. X-ray data, however indicates that the kk' form exists in the solid state[5]. Now in the kk' form the hydrogen atoms are in a more favourable position for hydrogen bonding with the anion and Baldwin[26] has suggested that those compounds which exist in the kk' form are stabilised by hydrogen bonding.

Hence compounds that show the greatest amount of hydrogen bonding as assessed from the NH_2 frequencies also give the simplest spectra. But compounds that are not fixed by specific interaction should contain both the kk and kk' form thus producing a greater complexity of band structure because of the lower symmetry of the kk form.

Experiments have been carried out on many trans-dihalobis(diamine) Co(III) cations to ascertain the structure of the chelate rings[17]. The results are summarised in the following table:

Structural Data for Compounds of the Type trans-$[M(AA)_2X_2](H_5O_2)Cl_2$

Compound	Conformation of diamine	Relation of rings	Position of substituents
Trans-$[Coen_2Cl_2](H_5O_2)Cl_2$	gauche	kk'	-
Trans-$[Coen_2Br_2](H_5O_2)Br_2$	"	"	-
Trans-$[Co(-pn)_2Cl_2](H_5O_2)Cl_2$	"	kk	equatorial
Trans-$[Co(+pn)(-pn)Cl_2](H_5O_2)Cl_2$	"	kk'	"
Trans-$[Coen_2Cl_2]Cl$	"	"	-

The chelate rings are all gauche and substituents are equatorial. The relation of the ethylenediamine rings in most cases is kk' and not the more stable kk. This has been explained as due to packing considerations

or to hydrogen bonding in the crystal. It is of interest that in the case of the bis- active diamine compounds the kk form predominates.

Trisethylenediamine Co(III) complexes have also been studied by X-ray analysis and in every case the kkk form is found as is shown in the following table;[17]

Structural Data on Trisethylenediamine Cobalt (III) Cation.

Compound	Chelate conformation	3 ring relationship	Reference
DL-$[Coen_3]Cl_3,3H_2O$	gauche	kkk	
2D-$[Coen_3]Cl_3,NaCl,6H_2O$	"	kkk	
2D-$[Coen_3]Br_3,H_2O$	"	kkk	

With regards to the conformation of the metal-ethylenediamine ring in complexes containing a metal ion other than cobalt considerable work has been done by Brown and Lingafelter.[28] Using X-ray crystallographic data they have shown the structure of $[Nien_2(NCS)_2]$ to be a nearly regular octahedron with the ethylenediamine molecule in the gauche form and the relation of the two ethylenediamine rings was found to be symmetrical or kk. They have also shown the structure of $[Cuen_2](SCN)_2$ to be a distorted octahedron with the ethylenediamine molecule in an unsymmetrical or kk' gauche- form. (See diagrams on page 20). It may be this distortion which is responsible for the intensity differences upon which the A/B classification of Powell and Sheppard is based.

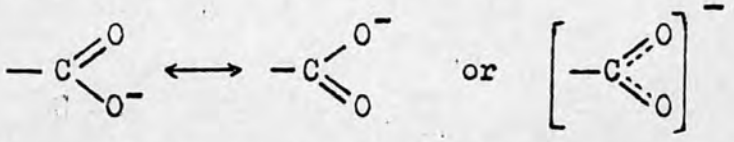
Infrared bands in the 590 - 465 $cm.^{-1}$ region have been assigned to (M-N) by Powell and Sheppard.[29] Since the bands suffer quite large frequency shifts on deuteration, it is postulated that there is vibrational coupling with $-NH_2$ rocking vibrations. Absorption at lower frequencies was tentatively assigned as δ(M-N-M). A recent report on $PdCl_2en_2$ by Durig *et al.*[30] is not consistent with Powell and Sheppard's work.

Vibrations of the Carboxyl and Carboxylate Groups

The infrared absorption spectra of the COO group in different environments are well established.[31]

The carboxyl group in a saturated acid, which can be regarded as unionised, exhibits a characteristic absorption band at ~ 1725-1700 $cm.^{-1}$ This band is strong and is due to the C=O stretching vibration. Dicarboxylic acids often have two bands in this region, e.g. malonic acid shows two peaks at 1740 and 1710 $cm.^{-1}$ This interaction effect is reduced in succinic acid which shows only a weak band at 1700 $cm.^{-1}$ Oxalic acid has only one strong absorption between 1710 and 1690 $cm.^{-1}$

The carboxyl group present in a salt however is ionised and resonance is possible between the two C-O bonds:-



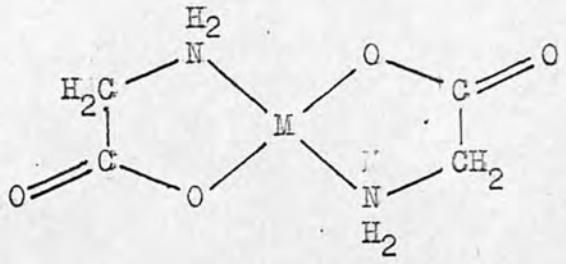
The characteristic carbonyl absorption is therefore replaced by two bands between 1610 and 1550 $cm.^{-1}$ and between 1400 and 1300 $cm.^{-1}$ which correspond to the antisymmetric and symmetric vibrations of the COO^- group. Of these bands the former is much more characteristic, as it is generally more constant in frequency whilst many other skeletal vibrations occur in the wide range 1400-1300 $cm.^{-1}$

When the ionised carboxyl group is coordinated to a metal it is seen to be somewhere between being an ionised group and an unionised group and the vibration due to the antisymmetric stretching mode of the COO^- group occurs around 1650-1590 $cm.^{-1}$ depending on the nature of the metal.

Therefore it is possible to distinguish between free and coordinated COO^- groups in these complexes and determine the degree of coordination.

Amino Acid Complexes

X-ray analysis indicates that in $[Ni(gly)_2]2H_2O$,[32] $[Zn(gly)_2]H_2O$ and $[Cd(gly)_2]H_2O$,[33] two glycinate ions coordinate to the metal by forming a trans square-planar structure:-



Also it has been shown that the oxygens of the carboxyl groups which are not coordinated to the metal are hydrogen-bonded either to the amino group of the neighbouring molecule or to the water of crystallisation, or are bonded weakly to the metal of the neighbouring complex. Thus the COO stretching frequencies of complexes of amino acids are affected by coordination as well as by intermolecular interaction.

Nakamoto et al.[34] have examined the effect of coordination and hydrogen bonding by making extensive measurements of the COO stretching frequencies of various metal complexes of amino acids in different physical states. They found that for any one physical state the antisymmetric frequencies increase, the symmetric frequencies decrease and the separation between the two frequencies increases in the following series of metals regardless of the nature of the ligand:-

$$Ni(II) < Zn(II) < Cu(II) < Co(II) < Pd(II) < Pt(II) < Cr(III)$$

Nakamoto et al. have explained this order by assuming that the covalent character of the M-O bond increases along the series, since an increase of covalent character leads to a more asymmetrical carboxyl group and results in an increase in the frequency separation of the two COO stretching bands.

But on the other hand Quagliano et al.[35] who have studied the infrared spectra of some glycine complexes have concluded that:

I. the M-O bonds in Cu(II), Ni(II) and Zn(II) glycinates are essentially ionic because their frequencies are almost the same as those of potassium glycinate and sodium acetate;

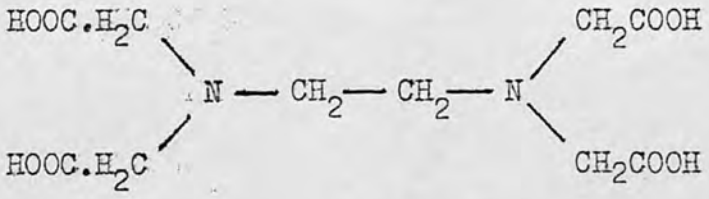
2. these metals use sp hybrid orbitals in forming linear bonds with the nitrogen atoms of the ligands;

3. the two oxygen atoms of the carboxyl group are symmetrically arranged with respect to the metal.

But the crystal structure of the nickel compound[32] shows quite clearly that all of the amine hydrogen atoms are involved in fairly strong hydrogen bonds and the uncoordinated carboxyl oxygen atoms are linked by fairly strong hydrogen bonds to the water molecules and NH_2 groups of other molecules. So it would seem that the near equivalence of the CO bonds as shown by Quagliano's work and by X-ray work could well be due to the fact that while one oxygen is forming a reasonably strong bond to the metal, the other is affected similarly by the several strong hydrogen bonds to it.

Ethylenediaminetetra-acetic Acid Complexes.

Ethylenediaminetetra-acetic acid can form complexes with many metals by coordination through the two nitrogen atoms and the four carboxylate groups:-



Of particular interest with regards to these compounds is the fact that infrared studies have been found to be of great use in distinguishing between unionised, coordinated and free ionised COO groups in these compounds.

Extensive work on this has been done by Sawyer and Paulsen[36] and they have concluded that the coordinated COO stretching frequency of these complexes shifts to higher frequencies as the M-O bond becomes more covalent. Examples of this can be seen in the following table which is taken from Sawyer's work on the infrared spectra of ethylenediaminetetra-acetic acid complexes of tri- and tetra-valent ions.

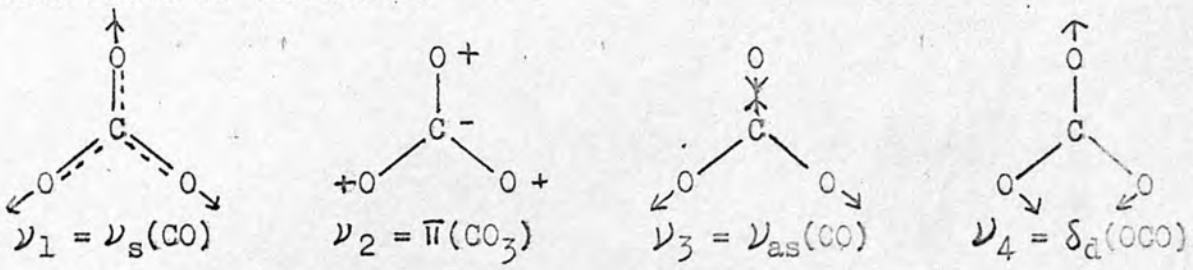
Chelate	Antisymmetric frequency $cm.^{-1}$	Symmetric frequency $cm.^{-1}$	Frequency difference
$Na[CrY]2H_2O$	1640	1360	280
$Na[CoY]2H_2O$	1645	1370	275
$Na[FeY]1H_2O$	1635	1385	250
$Na[AlY]xH_2O$	1670	1405	165
NaOAc	1580	1430	150

where H_4Y is ethylenediaminetetra-acetic acid.

These examples show not only that as the M-O bond becomes more covalent so the frequency due to the antisymmetric vibration of the carboxylate group increases but also that the frequency difference between the two different stretching vibrations of this group indicates the degree of covalent bonding. It is seen that as this frequency difference increases so the bonding becomes more covalent and Sawyer concluded that where the difference is 225 $cm.^{-1}$ or more the bonding is primarily covalent and where it is 225 $cm.^{-1}$ or less the bonding is primarily ionic.

Carbonato Complexes

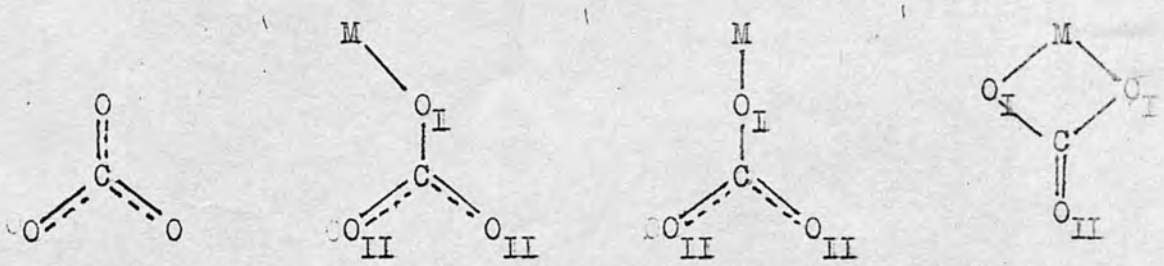
The free carbonate ion has D_{3h} symmetry and therefore has four normal modes of vibration:-



ν_2, ν_3 and ν_4 are infrared active and ν_1, ν_3 and ν_4 are Raman active.
36a
The frequencies of these vibrations are well established:-

1415 $cm.^{-1}$	ν_3	C-O asymmetric stretching vibration
1063 $cm.^{-1}$	ν_1	C-O symmetric stretching vibration
879 $cm.^{-1}$	ν_2	out-of-plane deformation vibration
680 $cm.^{-1}$	ν_4	in-plane deformation vibration

When the carbonate ion coordinates to a metal it can do so either as a unidentate or bidentate ligand. On coordination the carbonate ion becomes less symmetrical and therefore exhibits more vibrations. As a unidentate ligand it can have C_s or C_{2v} symmetry and as a bidentate ligand it can only have C_{2v} symmetry as the following diagrams show:-



On changing to C_s and C_{2v} when coordinated the ν_1 vibration becomes infrared active and the doubly degenerate vibrations ν_3 and ν_4 each split into two bands. Nakamoto et al. have demonstrated this effect experimentally.
37

Although the number of infrared active fundamentals is the same for C_s and C_{2v}, the splitting of the degenerate vibrations is larger in the bidentate than in the unidentate complex. This is also predicted quantitatively by the normal coordinate analysis carried out by Fujita [38] et al. for unidentate and bidentate carbonato complxes of Co(III). According to the results of these calculations, the CO stretching force constant, which is 5.46 for the free ion, becomes 6.0 for the CO_{II} bonds and 5.0 for the CO_I bond in the unidentate complex whereas it becomes 8.5 for the CO_{II} and 4.1 for the CO_I bonds in the bidentate complex. (All are UBF force constants in units of 10 dynes/cm.). Thus the difference between the CO_{II} and CO_I stretching force constants is larger in the bidentate than in the unidentate complex.

In organic carbonates such as dimethyl carbonate $(CH_3O_I)_2CO_{II}$, this effect is more striking because the CH_3-O_I bond is strongly covalent. In fact the CO_{II} stretching band is observed at 1870 $cm.^{-1}$, whereas the CO_I band is seen at 1260 $cm.^{-1}$

Gatehouse [39] et al. have shown that the separation of the CO stretching bands increase along the series:-

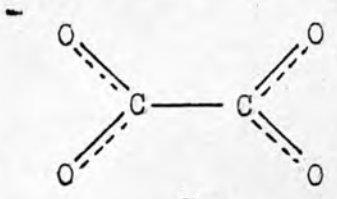
basic salt < carbonato complex < acid < organic carbonate

as shown by the following table:-

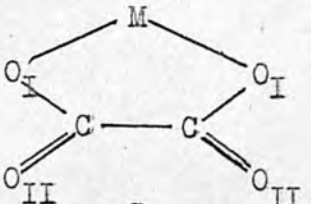
	asymmetric stretch	symmetric stretch
basic salt	1515-1470 ($cm.^{-1}$)	1425-1325 ($cm.^{-1}$)
complex	1577-1493	1338-1260
acid	1660-1655 1630-1620	1410-1400 1370-1295
organic carbonate	1870-1750	1280-1252

Oxalato Complexes

The structure of the free oxalate ion is planar with D_{2h} symmetry.[40]



D_{2h}



C_{2v}

The vibrational spectrum of the free oxalate ion has been examined by Murata and Kawai[41] who assigned three very strong infrared modes at 1627, 1338 and 768 $cm.^{-1}$ as an antisymmetric OCO stretch, a symmetric OCO stretch and an OCO out-of-plane bend respectively.

When the oxalate ion is coordinated to a metal its symmetry changes to C_{2v} and it exhibits more vibrations. Of these the two symmetric and the two antisymmetric stretching vibrations of the O-C-O linkages will be most sensitive, in a qualitatively predictable way, to changes in the strengths of the metal-oxygen bonds, since, as the metal-oxygen bonds become stronger, the bond orders in the ligand are increasingly altered. Fujita et al.[42] used this effect to relate their infrared data to the thermodynamic stability of the complexes. They reasoned that as the $M-O_I$ bond becomes stronger the $C-O_I$ bond lengthens and weakens while the $C-O_{II}$ bond becomes shorter and stronger. Such bond length changes are apparent from X-ray studies. They found that the lowering of the CO_I stretching vibration (corresponding to the 1338 $cm.^{-1}$ OCO stretch in the oxalate ion) does correlate with the stability order Cu(II) > Co(II) > Ni(II). For the trivalent metal oxalato complexes this study suggests the order Al(III) > Co(III) > Cr(III) > Fe(III), consistent with the order in other complexes involving coordination by six oxygen atoms.

Mizushima et al.[43] have made a vibrational study of oxalato complexes and have assigned the bands in their spectra by comparing them with the spectra of the oxalate ion and cis-dimethyloxalate which is presumed to be an approximate model for a hypothetical complex with fully covalent metal-oxygen bonds. The most characteristic features of the spectra of the complexes are:-

(i) strong doublet bands in the 1700 $cm.^{-1}$ region which were presumed to be essentially stretching vibrations of modified C=O groups;

(ii) a strong band at about 1400 $cm.^{-1}$ due to the OCO stretching vibration mainly attributable to C-O stretching vibration.

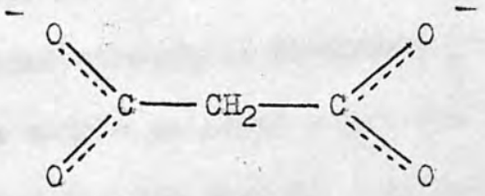
Mizushima et al.[43] have also attempted to determine the degree of covalency of the metal-oxygen bonds in the following way. Using sodium oxalate as a standard of zero covalency and dimethyloxalate as a standard of 100 per cent covalency in M-O bonds, they compared frequency shifts in certain C-O stretching frequencies in complexes with the total shift in going from sodium oxalate to dimethyoxalate for the same vibration. The OCO antisymmetric and OCO symmetric stretching vibrations were chosen for this purpose and tris oxalato complexes of Fe(III), Cr(III), Co(III) and Al(III) were examined. From a relation of the type:-

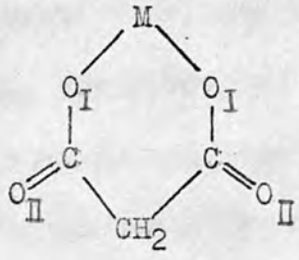
$$\text{Covalency} = \frac{\nu \text{ ester} - \nu \text{ complex}}{\nu \text{ ester} - \nu \text{ oxalate ion}}$$

they found covalency values of ~ 0.5 in all of the complexes using several vibrational modes.

Malonato Complexes

The free malonate ion can be seen from the following diagram to have C_{2v} symmetry:-





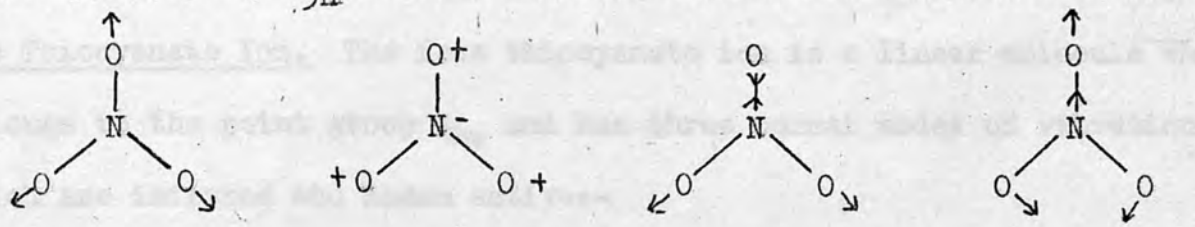
The infrared spectra of the malonate ion and malonic acid have been studied by Schmelz et al.[44] who have assigned all the observed frequencies. The antisymmetric and symmetric OCO stretching vibrations in the malonate ion have been assigned to strong bands at about 1600 and 1400 $cm.^{-1}$ respectively, both of which appear as doublets, the separation being of the order of 20 to 40 $cm.^{-1}$ The vibrations of malonic acid are very similar to those for the malonate ion except that the symmetric and antisymmetric OCO stretching vibrations of the malonate ion become the C=O stretching and C-O stretching vibrations of the acid and the latter couples with the in-plane OH deformation vibration. Also the out-of-plane deformations must be taken into account. For malonic acid the C=O stretching vibrations have been assigned to bands at 1735 and 1705 $cm.^{-1}$ and the C-O stretching vibrations, coupled with the in-plane OH deformation vibration, have been assigned to bands at 1439 and 1314 $cm.^{-1}$

Schmelz et al.[44] also interpreted the spectra of the tris-(malonato) complexes of Fe(III), Cr(III), Al(III), Cu(II), and Pd(II). They found that the antisymmetric and symmetric OCO stretching vibrations appear at about 1630 and 1380 $cm.^{-1}$ respectively. These authors compared these spectra with those of the oxalato metal complexes in which they had

determined the nature of the (M-O) bond from the values of the CO stretching frequencies.[43] For the malonato complexes they found that the OCO antisymmetric stretching frequency is higher than, and the OCO symmetric stretching frequency is lower than, the corresponding frequencies of the simple malonate ion. But these differences are less than those observed for the oxalato complexes and so it was concluded that the (M-O) bond of the malonato complexes was more ionic than that of the oxalato complexes.

Vibrations of the Anions

The Nitrate Ion. The nitrate ion is a planar molecule with the three oxygen atoms arranged symmetrically about the nitrogen atom. It belongs to the point group D_{3h} and therefore has four normal modes of vibration:-



$\nu_1 = \nu_s(NO)$ $\nu_2 = \pi(NO_3)$ $\nu_3 = \nu_d(NO)$ $\nu_4 = \delta_d(ONO)$

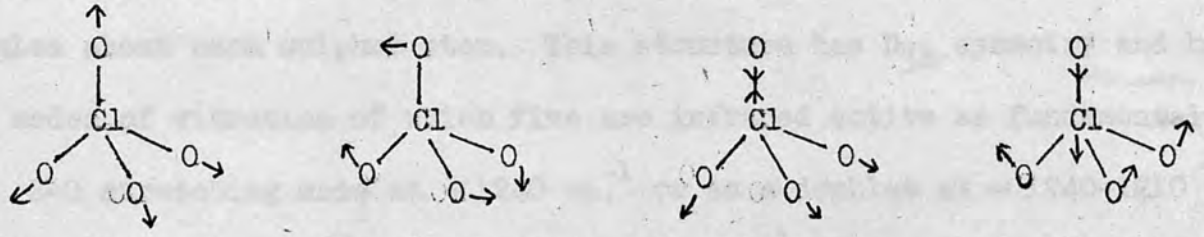
ν_2, ν_3 and ν_4 are infrared active and ν_1, ν_3 and ν_4 are Raman active. The frequencies of these vibrations are well known:-[45, 46]

1410-1340 $cm.^{-1}$ NO degenerate stretching vibration

860-800 $cm.^{-1}$ out-of-plane deformation vibration

730-690 $cm.^{-1}$ ONO in-plane deformation vibration

The Perchlorate Ion. The free perchlorate ion exists as a tetrahedral structure. As such it belongs to the point group T_d and has four normal modes of vibration:-



$\nu_1 = \nu_s(ClO)$ $\nu_2 = \delta_d(OClO)$ $\nu_3 = \nu_d(ClO)$ $\nu_4 = \delta_d(OClO)$

All four are Raman active but only ν_3 and ν_4 are infrared active the assignments being well established:-[45]

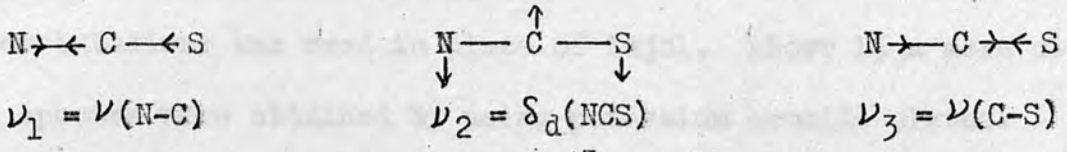
1170-1050 $cm.^{-1}$ Cl-O degenerate stretching vibration

~ 630 $cm.^{-1}$ O-Cl-O in-plane deformation vibration

Recent evidence[47] supports coordination of the perchlorate ion which

lower the symmetry to C_{3v} or C_{2v} so that the degenerate vibrations ν_3 and ν_4 are split and the symmetrical stretching vibration ν_1 becomes infrared active and occurs at about 935 $cm.^{-1}$

The Thiocyanate Ion. The free thiocyanate ion is a linear molecule which belongs to the point group $C_{\infty v}$ and has three normal modes of vibration which are infrared and Raman active:-



$\nu_1 = \nu(N\text{-}C)$ $\nu_2 = \delta_d(NCS)$ $\nu_3 = \nu(C\text{-}S)$

The following assignments have been made[45] for these vibrations:-

2200-2000 $cm.^{-1}$ C-N stretching vibration

750-740 $cm.^{-1}$ C-S stretching vibration

480 $cm.^{-1}$ N-C-S bending vibration

The Dithionate Ion. The assignment of the vibrational frequencies observed in the spectrum of the dithionate ion was carried out by Palmer.[48] The structure of the ion is $O_3S\text{-}SO_3$ with approximately tetrahedral bond angles about each sulphur atom. This structure has D_{3h} symmetry and has 11 modes of vibration of which five are infrared active as fundamentals:-

S-O stretching mode at ~1240 $cm.^{-1}$ or as a doublet at ~ 1240-1210 $cm.^{-1}$ and also at ~ 1000 $cm.^{-1}$

SO_3 deformation vibration at ~ 575 $cm.^{-1}$ (often as a doublet) and at ~ 516 $cm.^{-1}$ (again as a doublet)

SO_3 rocking vibration at ~ 204 $cm.^{-1}$

INFRARED ABSORPTION SPECTRA

EXPERIMENTAL

The infrared spectra were recorded on a Grubb-Parsons G.S.2A spectrometer. Solid samples in Nujol mulls were examined between rock-salt plates. The compounds were mostly studied in the regions 2.5 - 3.7 μ and 5 - 25 μ. For the region 6.5 - 8 μ where the Nujol peaks interfere hexachlorobutadiene was used in place of Nujol. Above 15 μ more clearly defined spectra were obtained by using potassium bromide plates.

Compounds of the type $[Coen_2CO_3]X$

The infrared spectra of these complexes were measured where X = chloride, bromide, iodide, nitrate, perchlorate, thiocyanate and dithionate. For each complex the infrared spectra of the anhydrous and hydrated forms have been obtained but only in the case of the bromide were the positions of the bands different. In order to separate the bands due to the vibrations of the carbonate group from those due to the ethylene-diamine rings the chloride, bromide and iodide have been deuterated and the corresponding infrared spectra have been incorporated with those of the undeuterated complexes. The deuteration was not complete but was enough to show the shift of the bands when there is a change from NH to ND. For simplicity the NH_2 bands that occur in the deutero complexes are not listed.

In addition the infrared spectra of the compound $Na_3[Co(CO_3)_3]$ was measured as a further attempt to separate the bands due to the carbonate group from those due to the ethylenediamine ring.

Compounds of the type $[Coen_2AA]Br$

The infrared spectra were measured for complexes containing the dicarboxylate groups oxalate, malonate and succinate so as to compare the positions of the bands due to the vibrations of the carboxylate groups in these complexes and in the corresponding carbonato complex $[Coen_2CO_3]Br$.

Compounds of the type trans-$[Coen_2Cl_2]Y$

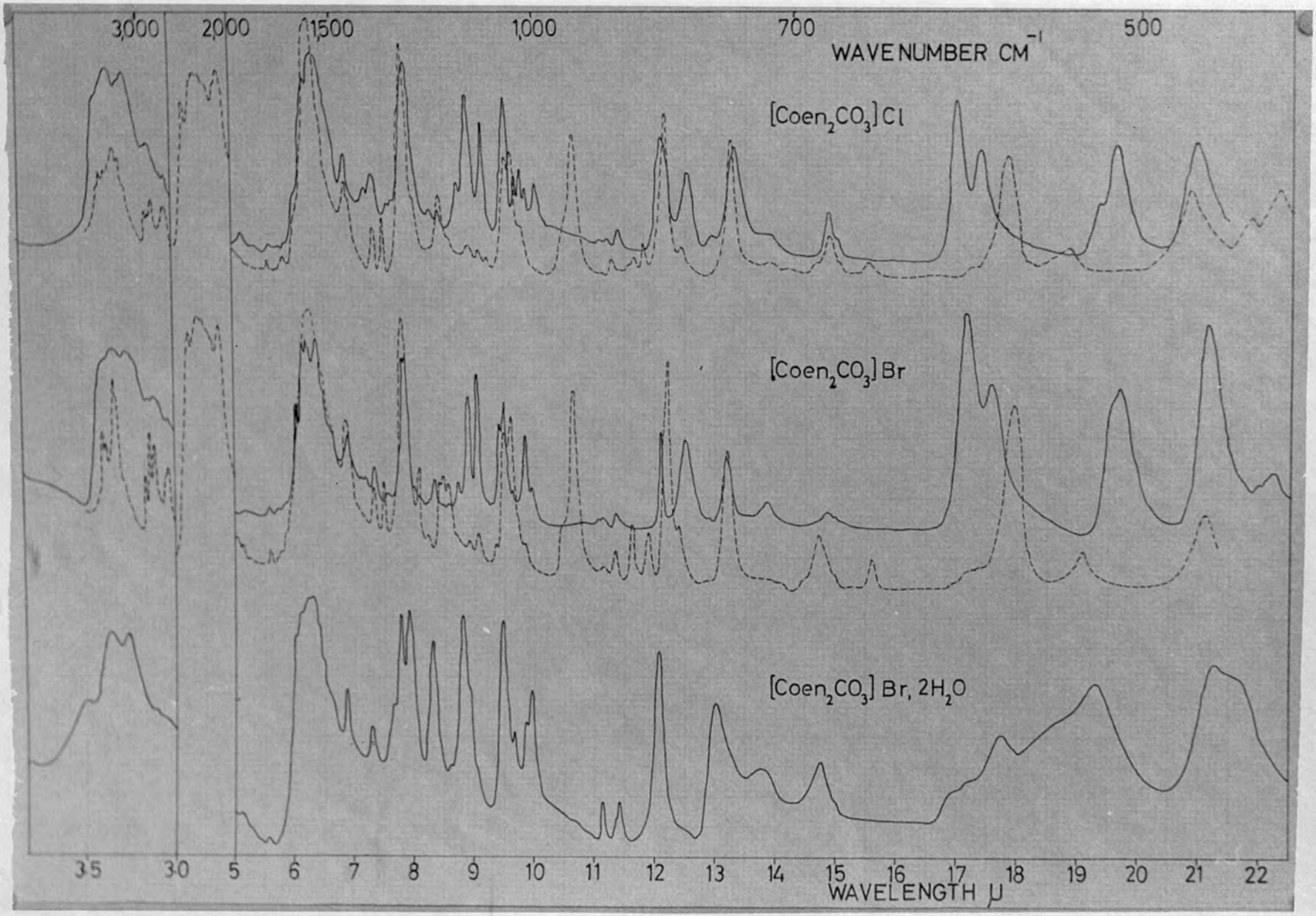
Infrared spectra of these complexes were measured where Y is the appropiate univalent anion from oxalic, malonic and succinic acids. These spectra were measured in order to compare the positions of the bands due the carboxylate group when it is present as an anion, as in these complexes, to the case when it is coordinated to the central metal ion. Also the infrared spectra was measured of the complex $[Coen_2CO_2CH_2CO_2]Y$ since this contains the malonate group as a bidentate ligand and as an anion.

The infrared spectra are reproduced on the following pages: page

The frequencies of the vibrations together with their assignments are set out on page 42 - 50.

Different conventions have been used for the assignments of the ethylenediamine rings and the carboxylate groups in order to remain consistent with previous papers. Abbreviations used are:-

ν, δ and π denote stretching, in-plane deformation and out-of-plane deformation vibrations respectively.


3,000
2,000
1,500
1,000
700
500
WAVENUMBER CM⁻¹
[Coen2CO3]Cl
[Coen2CO3]Br
[Coen2CO3]Br, 2H2O
3·5
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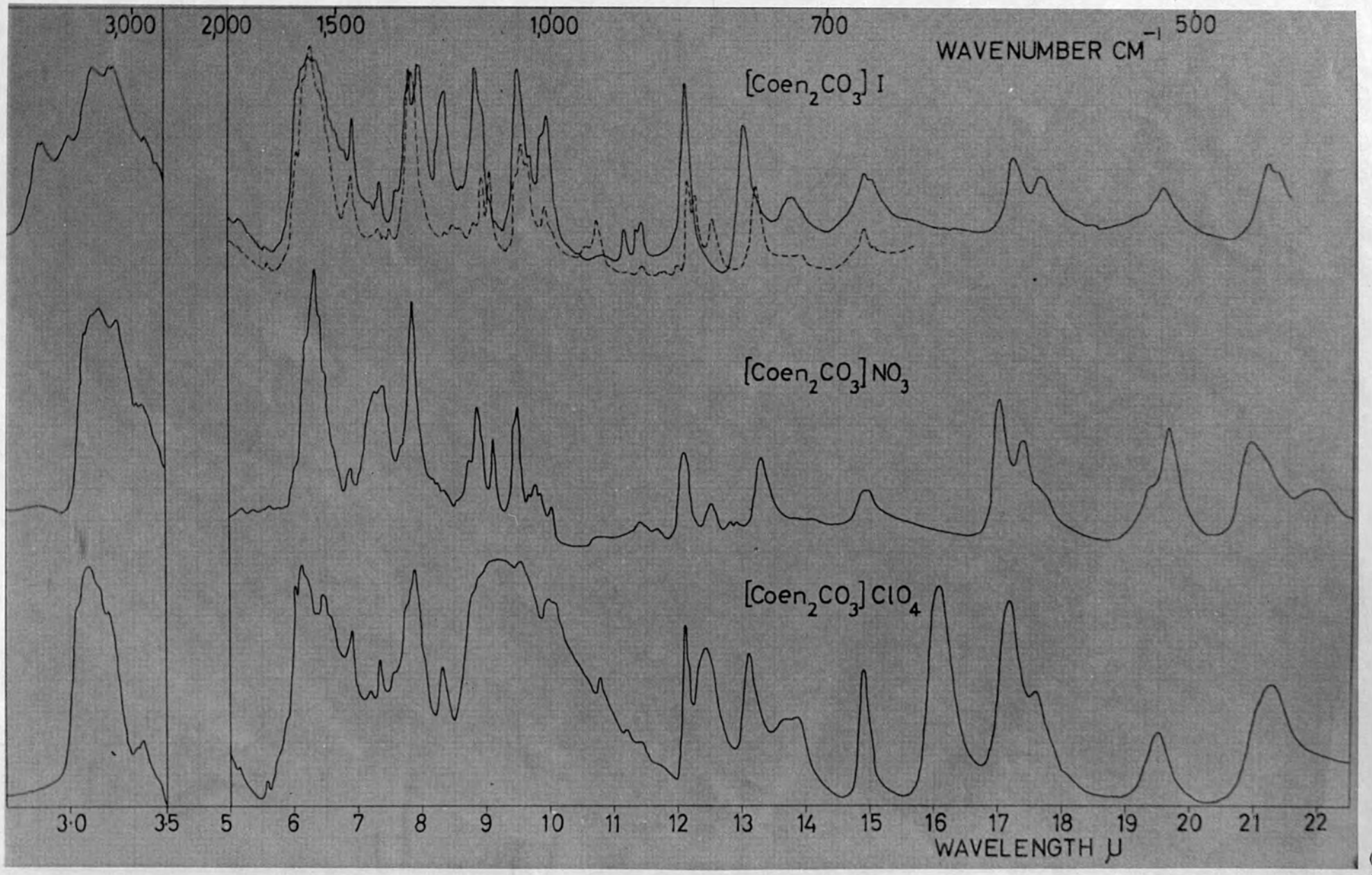
22
WAVELENGTH μ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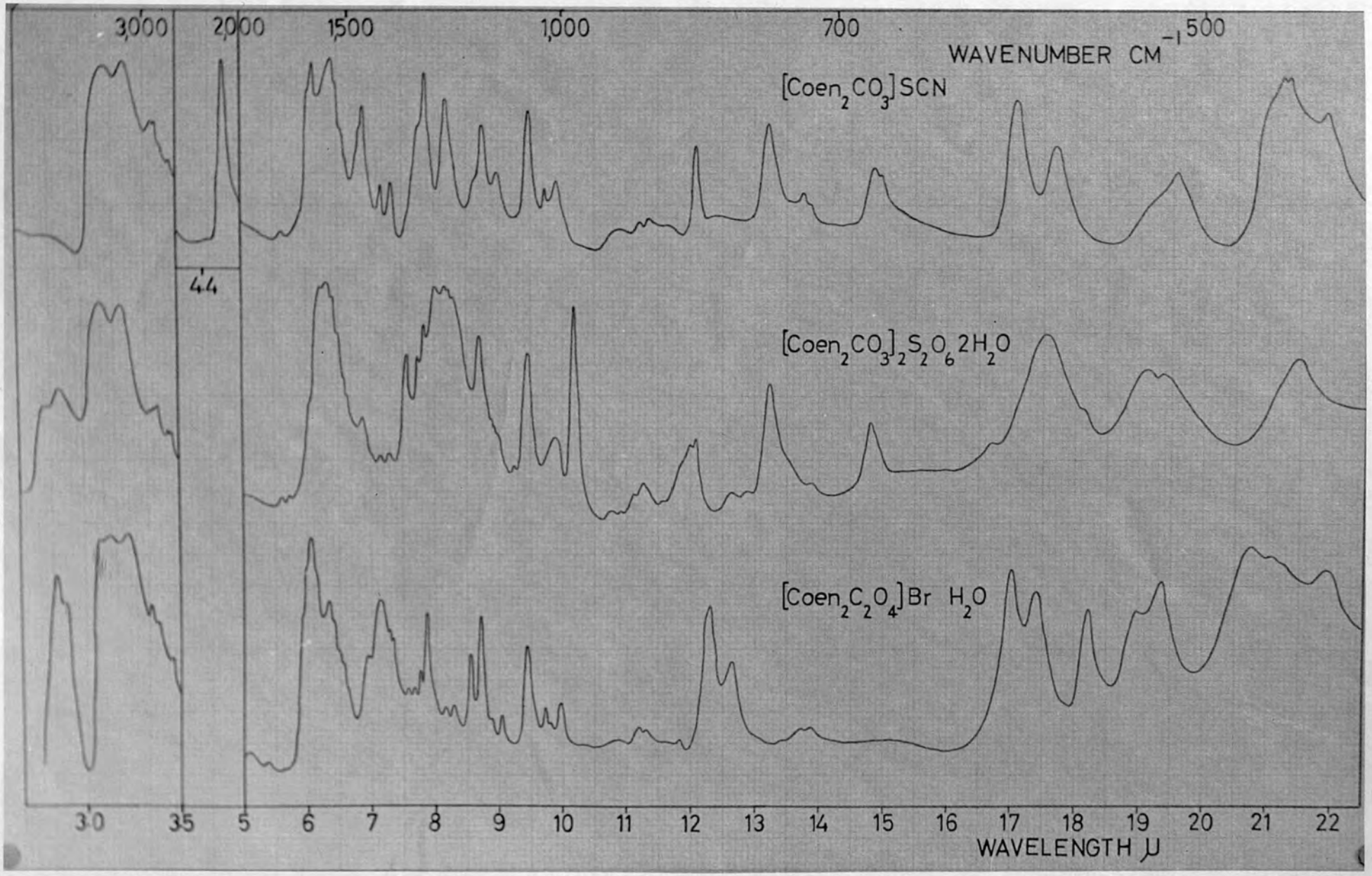
2,000
1,500
1,000
700
500
WAVENUMBER CM⁻¹
[Coen2CO3] I
[Coen2CO3] NO3
[Coen2CO3] ClO4
3·0
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ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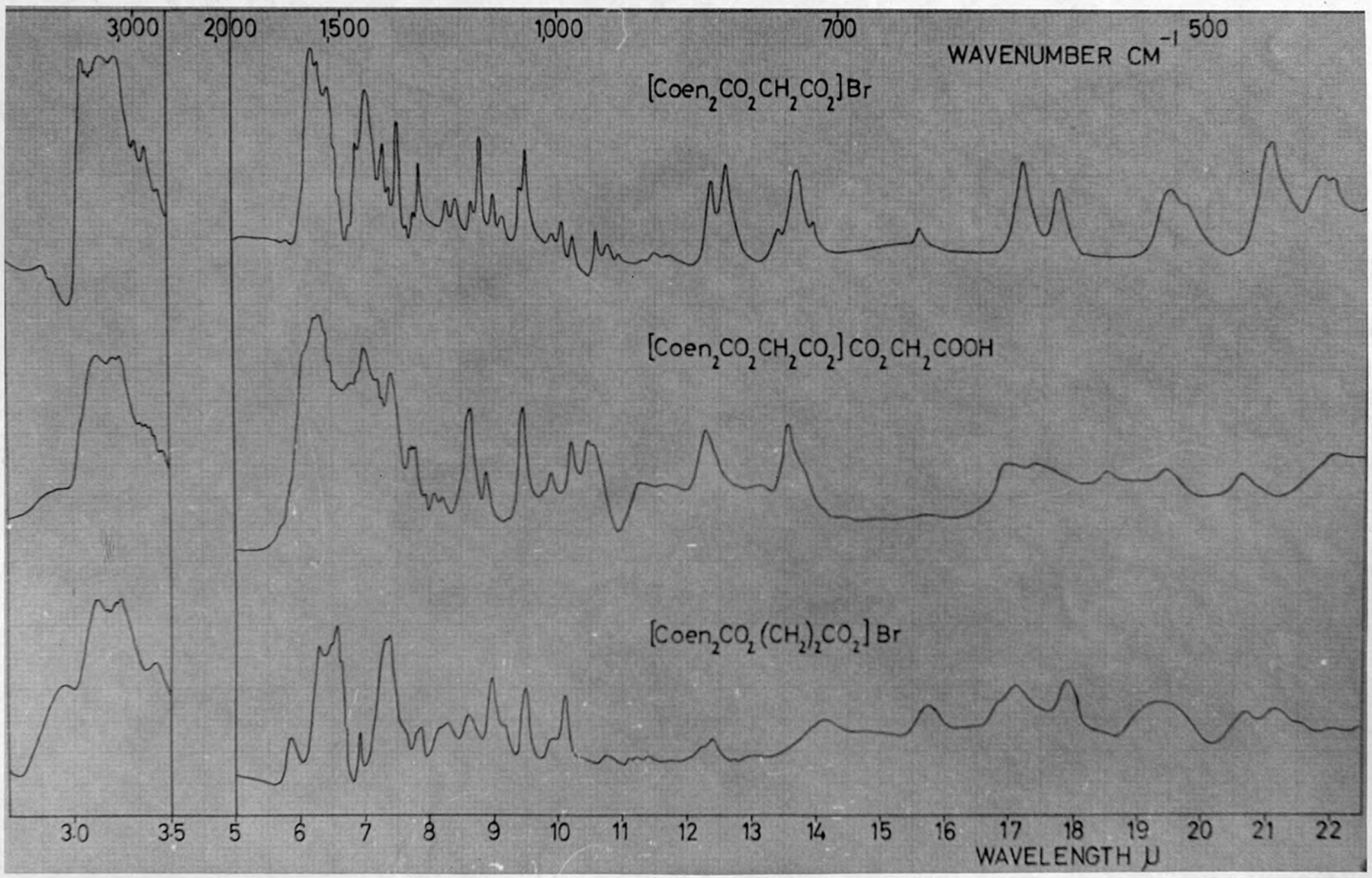
2,000
1,500
1,000
700
500
WAVENUMBER CM⁻¹
[Coen2CO3]SCN
4.4
[Coen2CO3]2S2O6 2H2O
[Coen2C2O4]Br H2O
3.0
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ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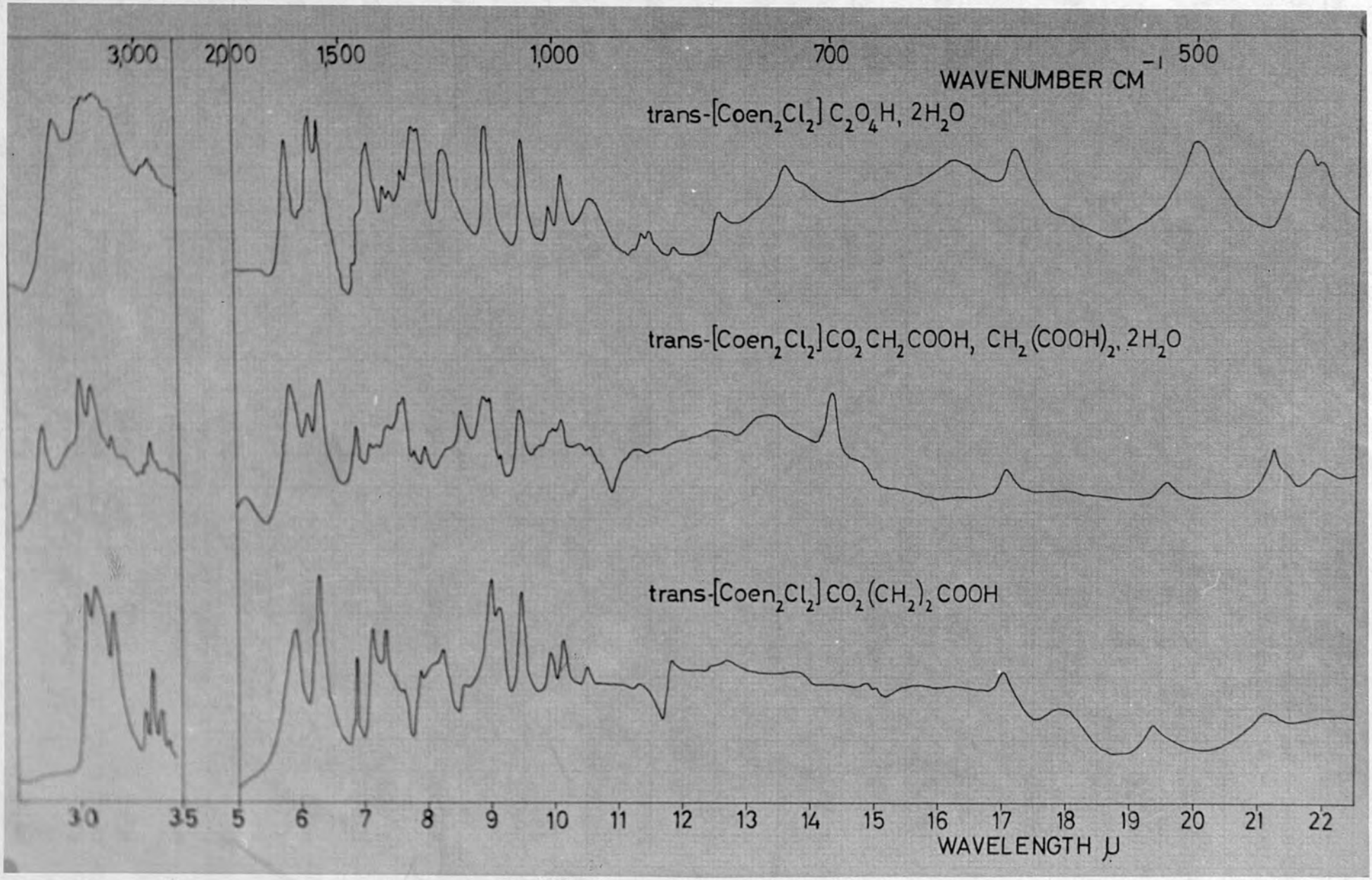
2,000
1,500
1,000
700
500
WAVENUMBER CM^{-1}
[Coen$_2$CO$_2$CH$_2$CO$_2$]Br
[Coen$_2$CO$_2$CH$_2$CO$_2$]CO$_2$CH$_2$COOH
[Coen$_2$CO$_2$(CH$_2$)$_2$CO$_2$]Br
3.0
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ


3,000
2,000
1,500
1,000
700
500
WAVENUMBER CM⁻¹
trans-[Coen2Cl2] C2O4H, 2H2O
trans-[Coen2Cl2]CO2CH2COOH, CH2(COOH)2, 2H2O
trans-[Coen2Cl2] CO2(CH2)2COOH
3.0
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ

Frequencies ($cm.^{-1}$) of vibrations of ethylenediamine rings in $[Coen_2AA]X$

Assignment	AA = oxalato X = bromide	AA = malonato X = bromide	AA = malonato X = malonate	AA = succinato X = bromide
NH_2 stretch		3261s		
	3242s	3242sh	3195s	3205s
	3192s	3145s	3125s	
	3096s	3091s	3086s	3100s
CH_2 stretch	2994s	3000m	2994sh	
	2955sh	2955m	2967sh	
	2899sh	2899sh	2941sh	2924w
	2817sh		2885sh	
NH_2 bend	1580s	1587sh	1582s	1582s
		1550s	1543sh	1538sh
CH_2 bend	1460sh	1473sh	1471sh	
	1449sh	1449s		
	1443m			1445m
CH_2 wag	1364sh	1350w	1391sh	
	1319w	1302w	1377sh	
	1304w	1282w		
CH_2 twist	1227w		1259sh	
	1205m	1210m	1220m	1206m
NH_2 wag	1171s	1155m	1157s	1159m
	1149s	1138s	1126m	
	1107m	1112m		1111s
		1094m		1087sh
Ring skeletal		1063sh		
	1058s	1054s	1058s	1052s
NH_2 twist	1029m	1012m	1011m	1007sh
	1001m	996m		987s
CH_2 rock			891w	893w
	885w	873w		877w
NH_2 rock	791s	797s		805m
	730w	749m	760w	
	720w	720sh	725sh	706m
Co-N stretch	588s	583s	588s	585s
	575s	565s	576s	559s
	528s, 517s	515s	515s	515s
Ring bend	476sh	477s		474s

Frequencies ($cm.^{-1}$) of vibrations of en. rings in trans-$[Coen_2Cl_2]X$

Assignment	X = oxalate	X = malonate	X = succinate
NH_2 stretch	3300s	3317s	3297s
	3280s	3257s	3252s
	3210s	3150m	3155s
	3045s	3086sh	
CH_2 stretch	2976w	3003w	
	2950m	2985w	2994m
	2930sh	2971m	2960s
	2910sh	2933sh	2915m
	2870sh	2885w	2882w
	2845sh	2857w	
NH_2 bend	1585s	1585s	1587s
CH_2 bend	1464sh		
	1445sh	1451m	1451s
CH_2 wag	1395sh	1385w	
	1368m	1351m	1364s
	1348w		
	1316m	1311m	1316sh
CH_2 twist		1282w	
		1255w	1267m
	1211s	1210sh	1215m
NH_2 wag	1121s	1126s	
	1110sh	1114sh	1111s
		1096w	1096s
Ring skeletal	1054s	1062s	1055s
NH_2 twist		1029w	
	1009m	1010w	1007m
	990s	990m	987s
CH_2 rock	882m	889w	885w
NH_2 rock	795s	800w	787w
	736s	725w	
Co-N stretch	582s	588m	588s
			562m
	501s	512m	514m
Ring bend	460s	472s	474m

Frequencies ($cm.^{-1}$) of vibrations of ethylenediamine rings in $[Coen_2CO_3]X$

Assignment	X = NO_3 (anhyd.)	X = ClO_4 (anhyd.)	X = SCN (anhyd.)	X = $\frac{1}{2}S_2O_6$ (anhyd.)
NH_2 stretch	3257s	3289sh		
	3200sh	3215s	3200s	3220s
	3165s	3175sh		
	3100sh	3115sh	3100s	3110s
	3077s			
CH_2 stretch	2981w	2990w		2985w
	2967w, 2950w	2960w	2970w, 2950w	2967w, 2950w
	2886w	2890w	2890w	2903w, 2885w
NH_2 bend	1664sh	1658sh	1660sh	1658sh
	1629sh	1629s	1640s	
	1582s		1563s	1587s
	1560sh	1546s		1560sh
	1540sh		1541sh	1541sh
CH_2 bend	1464sh			
	1453m	1449m	1451m	1458w
CH_2 wag	hidden	1391w	1397m	1399w
	by NO_3	1362m	1368m	1375w
	1305w	1316sh		1318m
CH_2 twist	1218w, 1192w	1203m	1221s	1203sh
NH_2 wag	1143m	1140sh	1140s	1148s
	1127s	1126s	1114m	
	1099s	1100s		
Ring skeletal	1055s	1048s	1055s	1056s
NH_2 twist	1025m	1003s	1010m	1012m
	1017m	995s		
	1000m			
CH_2 rock	890w	893w	894m	900m
	880m	874m	884m	886m
NH_2 rock	800m	805s		794w, 775w
	778w	721m	728m	720w
Co-N stretch	588s	583s	585s	570s
	576s	578s	565s	524s
	517sh, 510s	513s	510s	516s
Ring bend	478s	471s	471s	465s
Anion	1376m, 1350m	1083s	2060s	1250s, 1222s
	828s	927m		982s
	671s	623s		

Frequencies ($cm.^{-1}$) of vibrations of ethylenediamine rings in $[Coen_2CO_3]X$

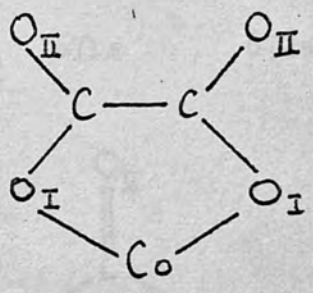
Assignment	X = Br (1 H_2O)	X = I (anhyd.)	X = I (deuterated)	$\frac{\nu NH}{\nu ND}$
NH_2/ND_2 stretch	3195s	3200s	2364s	1.35
		3160sh	2315s	1.37
	3096s	3106s	2247s	1.38
CH_2 stretch	2985w	2967w		
	2959w	2955w		
		2946w		
	2899w	2874w		
NH_2/ND_2 bend	1660sh	1653s		
	1634s	1630s	1198w	1.36
	1577s	1577s	1179w	1.34
	1562sh	1560sh	1166w	1.34
	1546sh	1540sh		
CH_2 bend		1476w		
	1456m	1449m	1449m	
CH_2 wag		1391w	1364w	
	1376m	1370sh	1348w	
		1364m	1335w	
	1319sh	1321w		
	1309w			
CH_2 twist	1208s	1200s		
NH_2/ND_2 wag	1138s	1135s	951m	1.19
	1124sh	1122sh	935m	1.20
Ring skeletal			1058s	
	1057s	1055s	1052s	
NH_2/ND_2 twist	1016sh	1014sh		
	1006s	1008s	836w	1.20
CH_2 rock	898m	888m		
	881sh	884sh		
	876m	877m	877w	
NH_2/ND_2 rock	726m	728m		
Co-N stretch		582s		
	563s	568s		
	518s	512s		
Ring bend	470s	473s		

Frequencies ($cm.^{-1}$) of vibrations of the ethylenediamine rings in $[Coen_2CO_3]X$

Assignment	X = Cl (anhyd.)	X = Cl (deuterated)	$\frac{\nu NH}{\nu ND}$	X = Br (anhyd.)	X = Br (deuterated)	$\frac{\nu NH}{\nu ND}$
NH_2/ND_2	3257s	2439s	1.34	3236s	2430s	1.33
	3195sh					
stretch	3165s	2387s	1.33	3170s	2387s	1.33
	3101sh			3140sh		
	3077s	2283s	1.35	3086s	2288s	1.35
CH_2 stretch	2976w			2981w		
	2963w, 2950w			2959w		
	2920w			2933w		
	2882w, 2845w			2886w, 2874w		
NH_2/ND_2 bend	1660sh			1658m		
	1631sh	1189m	1.37	1629s	1190m	1.37
	1577s	1168sh	1.35	1577sh	1182m	1.35
	1538sh			1570s	1170m	1.34
				1543sh		
CH_2 bend	1464sh	1453m		1464sh	1464m	
	1453m	1445sh		1453m	1456m	
CH_2 wag	1393w	1364m		1391w	1370m	
	1369w	1337m		1365m	1339m	
	1324w	hidden		1325w		
	1308w	by CO_3				
CH_2 twist	1250sh	1255sh		1250sh	1247m	
	1214w	1212w			1218w	
	1192w					
NH_2/ND_2 wag	1147m			1148m	957sh	
	1127s	941s	1.20	1124s	940s	1.20
	1099s			1106s		
Ring skeletal		1053s		1062s	1055s	
	1054s	1041s		1054s	1043s	
NH_2/ND_2 twist	1025m	865sh	1.19			
	1016m	858m	1.18	1016s	861m	1.18
	1000m	847m	1.18	1005m	841m	1.20
CH_2 rock	893w	899w		899w	896w	
	878m	885m		881m	884m	
NH_2/ND_2 rock	800s	hidden by CO_3		800s	hidden by CO_3	
	772w	645m	1.20	725m	642m	1.13
Co-N stretch	589s	562s		583s	557s	
	576s	532m		569s	525m	
	518sh 512s	483s		508s	474s	
Ring bend	479s	451s		474s		

Frequencies ($cm.^{-1}$) of vibrations of the oxalate group in $[Coen_2C_2O_4]Br$ and trans-$[Coen_2Cl_2]C_2O_4H$

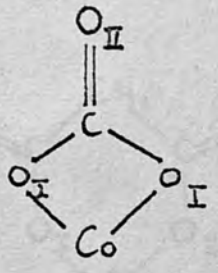
Assignment	$[Coen_2C_2O_4]Br$	trans-$[Coen_2Cl_2]C_2O_4H$
$\nu_a(CO_{II})$	1689sh	1724s
	1672sh	
	1650s	1618s
$\nu_s(CO_I)$		1425sh
	1405s	1416s
	1289m	1285s
	1271s	1269s
ν (C-C)		948s
	893m	871m
δ (OCO)	813s	842w
δ (OCO) or ν (Co-O)	549s	616b
δ (OCO) or ring def.	482s	
ν (Co-O)	455s	



Frequencies ($cm.^{-1}$) of vibrations of the carbonate group in $[Coen_2CO_3]X$

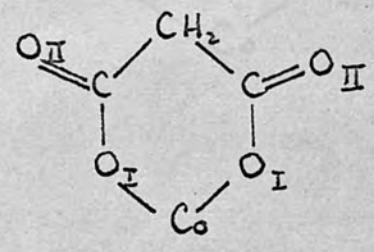
Assignment	X = Cl (anhyd.)	X = Cl (anhyd.) (deut.)	X = Br (anhyd)	X = Br (anhyd) (deut.)	X = Br ($1\ H_2O$)
$\nu_a(CO_{II})$	1613s 1590sh	1610s 1580s	1613s 1607sh	1608s 1595s	1603s
$\nu_s(CO_I)$	1271s	1294sh 1282s	1282s 1276s	1284s	1290s 1266s
$\nu\ (CO_I)$	1034m	1024sh	1039w		1037m
$\pi\ (CO_3)$	828s	822s	826s	821s	829s
$\delta(OCO)$	754s	754s	758s	758s	766s
$\delta(OCO)$	670m	671m	674m	680m	677s

	X = I (anhyd.)	X = I (deut.)	X = NO_3 (anhyd.)	X = ClO_4 (anhyd.)	X = SCN (anhyd.)	X = $\frac{1}{2}S_2O_6$ (anhyd.)
$\nu_a(CO_{II})$	1608s	1605s	1613s	1603s	1600sh	1620sh 1607s
$\nu_s(CO_I)$	1285s 1264s	1280s	1272s	1287sh 1267s	1285sh 1267s	1277s
$\nu\ (CO_I)$	1034m	1041s	1034m	hidden by ClO_4	1030m	
$\pi\ (CO_3)$	828s	826s	828s	826s	828s	826s
$\delta(OCO)$	770s	760s	753s	763s	757s	757s
$\delta(OCO)$	672s	673s	671s	672s	673s	676s



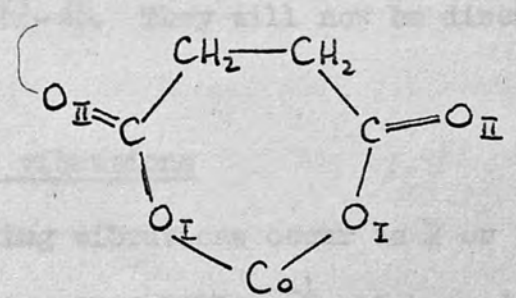
Frequencies ($cm.^{-1}$) of vibrations of the malonate group in $[Coen_2AA]Br$, $[Coen_2AA]AAH$ and trans-$[Coen_2Cl_2]AAH, AAH_2$, where $AA = (CO_2CH_2CO_2)^{2-}$

Assignment	$[Coen_2AA]Br$	$[Coen_2AA]AAH$	trans-$[Coen_2Cl_2]AAH_2$
			1715s
$\nu_a(CO_{II})$	1618s	1642sh	1634s
	1610s	1600s	1600sh
$\nu_s(CO_I)$	1420b	1431s	1408m
	1368m	1347s	1323sh
	1330s	1299sh	
		1294m	
	1272s	1285sh	
		1240m	
$\nu_a(C-C)$	1189s		1175s
$\nu_s(C-C)$	980m	980s	
		957s	965w
	946m	947sh	948w
CH_2 rock	930m		
	917m		
δ (OCO)	812s	815s	
	733s	739s	755b
	644m		698s
δ (OCO) or ν(Co-O)		540s	
δ (OCO) or ring def.		486s	
ν (Co-O)	460s		



Frequencies ($cm.^{-1}$) of vibrations of the succinate group in $[Coen_2AA]Br$ and trans-$[Coen_2Cl_2]AAH$, where $AA' = (CO_2(CH_2)_2CO_2)^{2-}$

Assignment	$Coen_2AA$ Br	trans- $Coen_2Cl_2$ AAH
$\nu_a(CO_{II})$	1698m 1520s	1700s 1608sh
$\nu_s(CO_I)$	1370s 1351s	1404s
	1271m	1235b
$\nu_a(C-C)$		1170m
$\nu_s(C-C)$		952m
CH_2 rock	929m 901w	
$\nu(C-C)$		846m
$\delta(OCO)$	634s	
$\delta(OCO)$ or ring def.	483s	



INFRARED ABSORPTION SPECTRA

DISCUSSION

Vibrations due to the ethylenediamine rings

The assignment of bands arising from vibrations of the ethylenediamine rings has been made with reference to the infrared spectra of ethylenediamine itself [49 50 51] and molecules similar to ethylenediamine such as 1:2 dichloroethane [52], ethylenethiocarbamide and tetrabis(en thiocarbamide)Cu(I) [53] and 1,2 dithiocyanatoethanedichloro Pt(II) [54]. The infrared spectra of some ethylenediamine complexes were also referred to, [55 56 57 58] and those by Powell and Sheppard [29], Baldwin [26] and James [59] were found to be particularly useful. The assignment was also assisted by the deuteration experiments made in the present study.

From an overall inspection of the spectra of all the complexes studied it can be seen that all the vibrations due to the NH_2 group are stronger than the corresponding vibrations due to the CH_2 group. This is in contrast with ethylenediamine in the free state where they are of about equal strength.

The vibrations of the ethylenediamine rings and their assignments are set out on page 42-46. They will now be discussed under five headings.

NH and CH stretching vibrations

The N-H stretching vibrations occur as 2 or 3 strong bands with shoulders in the region 3300-3050 $cm.^{-1}$ which on deuteration shift to 2450-2250 $cm.^{-1}$ and show the expected value for the ratio $\nu NH/\nu ND = 1.34$. The absorption is lower than that in free ethylenediamine due to coordination

Comparing the positions of these bands in the carbonato complexes for different anions it can be seen that the lowest frequencies occur in the spectra of the chloride and bromide and the highest for the perchlorate showing that the former most easily form hydrogen bonds. Also the spectra of the chloride, bromide and nitrate show three main bands indicating vibrations of hydrogen-bonded and free NH groups whereas the other spectra contain two main bands.[31]

The C-H stretching vibrations occur in the region 3000-2800 $cm.^{-1}$ They are weak and often difficult to detect compared with the same bands in ethylenediamine itself which occur in the same region but are strong. As expected they do not move on deuteration.

NH_2 angle deformations

These are the vibrations of the type: bending, wagging, twisting and rocking. There would be expected to be two vibrations of each type per (en) group which gives a maximum of four vibrations of each type for each complex studied.

The NH_2 bending vibrations are seen to occur in the cis-complexes as two strong bands at about 1630 and 1570 $cm.^{-1}$, with shoulders, which shift on deuteration to 1200-1160 $cm.^{-1}$ giving the ratio $\nu NH/\nu ND = 1.35$. In addition these complexes have a distinct shoulder at about 1660 $cm.^{-1}$ which remains constant in position for all the complexes except the oxalato, malonato and succinato complexes where it is hidden by the CO absorption.

For the trans-complexes studied the NH_2 bending vibration occurs as a single strong band at 1585 $cm.^{-1}$

The NH_2 bending vibration is seen to be in the same position as that for free ethylenediamine[10] but it has been noted that this vibration is the least sensitive to coordination to a metal.

The NH_2 wagging vibration in the carbonato (cis-) complexes appears in a different form depending on the anion. There are seen to be two forms:
1) produced by complexes containing the anions: chloride, anhydrous bromide, nitrate and perchlorate (group A), consists of a medium band at ~ 1145 $cm.^{-1}$ and two strong bands at about 1125 and 1100 $cm.^{-1}$; they shift on deuteration to 957 and 940 $cm.^{-1}$ giving the $\nu NH/\nu ND$ ratio of 1.20.
2) produced by complexes containing the anions: hydrated bromide, iodide, thiocyanate and dithionate (group B), consists of one strong band at about 1140 $cm.^{-1}$ with a shoulder or medium band attached to it at about 1120 $cm.^{-1}$; on deuteration of the iodide these bands shift to 951 and 935 $cm.^{-1}$ giving the $\nu NH/\nu ND$ ratio of 1.20.
The spectra of the complexes of the type $[Coen_2AA]X$, where AA is oxalato, malonato and succinato and X is bromide are seen to belong to type A.
That where AA is malonato and X is malonate belongs to type B.

The NH_2 wagging vibration in the trans-complexes of the type $[Coen_2Cl_2]X$ appears as a doublet in the region 1120-1100 $cm.^{-1}$

The NH_2 twisting vibration also appears in a different form depending on the anion: for the group A complexes it occurs as two medium bands at about 1020 and 1000 $cm.^{-1}$, sometimes with shoulders, which shift on deuteration to 860-840 $cm.^{-1}$ giving the $\nu NH/\nu ND$ ratio of 1.19.
For the group B complexes it occurs as one strong band at about 1010 $cm.^{-1}$ with a shoulder at a higher frquency; on deuteration of the iodide the band shifts to 836 $cm.^{-1}$ giving the $\nu NH/\nu ND$ ratio of 1.20.

The NH_2 twisting vibration occurs in the trans-complexes as a medium band at about 1010 $cm.^{-1}$ and a strong band at about 990 $cm.^{-1}$

The corresponding vibrations in free ethylenediamine are at 995 and 905 $cm.^{-1}$ so that the vibration is seen to be at a higher frequency in the complex due to coordination.

The NH_2 rocking vibration is said to be the most sensitive of the NH_2 angle deformations to coordination to a metal[10] and this is seen to be so in these complexes. Again the two groups of cis-complexes show a different form of spectra:

the group A complexes all have a strong band at 800 $cm.^{-1}$ and a medium band at about 775 or 725 $cm.^{-1}$; the deuteration shift giving $\nu NH/\nu ND = 1.20$.

the group B complexes have no band at 800 $cm.^{-1}$ but just a medium band at about 725 $cm.^{-1}$

In the trans-complexes the NH_2 rocking vibration appears as two bands at about 800 and 730 $cm.^{-1}$

The corresponding vibration in free ethylenediamine occurs at 327 $cm.^{-1}$ so it can be seen that this vibration is considerably raised to higher frequencies by coordination.

CH_2 angle deformations

These are the bending, wagging, twisting and rocking vibrations. Again there would be expected to be a maximum of four vibrations of each type. Their positions are found from the fact that they show only small frequency shifts on deuteration.

The CH_2 bending vibration is a most consistent vibration; in all the complexes studied it occurs as two medium or weak bands at ~1464 and 1453 cm^{-1}

and these shift on deuteration by only about 10 $cm.^{-1}$ to lower frequencies. This vibration occurs at exactly the same frequency as that in free ethylenediamine and in fact occurs at the same place in all molecules containing two CH_2 groups with the gauche-configuration. In some of the complexes the 1464 $cm.^{-1}$ band is hidden by the absorption due to the NH_2 bending vibration.

The CH_2 wagging vibration occurs as 2-4 weak or medium bands in the region 1400-1300 $cm.^{-1}$ and on deuteration they shift about 20 $cm.^{-1}$ to lower frequencies.

The CH_2 twisting vibration occurs as 2 or 3 weak or medium bands in the region 1255-1192 $cm.^{-1}$ and on deuteration they shift by about 5 $cm.^{-1}$ to lower frequencies. Of particular interest in this region is a band at about 1200 $cm.^{-1}$ which varies considerably in intensity in different complexes. In the group A complexes it is either a single weak or medium band (anhydrous bromide and perchlorate) or a weak doublet (chloride and nitrate). But in the group B complexes there is just a single strong absorption at about 1200 $cm.^{-1}$

In the trans-complexes of the type $[Coen_2Cl_2]X$ this band occurs as a single strong absorption at about 1210 $cm.^{-1}$ for X = oxalate and succinate but it occurs as a weak shoulder at 1210 $cm.^{-1}$ for the malonate.

The CH_2 rocking vibration gives rise to two weak or medium bands in all the cis-complexes in the region 900-870 $cm.^{-1}$ which are very constant in their position. They shift on deuteration by not more than 5 $cm.^{-1}$ to higher frequencies. In the trans-complexes however this vibration occurs as a single weak or medium band at about 885 $cm.^{-1}$ This variation in the spectra of cis- and trans-complexes is as predicted by Baldwin.[26]

Skeletal stretching vibrations

These involve the C-C and C-N bonds and three vibrations are expected per ethylenediamine group. For ethylenediamine itself they occur at 1130, 1095 and 830 $cm.^{-1}$ A strong band appears consistently in all the complexes at about 1050 $cm.^{-1}$ and has been assigned by Powell and Sheppard[29] and Baldwin[26] to one of these vibrations due to its small shift on deuteration. In several of the complexes studied this band seems to appear as a doublet.

Co-N vibrations

These occur in the region 600-500 $cm.^{-1}$ and they shift by about 30 $cm.^{-1}$ on deuteration showing that there must be vibrational coupling with the NH_2 rocking vibrations. All the cis-complexes studied have very similar spectra in this region: three strong bands at about 585, 570 and 510 $cm.^{-1}$ and some have an additional band at about 520 $cm.^{-1}$ The trans complexes however have only two or three bands in this region. This difference between the spectra of the cis- and trans-complexes is as suggested by Hughes and McWhinnie.[58]

All the complexes studied have a strong band at about 475 $cm.^{-1}$ in their spectra and this is probably due to ring deformation.

Explanation of type A and type B spectra

It has been noted that the infrared spectra of the cis-complexes studied fall into two classes, A and B. The main difference between the spectra of each group lies in the bands due to vibrations of the NH_2 group and also in one band attributed to the CH_2 group:-

Vibration	Spectrum type	Approximate positions of bands ($cm.^{-1}$)
NH_2 wag	A	1145m 1125m 1100s
	B	1140s 1120sh
NH_2 twist	A	1020m 1000m
	B	1010s + shoulder at higher frequency
NH_2 rock	A	800s 775m or 725m
	B	725m
CH_2 twist	A	1200w or absent
	B	1200s

The nature of the crystals and the state of hydration of the complexes together with the spectrum type are set out in a table on the following page to find some cause of the difference. From this table there is no apparent correlation between the state of hydration and the spectrum type. The nature of the crystals, however, does give rise to a rough correlation since it is seen that in several cases the type B spectrum is obtained for those complexes which are formed as hexagonal or prismatic crystals, whereas the type A spectrum is obtained for those complexes which are formed as a powder or micro-crystalline

Complex	State of hydration	Nature of crystals	Spectrum type
$[Coen_2CO_3]Cl$	anhydrous	blue-red powder	A
$[Coen_2CO_3]Br$	1 H_2O	hexagonal pillars	B
	anhydrous	small, cubic crystals	A
$[Coen_2CO_3]I$	anhydrous	prismatic crystals	B
$[Coen_2CO_3]NO_3$	hydrated	flaky crystals	A
	anhydrous	powder	A
$[Coen_2CO_3]ClO_4$	anhydrous	crystalline powder	A
$[Coen_2CO_3]SCN$	hydrated	hexagonal prisms	B
	anhydrous	needles	B
$[Coen_2CO_3]_2S_2O_6$	hydrated (2 H_2O)	prismatic crystals	B
	anhydrous	powder	B
$[Coen_2C_2O_4]Br$	1 H_2O	leaf-like crystals	A
$[Coen_2C_3H_2O_4]Br$	anhydrous	leaf-like crystals	A
$[Coen_2C_3H_2O_4]C_3H_3O_4$	anhydrous	fine crystals	B
$[Coen_2C_4H_4O_4]Br$	hydrated (1 H_2O)	powder	A

powder, or as flaky or leaf-like crystals. But not all the spectra follow this correlation.

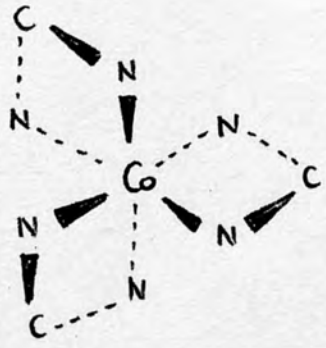
Another factor which could account for the difference in spectra is the conformations of the cobalt-ethylenediamine rings. Each ring

being in the gauche form, can adopt either of two conformations, k and k'. In the first of these the C-C bond is nearly parallel to the three-fold axis of the metal complex, and in the second it forms an obtuse angle with this axis. Considering only the interactions of the NH_2 groups the kk form is expected to be more stable[25] but in cases where the complex is stabilised by hydrogen bonding between the NH_2 groups and an anion then the kk' form is more stable.

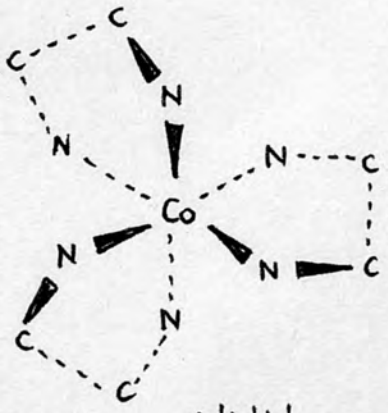
For tris(ethylenediamine) complexes the kkk form is predicted to be the more stable form from calculations on the interactions of NH_2 groups.[25] But the k'k'k' form contains NH_2 groups which are in a more favourable position to form hydrogen bonds with an anion, so that hydrogen bonding specifically favours the k' conformation relative to the normally more stable k form.[65] A recent X-ray study has shown the existence of three new conformers of tris(ethylenediamine)chromium(III):-

$[Cren_3][Ni(CN)_5]1.5H_2O$ contains one $[Cren_3]^{3+}$ ion having the conformation kk'k' and the other the conformation kkk'. And in the complex $[Cren_3][Co(CN)_6]6H_2O$ the $[Cren_3]^{3+}$ ion has the k'k'k' form.

Complexes containing two ethylenediamine rings which are stabilised by hydrogen bonding would therefore be expected to give rise to simpler spectra than those which are not fixed by specific interaction and can contain both the kk and the kk' form. The type B spectrum is seen to be the simpler of the two spectra so that this could be attributed to the kk' form only and thus implying that hydrogen bonding stabilises these complexes, whereas hydrogen bonding is negligible in those complexes giving rise to the type A spectrum.

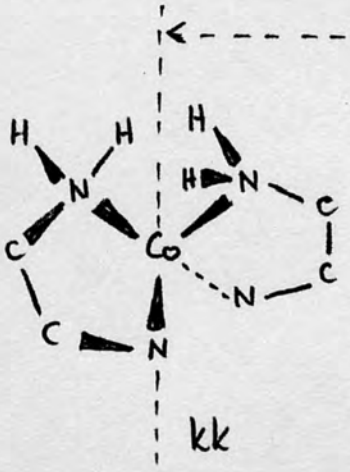


kkk

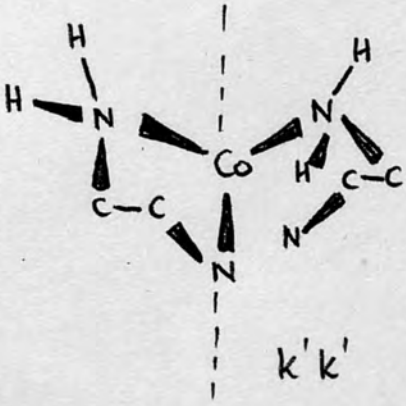


k'k'k'

The conformations of D^{*}-$[Coen_3]^{3+}$ in the two extreme forms kkk (eclipsed C-C axes) and k'k'k' (staggered C-C axes), viewed along the 3-fold axis of symmetry. In L^{*}-$[Coen_3]^{3+}$ the k'k'k' form contains the eclipsed C-C axes and the kkk form the staggered C-C axes.



kk



k'k'

Two ethylenediamine rings shown in the kk and k'k' conformations, viewed parallel to the 3-fold axis, showing in the kk form how the axial amine hydrogens are directed towards a point on the 3-fold axis whereas in the k'k' form there is a general broadening of the complex and the axial amine hydrogens point away from the 3-fold axis.

Vibrations due to the carboxylate groups

The assignment of bands arising from vibrations of the carbonate group was made using the work of Nakamoto [37] et al., Fujita [38] et al. and Gatehouse [39] et al. Two of these reports [37, 39] also contained the frequencies of the vibrations of the free carbonate group needed for comparison with th those due to the coordinated group.

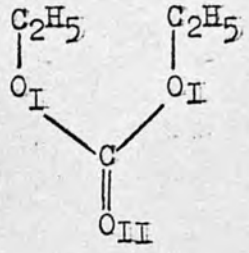
The assignment of bands arising from vibrations of the oxalate group has been made mainly using the work of Fujita [60] et al. Other reports that were studied were those of Nakamoto [37] et al., an earlier work by Fujita [42] et al. and that of Schmelz [43] et al. These also contained the frequencies of the vibrations due to the free oxalate group as does also the work done by Kurod and Kubo [61] which was found to be of use.

The assignment of bands arising from vibrations of the malonate group was made using the work of Schmelz [44] et al. This work also contained the infrared spectra of malonic acid and sodium and potassium malonates. The infrared spectrum of sodium malonate was also found in the work of Kurod and Kubo [61].

In general the vibrations of the carboxylate groups give rise to strong bands similar in intensity to the bands due to the NH_2 group. They were distinguished from these by the fact that the bands due to the vibrations of the carboxylate groups show only small shifts on deuteration. In this study the vibrations of the carboxylate groups in the complexes are compared with those that are ionised, as in the alkali metal carboxylates, and those that are unionised as in the organic carboxylates and in the carboxylic acids. Hence the degree of covalency in the metal-oxygen bond for the various complexes studied could be obtained in a qualitative way.

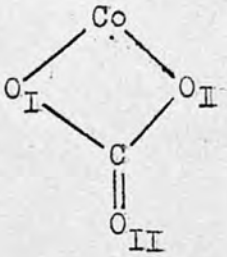
Vibrations of the carbonate group

When the carbonate group is coordinated as a bidentate ligand it is seen to give rise to six main vibrations in the region 1630 - 670 $cm.^{-1}$



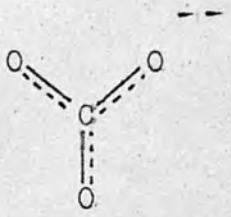
diethyl carbonate

covalent



bidentate

carbonate ligand



carbonate ion

ionic

The degenerate C-O stretch vibration of the symmetrical carbonate ion, which appears as one band at 1415 $cm.^{-1}$, is split into two bands in the complex:- the band due to the $C\text{-}O_{II}$ stretch appears as a single band or a doublet at about 1610 $cm.^{-1}$ and the band due to the $C\text{-}O_{I}$ stretch appears as a doublet in the region 1290-1260 $cm.^{-1}$ The corresponding bands arising from a covalently bound carbonate group, as in diethyl carbonate, appear at 1750 and 1262 $cm.^{-1}$ In all the carbonato complexes studied the band due to the $C\text{-}O_{II}$ stretch is a strong band at 1613-1603 $cm.^{-1}$ with or without another band which moves slightly to a lower frequency on deuteration. The band due to the $C\text{-}O_{I}$ stretch always appears as a doublet or as a broad band as in the chloride, nitrate and dithionate where it appears at 1271-1277 $cm.^{-1}$ The frequency separation between the bands of the doublets increases along the series:- anhydrous bromide (6 $cm.^{-1}$), thiocyanate (18 $cm.^{-1}$), perchlorate (20 $cm.^{-1}$), iodide (21 $cm.^{-1}$), hydrated bromide (24 $cm.^{-1}$). These bands move to slightly higher frequencies on deuteration.

The symmetric C-O stretch vibration which is infrared inactive in the free carbonate ion becomes infrared active when the carbonate group is covalently bound. It appears as a medium band in all the carbonato complexes at about 1034 $cm.^{-1}$ There is no appreciable shift on deuteration. The corresponding band in the ionic carbonate group appears in the Raman spectrum at 1063 $cm.^{-1}$ and that in a covalently bound group as in diethyl carbonate appears at 1021 $cm.^{-1}$

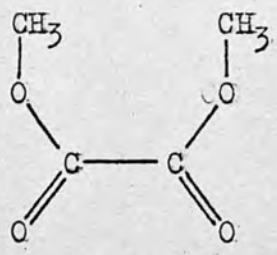
The out-of-plane deformation vibration occurs in all the complexes at 826 or 828 $cm.^{-1}$ as a strong band which shifts slightly to lower frequencies on deuteration. The corresponding bands in the free carbonate ion and in diethyl carbonate occur at 879 and 790 $cm.^{-1}$ respectively.

The degenerate in-plane deformation vibration which occurs as one band in the free carbonate ion, at 680 $cm.^{-1}$, is split into two bands in the complexes at 770-753 $cm.^{-1}$ and at 677-670 $cm.^{-1}$ These bands are all strong and easy to detect and they show no appreciable shift on deuteration.

A comparison of the spectra of all the carbonato complexes shows that the spectra of the chloride and nitrate are almost identical as were their vibrations due to the ethylenediamine rings. Also for all the vibrations, except the $C-O_{II}$ stretch, the hydrated carbonato bromide has the highest or second to highest frequency.

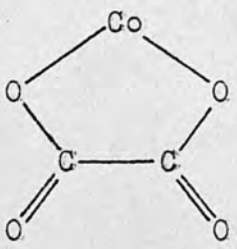
Vibrations of the oxalate group

When the oxalate group is coordinated as a bidentate ligand, as in $[Coen_2C_2O_4]Br$, it gives rise to vibrations due to the two COO groups and to the C-C bond.

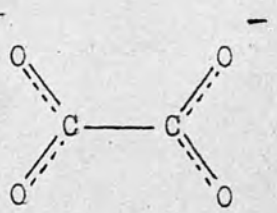


dimethyl oxalate

covalent



bidentate oxalate ligand



oxalate ion

ionic

In the complex $[Coen_2C_2O_4]Br$ the vibration due to the antisymmetric CO stretch is easily found as a group of three bands at 1689, 1672 and 1650 $cm.^{-1}$ in comparison with corresponding bands in trans-$[Coen_2Cl_2]C_2O_4H$ which occur at 1724 and 1618 $cm.^{-1}$ and which are the frequencies for the covalent acid group and the ionic oxalate group respectively as can be seen by comparison with the spectra of dimethyl oxalate and sodium oxalate It is perhaps significant that the mean of 1724 and 1618 $cm.^{-1}$ is 1671 $cm.^{-1}$ and that the mean of the three bands of the oxalato complex is 1670 $cm.^{-1}$ suggesting that the cobalt-oxygen bond in the oxalato complex is 50% covalent as put forward by Mizushima et al.[43]

The vibration due to the symmetric CO stretch occurs as a strong band at 1405 $cm.^{-1}$ and as two bands at 1289 and 1271 $cm.^{-1}$ in the $[Coen_2C_2O_4]Br$ and as doublets at 1425, 1416 and 1285, 1269 $cm.^{-1}$ in trans-$[Coen_2Cl_2]C_2O_4H$ The frequencies of the corresponding vibrations in dimethyl oxalate and sodium oxalate again show that the vibrations of the oxalato complex lie

midway between the two sets of values suggesting that the bonding is 50% covalent in the complex.

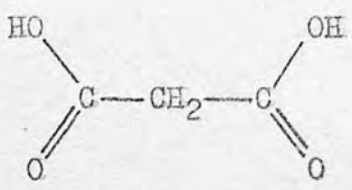
There is then a gap in the spectrum of the vibrations of the oxalato group until a medium band at 893 $cm.^{-1}$; this band is in the same place as that due to the CH_2 'rock' but it is seem to be relatively more intense. This band is assumed to arise from the C-C stretch vibration by comparison with that in sodium oxalate at 898 $cm.^{-1}$ and that in dimethyl oxalate at 862 $cm.^{-1}$ The corresponding bands in trans-$[Coen_2Cl_2]C_2O_4H$ are at 948 and 871 $cm.^{-1}$

The next band in the spectrum of $[Coen_2C_2O_4]Br$ is a strong one at 813 $cm.^{-1}$ which is probably due to deformation of the OCO group (by comparison with the spectra of sodium oxalate and dimethyl oxalate where this band appears at 768 and 851 $cm.^{-1}$ respectively). The mean of these two bands is $\sim$ 810 $cm.^{-1}$ which is close to the 813 $cm.^{-1}$ reported for the oxalato complex again showing that the cobalt-oxygen bonding in the oxalato complex is probably 50% covalent.

Lastly there are two bands at 549 and 482 $cm.^{-1}$ in the spectrum of $[Coen_2C_2O_4]Br$ which are probably due to deformation vibration of the OCO group by comparison with the spectrum of sodium oxalate where they occur at 545 and 518 $cm.^{-1}$

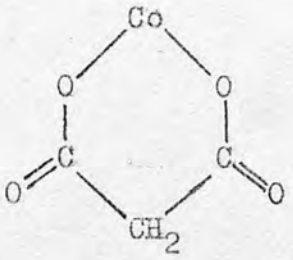
Vibrations of the malonate group

Three complexes were studied that contain the malonate group:- $[Coen_2AA]Br$, $[Coen_2AA]HAA$, trans-$[Coen_2Cl_2]HAA,H_2AA$ where $AA=CO_2CH_2CO_2^{2-}$.



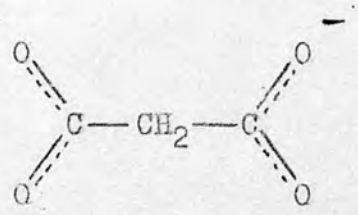
malonic acid

covalent



bidentate

malonate ligand



malonate ion

ionic

The antisymmetric CO stretch was found to occur in the spectrum of $[Coen_2AA]Br$ as a doublet at 1618 and 1610 $cm.^{-1}$ by comparison with the same vibration in sodium malonate and malonic acid where it occurs as a doublet at 1600, 1562 $cm.^{-1}$ and at 1735, 1705 $cm.^{-1}$ respectively. Thus the frequency of the band due to the complex is nearer to that of the sodium malonate suggesting that the cobalt-oxygen bond is more ionic than covalent. The same vibration gave rise to two bands in the spectrum of $[Coen_2AA]HAA$ at 1642 and 1600 $cm.^{-1}$ The corresponding bands in the spectrum of trans-$[Coen_2Cl_2]HAA,H_2AA$ are at 1715, 1634 and 1600 $cm.^{-1}$ showing that there is an ionic and a covalent malonate group in the anion of this complex as expected.

The vibration due to the symmetric CO stretch occurs as a strong band at 1420 $cm.^{-1}$ and as two bands at 1368 and 1330 $cm.^{-1}$ in the spectrum for $[Coen_2AA]Br$. These bands are at similar positions as those in potassium malonate where they occur at 1405 and 1370 $cm.^{-1}$ In the spectrum of the complex trans-$[Coen_2Cl_2]HAA,H_2AA$ there are two bands in this region

at 1408 and 1323 $cm.^{-1}$; the former corresponds to the 1405 $cm.^{-1}$ band in the spectrum of potassium malonate and the latter to a band at 1314 $cm.^{-1}$ in the spectrum of malonic acid again showing that this complex contains an ionic and a covalent malonate group in the anion.

The band at 1272 $cm.^{-1}$ in the spectrum of $[Coen_2AA]Br$ is assumed to be due to the wagging vibration of the CH_2 group in the malonato group. A similar band appears in the spectrum of $[Coen_2AA]HAA$ at 1285 $cm.^{-1}$ and at 1240 $cm.^{-1}$

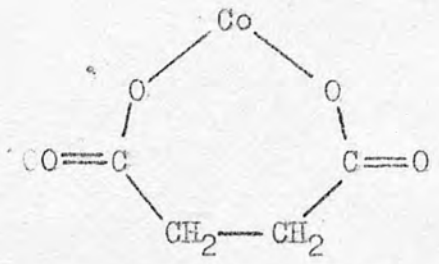
The vibration due to the C-C stretch in $[Coen_2AA]Br$ gives rise to bands at 1189, 980 and 946 $cm.^{-1}$ The corresponding bands in potassium malonate occur at 1190 and 955 $cm.^{-1}$ again showing how close the values of the complex are to the ionic salt.

Another vibration of $[Coen_2AA]Br$ which is very close to that of the ionic salt is the (OCO) bending vibration which occurs at 812 $cm.^{-1}$ in the spectrum of the complex and at 813 $cm.^{-1}$ in that of sodium malonate.

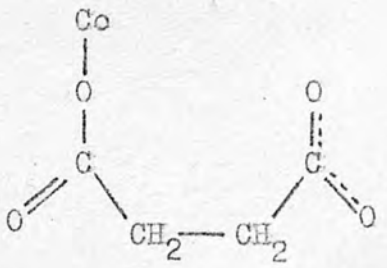
Vibrations of the succinate group

Two complexes were studied containing the succinate group:- $[Coen_2AA]Br$ and trans-$[Coen_2Cl_2]HAA$ where $AA = CO_2(CH_2)_2CO_2^{2-}$.

The antisymmetric CO stretch vibration was found to appear in the spectrum of $[Coen_2AA]Br$ at 1698 and 1520 $cm.^{-1}$, the former being characteristic of the C=O stretch vibration as found in carboxylic acids and the latter being characteristic of the antisymmetric vibration of the CO_2^- group,



bidentate succinate ligand



unidentate succinate ligand

as found in ionised carboxylic salts. This suggests that in the succinato complex as prepared the succinate group is present as a unidentate ligand with one end containing an ionic CO_2^- group and the other end containing a covalent group. The symmetric CO stretch vibration was found to appear as a doublet at 1370 and 1351 $cm.^{-1}$ close to the value obtained for the corresponding ionic salts.

In the spectrum of <u>trans</u>-$[Coen_2Cl_2]HAA$ the antisymmetric CO stretch vibration again appears as two bands at 1700 and 1608 $cm.^{-1}$ showing the presence of an ionic and a covalent succinate group in the anion. The symmetric CO stretch vibration appears at 1404 $cm.^{-1}$, being characteristic of an ionic CO_2^- group.

On inspection the spectrum of <u>trans</u>-$[Coen_2Cl_2]HAA$ is seen to be quite similar to that of the corresponding malonate and the spectrum of $[Coen_2AA]Br$, except for the antisymmetric CO vibrations, is similar to that of the malonato complex.

Comparison of the Spectra of the Carboxylate Groups

Use is made of the generalisation that the spectra of carboxylic acids contain absorption in the region 1725-1700(s) $cm.^{-1}$ due to the C=O stretch and in the regions 1400-1395(w) and 1320-1211(s) $cm.^{-1}$ due to the C-O stretch. Whereas the spectra of the salts of carboxylic acids contain absorptions in the regions 1610-1550(s) and 1420-1300(s) $cm.^{-1}$ due to the antisymmetric and symmetric vibrations of the CO_2^- group. Also the frequency difference between the antisymmetric and symmetric vibrations of the CO_2^- group in the complex increases as the bonding becomes more covalent.

The frequency differences for the complexes can be calculated in $cm.^{-1}$:-

$[Coen_2AA]Br$	carbonato	oxalato	malonato
$\nu_a(CO)$	1613, 1607	1689, 1672, 1650	1618, 1610
mean	1610	1670	1614
$\nu_s(CO)$	1282, 1276	1289, 1271	1368, 1330
mean	1279	1280	1349
separation ($cm.^{-1}$)	331	390	265

This gives an order for the degree of covalency in the cobalt-oxygen bond:- oxalato > carbonato > malonato. Since the oxalato complex has been shown to have a covalency of about 50% it can be assumed that the other complexes contain cobalt-oxygen bonds which are more ionic than covalent which is also reflected in some of their properties and can be understood when reference is made to models of these complexes since it is then seen that the bidentate oxalate group forms the most stable ring (5-membered) with a minimum of strain whereas the carbonate group forms a strained ring

and the malonate group a puckered ring.

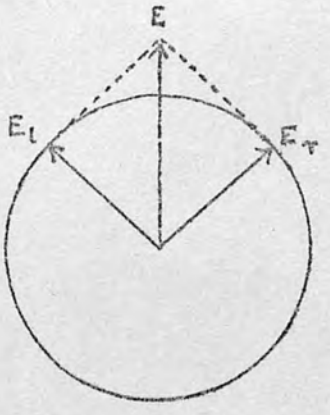
In the case of the succinate group, if this group were to form a bidentate ligand it would be under considerable strain and the spectrum is seen to support the fact that it more likely exists as a unidentate ligand. This would also help to explain the fact that the succinato complex was never obtained in a crystalline form but only as a gel or an amorphous powder.

OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

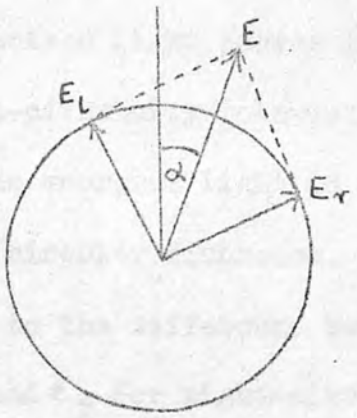
INTRODUCTION

Optical activity is the phenomenon exhibited by substances which will rotate the plane of linearly polarised light. In the case of complex compounds optical activity arises because the structure of the molecule is disymmetric, i.e. the compound can exist in two forms whose structures are non-superimposable mirror images which have no plane of symmetry or centre of symmetry.

A ray of linearly polarised light may be regarded as equivalent to equal components of left- and right-circularly polarised light, i.e. the electric field vector traces out a left- and a right-handed helix, E_l and E_r, to give the resultant electric field vector, E, of linearly polarised light.



In an optically active medium the two circularly polarised components travel with different velocities so that the plane of polarisation is rotated through an angle, α. Since the velocity of a light wave travelling through a medium is proportional to the refractive index of the medium a substance is optically active if it has different refractive indices n_l for left- and n_r for right-circularly polarised light, i.e. it is circularly birefringent.



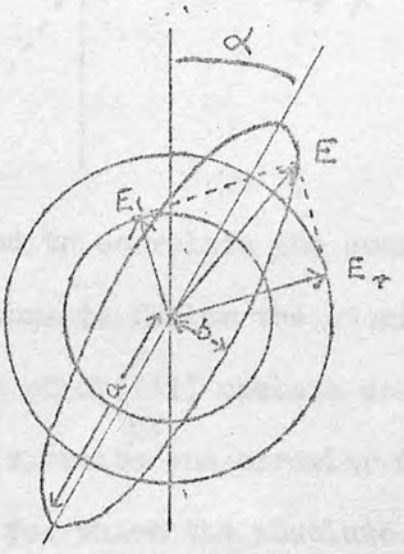
The angle of rotation depends on the difference between n_l and n_r, the thickness of the medium, the concentration of the solution, the nature of the solvent, the wavelength of the light used and the temperature. The specific rotation $[\alpha]_\lambda$ at a given wavelength and temperature for a particular solvent is given by Biot's Law: $$[\alpha]_\lambda = \frac{\alpha}{l \times c}$$ where l is the thickness of the medium in decimetres,

c is the concentration of the solution in grams per c.c.

The molecular rotation is given by: $$[M]_\lambda = \frac{M \times [\alpha]_\lambda}{100}$$ where M is the molecular weight.

The variation of the optical rotation with wavelength is known as optical rotatory dispersion. For a compound containing no chromophore the optical activity progressively increases or decreases with increasing wavelength to give a plain dispersion curve. For a compound with one or more optically active absorption bands the dispersion curve is anomalous and shows one or more $\int$-shaped curves in the region in which the chromophores absorb. In the ideal case where an optically active absorption band is not affected by other bands the mean of the wavelengths at which the peak and trough occur coincides almost exactly with the point of zero rotation and is also approximately identical with the wavelength of maximal ultra-violet absorption.

If, when linearly polarised light passes through an optically active medium, the left- and right-circularly polarised light are absorbed to a different extent, then the emergent light is elliptically polarised and the phenomenon is known as circular dichroism. The minor axis of the resulting ellipse is equal to the difference between the molar extinction coefficients ϵ_l for left- and ϵ_r for right-circularly polarised light.

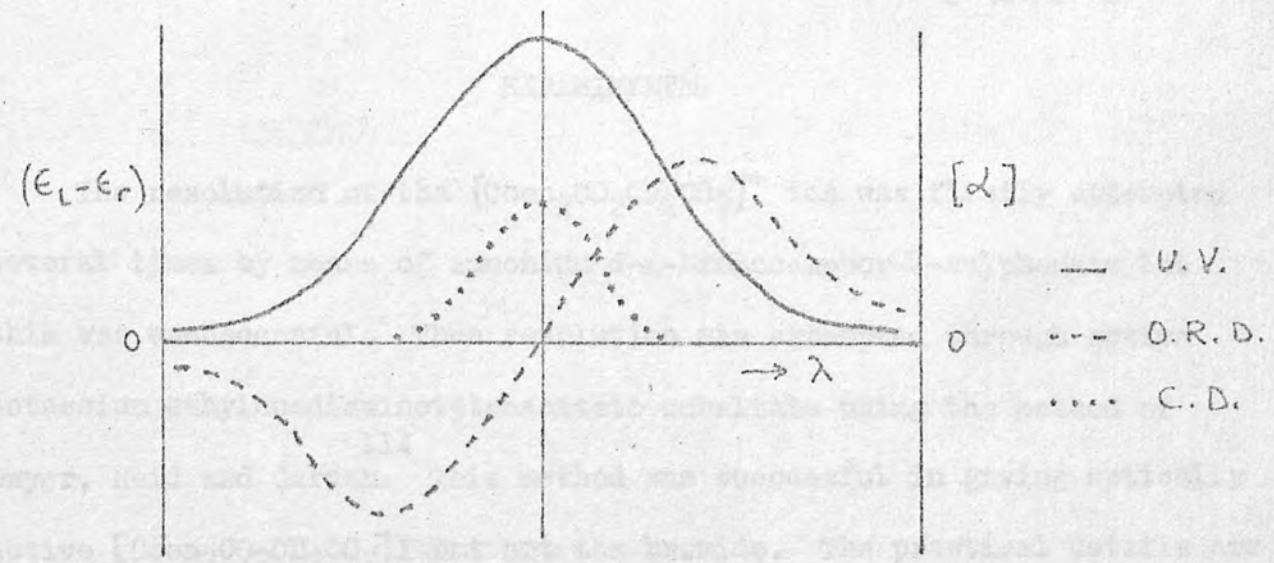


$$a = \epsilon_l + \epsilon_r$$
$$b = \epsilon_l - \epsilon_r$$

The variation of $(\epsilon_l - \epsilon_r)$ with wavelength is observed as a peak or trough, the maximum wavelength of which almost coincides with the maximum of an ultra-violet absorption band.

The combination of optical activity and circular dichroism is observed in what is termed the "Cotton effect". The Cotton effect associated with an optically active absorption band of a given compound is seen as an anomalous optical rotatory dispersion curve and a circular dichroism curve. If the dispersion curve consists of one peak and one trough it is referred to as a single Cotton effect and if the peak occurs at higher wavelength than the trough it is a positive Cotton effect and the circular dichroism curve will occur as a peak. For one enantiomorph the Cotton effect will be the reverse of that of the other enantiomorph.

Positive Cotton Effect



Cotton effects are used to correlate the configurations of related disymmetric molecules and thus to follow the steric course of reactions. The absolute configurations of Co(III) chelate complexes have been related through optical rotatory dispersion[62] and circular dichroism[63] spectra to optically active $[Coen_3]^{3+}$ for which the absolute configuration is known by means of anomalous X-ray dispersion.[64]

Also the kinetics of a reaction which results in loss of optical activity can be examined by observing the change in the optical rotation of the substance at a particular wavelength. The optimum wavelength for this can be obtained from the optical rotatory dispersion curve, that is the point of highest rotatory power.

OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

EXPERIMENTAL

The resolution of the $[Coen_2CO_2CH_2CO_2]^+$ ion was firstly attempted several times by means of ammonium d-α-bromocamphor-π-sulphonate but this was unsuccessful. Then resolution was attempted through active potassium ethylenediaminetetraacetato cobaltate using the method of Dwyer, Reid and Garvan.[114] This method was successful in giving optically active $[Coen_2CO_2CH_2CO_2]I$ but not the bromide. The practical details are in the section on preparation of compounds, (page 147).

Optical rotation measurements were carried out on a Hilger Standard polarimeter using a mercury arc lamp. A 0.05% solution of the active $[Coen_2CO_2CH_2CO_2]I$ was made up and its angle of rotation was measured on the yellow, green and blue lines. The solution was then kept for three days and the readings were repeated to see if there was any change in the optical rotation.

The optical rotatory dispersion was then measured using a 0.2% solution of the complex in a Hilger photoelectric polarimeter with a Zenon lamp which had been especially adapted for the purpose by Dr. Hargreaves of Queen Elizabeth College, University of London. The angles of rotation for each wavelength were converted to the molecular rotation [M] and a graph was plotted of [M] against wavelength to give the optical rotatory dispersion curve.

The visible and ultra-violet absorption spectra of a solution of the active iodide was also obtained so as to compare it with the rotatory dispersion curve.

OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

1st preparation 0.05% solution in 2 dec. tube

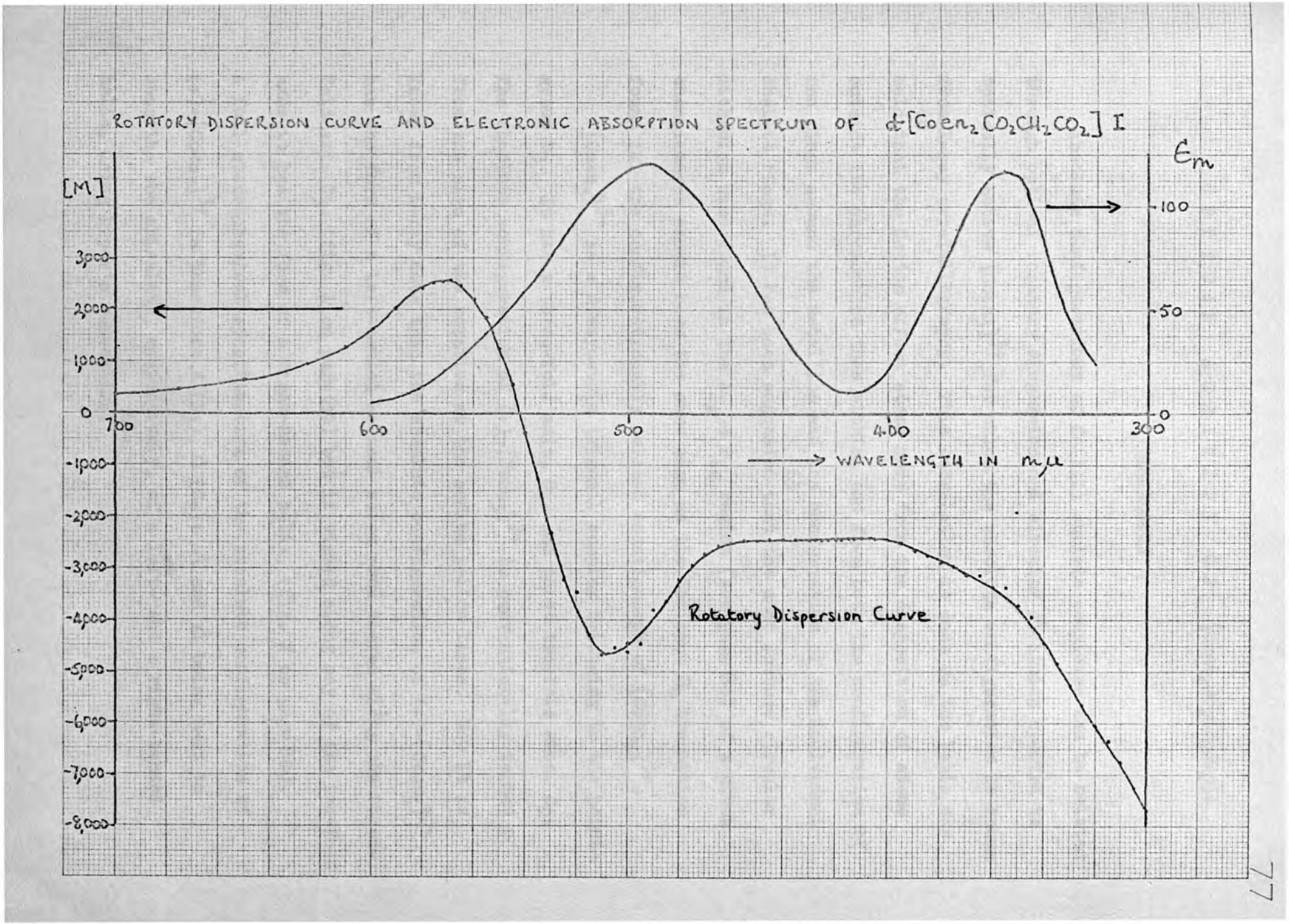
wavelength Å		α	$[\alpha]_\lambda$	$[M]_\lambda$
yellow	5791	+0.54°	+540°	+2204°
green	5461	+0.37°	+370°	+1510°
blue	4047	-0.56°	-560°	-2285°

Above solution after three days

wavelength Å		α	$[\alpha]_\lambda$	$[M]_\lambda$
yellow	5791	+0.56°	+560°	+2285°
green	5461	+0.37°	+370°	+1510°
blue	4047	-0.62°	-620°	-2530°

2nd preparation 0.05% solution in 2 dec. tube

wavelength Å		α	$[\alpha]_\lambda$	$[M]_\lambda$
yellow	5791	+0.55°	+550°	+2245°
green	5461	+0.39°	+390°	+1592°
blue	4047	-0.57°	-570°	-2326°


ROTATORY DISPERSION CURVE AND ELECTRONIC ABSORPTION SPECTRUM OF d-[Coen2CO2CH2CO2] I
[M]
3,000
2,000
1,000
0
-1,000
-2,000
-3,000
-4,000
-5,000
-6,000
-7,000
-8,000
700
600
500
400
300
WAVELENGTH IN mμ
εm
100
50
0
Rotatory Dispersion Curve

OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

DISCUSSION

Absolute configurations of Co(III) chelate complexes can be related through optical rotatory dispersion and circular dichroism spectra to optically active $[Coen_3]^{3+}$ for which the absolute configuration is known from X-ray crystallography. This correlation is made on the basis now held that the Cotton effect stems more from the disposition of atoms outside the chromophore than within, and from both the configuration of the rings around the metal ion and the conformation of the individual chelate rings.[66] It has been suggested[63] that the most intense circular dichroism band found in the $A_{1g} \rightarrow T_{1g}$ region (see page 84) of a given enantiomorph should have the same sign as the dominant E_a transition found for the configurationally related enantiomorph of $[Coen_3]^{3+}$.

$[Coen_3]^{3+}$ is a dissymetric trigonal complex belonging to the point-group D_3. It has a three-fold axis, C_3, and three two-fold axes, C_2. The absolute configuration of (+)-$[Coen_3]^{3+}$ is conventionally termed D from the sign of the rotation at the sodium yellow lines. Now it is known from X-ray data that the absolute configuration of (+)-$[Coen_3]^{3+}$ has the form of a left-handed helical screw when viewed along the three-fold axis C_3, (fig. 1 on page 80) but if viewed along any of the two-fold axes it has the form of a right-handed helix, (fig. 2 on page 80). A full stereochemical specification of the absolute configuration of (+)-$[Coen_3]^{3+}$ is therefore Λ (C_3), Δ (C_2); Λ and Δ being used to describe the chirality, respectively, of a left- and a right-handed helix, using Piper's convention.[66a]

Bisdiamine complexes of the type cis-$[Coen_2X_2]^+$ belong to the point-group C_2 and are related to the tris(diamine)$[Coen_3]^{3+}$ by a common two-fold axis (C_2). A bisdiamine complex and the corresponding trisdiamine have a similar stereochemical configuration if the handedness of the chelate rings around the metal ion is the same when viewed along the common two-fold axis. So that a bisdiamine for which the stereochemical arrangement of the chelate rings about the metal ion is right-handed when viewed along the two-fold axis C_2 is designated Δ (C_2), (fig.4 on page 80).

The isomer (+)-$[Coen_3]^{3+}$ gives rise to a positive Cotton effect,[67] its stereochemical chirality is left-handed along the three-fold axis C_3 and right-handed along the two-fold axis C_2 so that the isomer is designated Λ (C_3), Δ (C_2). The malonato complex was resolved and the isomer studied was termed (+)-$[Coen_2CO_2CH_2CO_2]^+$ from the sign of the rotation at the sodium yellow lines. From the rotatory dispersion curve of the isomer it is seen to give rise to a positive Cotton effect so that it is configurationally related to (+)-$[Coen_3]^{3+}$ and hence its absolute configuration is Δ (C_2) from the right-handed chirality of the complex along the two-fold axis C_2. The configuration of this complex can also be designated Λ (C_3) using the pseudo-C_3 axis (fig.3 on page 80).

The isomer studied did not lose its optical activity when left for three days at room temperature in aqueous solution. This behaviour is similar to that obtained for the optically active isomer of the oxalato complex $[Coen_2C_2O_4]Cl$.[114] This isomer has been shown to undergo no racemisation after five days at 18°C and to be decomposed on long boiling.[114]

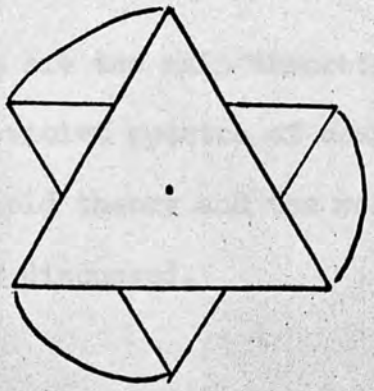


fig 1

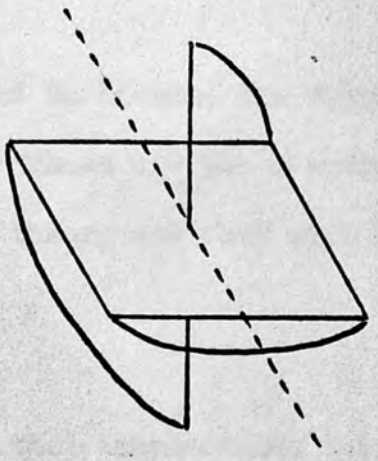


fig 2

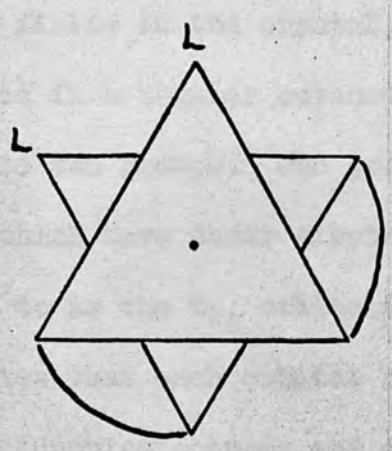


fig 3

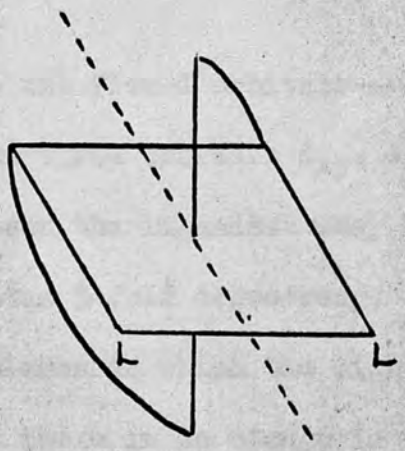


fig 4

VISIBLE AND ULTRA-VIOLET SPECTRA

INTRODUCTION

There are two main theoretical methods used to discuss the visible and ultra-violet spectra of complex compounds. These are the electrostatic crystal field theory and the molecular orbital theory and they will now be briefly discussed.

The Electrostatic Crystal Field Theory assumes that interactions between metal ions and ligands are strictly electrostatic in the sense that the metal ion orbitals do not in any way mix with ligand atom orbitals, that is, covalent bonding is neglected. The essence of the crystal field theory is to use group theory as applied to symmetry operations to deduce the splitting of atomic energy levels due to symmetry properties of the electric fields in the crystal.

Hence in a regular octahedral environment the five d orbitals are split into two groups. One group comprises the three orbitals d_{xy}, d_{yz}, and d_{xz} which have their electron density between the ligands. They are referred to as the t_{2g} orbitals where t indicates 3-fold degeneracy, 2 indicates that each orbital has two mirror planes in which the sign of the wave function changes and g indicates that there is no change in the wave function on inversion through the origin. The other group of orbitals, $d_{x^2-y^2}$ and d_{z^2}, have their electron density directed towards the ligands and are therefore less stable than the former group. They are referred to as the e_g orbitals where e indicates 2-fold degeneracy.

There is thus an energy level splitting between the two groups of

orbitals referred to as Δ_o where o indicates octahedral environment. But from group theory it is not possible to obtain the magnitude of this splitting.

Mention must also be made of the ligand field theory which uses the basic electrostatic viewpoint and the methods of calculation of the crystal field theory, but the effective field is considered to be imposed not by the whole crystal but by the ligands which surround the atom in question so that covalent forces are taken into account.

The Molecular Orbital Theory starts with the premise that overlap of orbitals will occur, to some degree, wherever symmetry permits. It thus includes the electrostatic situation (no overlap) as one extreme, maximal overlapping of orbitals as the other extreme, and all intermediate degrees of overlap. To find out which orbitals have suitable symmetry requirements for overlap, group theory is used.

A metal ion in the first transition series has 9 orbitals available for bond formation: 4s, 4p and 3d. But only six of these have suitable symmetry requirements to overlap with σ ligand orbitals. They are the 4s, 4p and the $3d_{x^2-y^2}$ and $3d_{z^2}$ (the e_g d orbitals). They therefore combine to form six bonding and six anti-bonding orbitals of which the two e_g anti- bonding orbitals are in the lowest energy state. The three t_{2g} d orbitals (d_{xy}, d_{xz}, and d_{yz}) are unaffected by σ bonding and remain as non-bonding orbitals. The twelve electrons from the six ligands will all go in the six bonding orbitals and the electrons from the metal ion will be located in the t_{2g} non-bonding and the e_g anti-bonding orbitals. So, as in the crystal field theory, there is an energy level splitting Δ_o between t_{2g} and e_g orbitals.

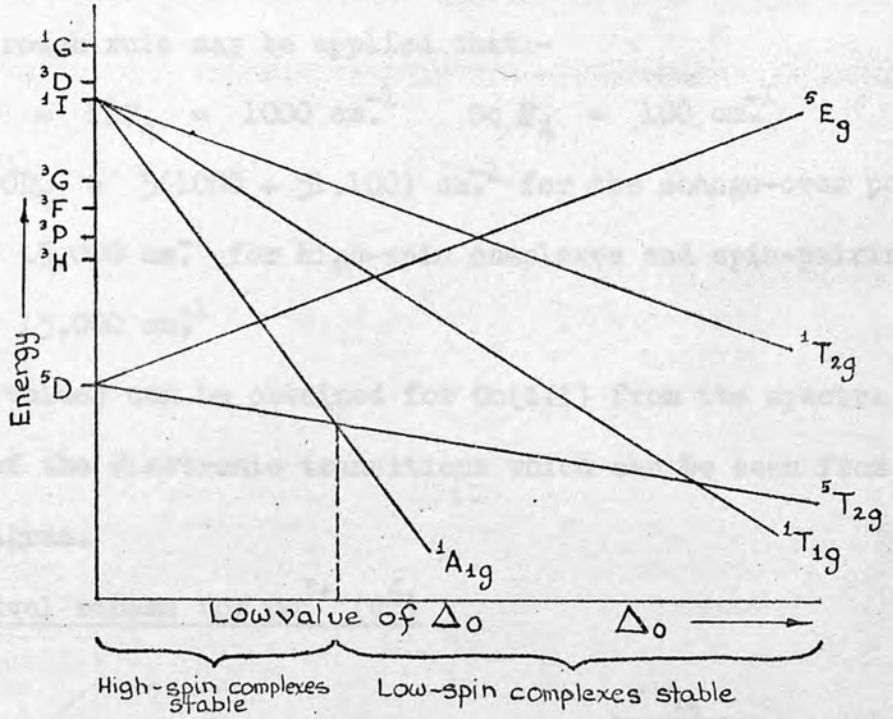
Absorption Spectra

The absorption spectra of a complex ion is caused by electronic transitions between the different energy levels into which the d orbitals are split. The nature of the spectra is determined by the extent of the splitting of the d orbitals. If the splitting is small, i.e. weak ligand field, then the electrons will be unpaired with their spins parallel, called the spin-free case. But if the splitting is large, i.e. strong ligand field, then the electrons will be forced to fill the t_{2g} orbitals before occupying the e_g orbitals. The electrons are therefore forced into pairing and this is called the spin-paired case.

Before the spectra can be interpreted for a metal ion with more than one d electron it is necessary to know the lowest energy state. In the free ion the d electrons couple into the various Russell-Saunders states and all these are split in the presence of a ligand field.

In the case of Co(III) (d^6 system) the electronic ground state for the free ion is ^5D (L=2, S=2) so that the spins are unpaired. In a weak ligand field the lowest state originating from ^5D is $t_{2g}^4 e_g^2$ with a $^5T_{2g}$ ground term and this is the high-spin case. Complexes with a high spin are $[CoF_6]^{3-}$ (μ_{eff} = 5.2 B.M.) and also $[CoF_3(H_2O)_3]$ (μ_{eff} = 4.47 B.M.)[70] so that the moment indicates four unpaired spins with some orbital contribution.

However, there are very few high-spin cases for Co(III) because at a low value of Δ_o the electrons pair up their spins to give the configuration t_{2g}^6. The Orgel diagram (see next page) shows that the $^1A_{1g}$ state arising from the high energy singlet state ^1I of the free ion becomes the ground term at a low value of Δ_o.



The condition for the change from high-spin to low-spin complexes occurs at:-

$$20D_q = 5 (F_2 + 51F_4)$$

This is the cross over point between the $^5T_{2g}$ and $^1A_{1g}$ states.

The F terms are the Condon and Shortley ligand field stabilisation parameters, values for which can be obtained from the spectra of the free ion, and $10D_q = \Delta_o$.

Ballhausen[71] states that in the weak-field case ($t_{2g}^4 e_g^2$) the field stabilisation is only $4D_q$ but in the strong-field case (t_{2g}^6) it becomes $24D_q$ because $10D_q$ is gained by every electron transferred from an e_g shell to a t_{2g} shell. But this stabilisation is achieved at the expense of some $5(F_2 + 51F_4)$ in promotional energy. Hence the changeover from weak-field case to strong-field case occurs at:-

$$24D_q - 4D_q = 5 (F_2 + 51F_4)$$

$$\text{i.e. } 20D_q = 5 (F_2 + 51F_4)$$

Ballhausen[71] indicates that for the Fe(II) case, another characteristic d^6 case, the rough rule may be applied that:-

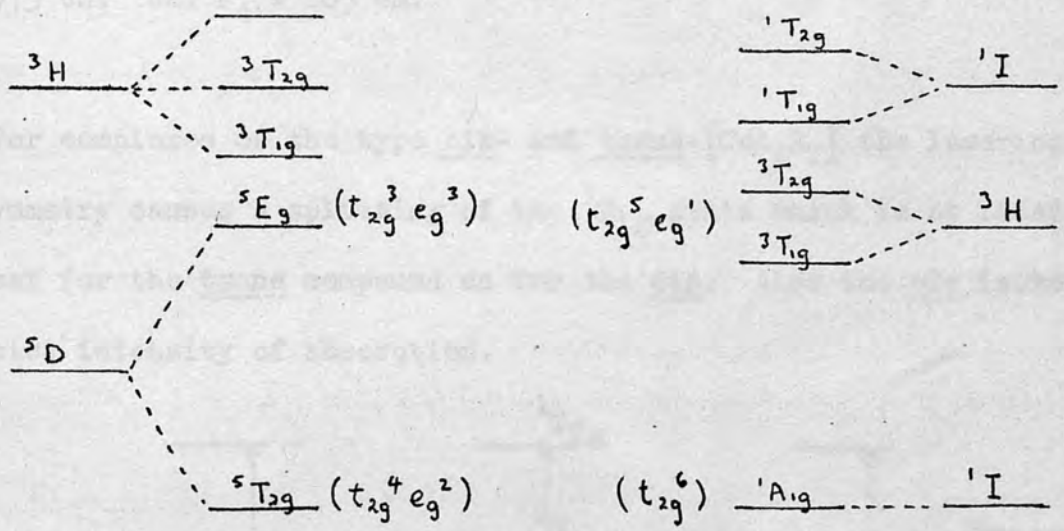
$$F_2 = 10F_4 = 1000 \text{ cm.}^{-1} \quad \text{So } F_4 = 100 \text{ cm.}^{-1}$$

whence $20D_q = 5(1000 + 51.100) \text{ cm.}^{-1}$ for the change-over point

Hence $10D_q < 15{,}000 \text{ cm.}^{-1}$ for high-spin complexes and spin-pairing occurs when $10D_q > 15{,}000 \text{ cm.}^{-1}$

Similar values can be obtained for Co(III) from its spectra and from a knowledge of the electronic transitions which can be seen from the following diagram.

The energy level scheme for Co^{3+} (d^6)



weak field
high-spin complex

strong field
low-spin complex

For Co(III) in the spin-free $[CoF_6]^{3-}$ complex the spectroscopic transition $^5T_{2g} \rightarrow {}^5E_g$ occurs at 13,000 cm.^{-1} [72]

For spin-paired complexes the spectra should be made up of two strong bands corresponding to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In addition some singlet-triplet bands could appear.

So that for the singlet--singlet bands

$$\Delta E\ (^1T_{1g} - {}^1A_{1g}) = -35F_4 + 10D_q$$

$$\Delta E\ (^1T_{2g} - {}^1A_{1g}) = 16F_2 - 115F_4 + 10D_q$$

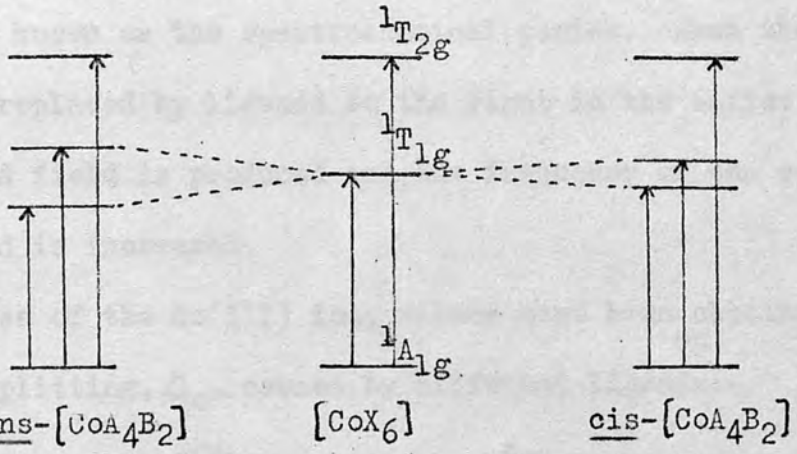
and for the singlet-triplet bands

$$\Delta E\ (^3T_{1g} - {}^1A_{1g}) = -105F_4 + 10D_q$$

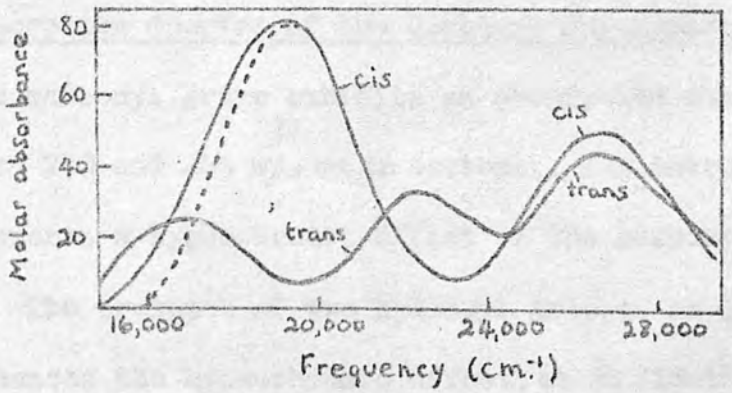
$$\Delta E\ (^3T_{2g} - {}^1A_{1g}) = 8F_2 - 245F_4 + 10D_q$$

In the spectrum of the spin-paired complex $[Coen_3]^{3+}$ [73] two strong bands occur at 21,400 $cm.^{-1}$ ($^1A_{1g} \rightarrow {}^1T_{1g}$) and 29,600 $cm.^{-1}$ ($^1A_{1g} \rightarrow {}^1T_{2g}$) and a very broad spin-forbidden band at $\sim$14,000 $cm.^{-1}$ ($^1A_{1g} \rightarrow {}^3T_{1g}$). From this the following values are obtained:- D_q = 2,510 $cm.^{-1}$, F_2 = 975 $cm.^{-1}$ and F_4 = 105 $cm.^{-1}$

For complexes of the type <u>cis</u>- and <u>trans</u>-$[CoA_4B_2]$ the lowering of the symmetry causes a splitting of the $^1T_{1g}$ state which is at least twice as great for the <u>trans</u> compound as for the <u>cis</u>. Also the <u>cis</u> isomer shows a greater intensity of absorption.



[74] The measurements of Basolo, Ballhausen and Bjerrum show this to be approximately true for a variety of substituted Co(III) complexes. [75] Similar results have been obtained by Nakamoto <u>et al</u>.



The visible spectra of cis- and trans-$[Coen_2F_2]^+$. The dotted line shows where the low frequency side of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band of the cis isomer would be if the band were completely symmetrical.

The Spectrochemical Series

It has been found by study of the spectra of complexes containing various metal ions and ligands, that the ligands may be arranged in a series according to their capacity to cause d-orbital splitting. The order of increasing ligand field strength, Δ_o, is as follows:-

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < -NCS^- < NH_3 < en < NO_2^- < CN^-$

This series is known as the spectrochemical series. When the ligands in a complex are replaced by ligands to the right in the series then a stronger ligand field is produced and the frequency of the corresponding absorption band is increased.

In the case of the Co(III) ion, values have been obtained for the ligand field splitting, Δ_o, caused by different ligands:- [76]

$6H_2O$	$6NH_3$	3en	$6CN^-$
18,600	23,000	23,300	34,000 $cm.^{-1}$

Ultra-Violet Absorption Spectra of the Carbonyl Chromophore

The ketonic carbonyl group exhibits an absorption maximum of low intensity between 270 and 285 mμ.[77] as in acetone. The introduction of a hydroxyl group exerts a hypsochromic effect on the carbonyl absorption as in acetic acid. The presence of two hydroxyl groups, as in carbonic acid derivatives, enhances the hypsochromic effect, as in dimethyl carbonate.

	λ_{max}	ϵ_{max}	Reference
CH_3COCH_3	274 mμ	13.5	78
CH_3COOH	204 mμ	44.5	78
$(CH_3)_2CO_3$	< 180 mμ	> 50	78

Dimethyl oxalate and anhydrous oxalic acid exhibit a characteristic band of low intensity in the region 210-260 mμ.[79] which is identified with the covalently bound carboxyl group and is most likely due to transitions of the π electrons of the $>C=O$ group. This band is absent in the ultra-violet absorption spectrum of aqueous potassium oxalate solution and there is only an inflexion in the case of aqueous oxalic acid indicating that there are no covalently bound carboxyl groups present in these compounds.

The ultra-violet absorption spectra of a great majority of metal oxalato complexes resemble that of dimethyl oxalate with a low intensity band in the region 250-270 mμ.[79] Graddon has found that the maxima varies with the cation. The absorption maximum is seen to increase smoothly with z/d^2, where z is the oxidation number of the cation and d is the "ideal" covalent-bond distance from metal to oxygen. Thus, the low intensity band, which is characteristic of a covalently bound oxalate, is displaced towards longer wavelengths as the coulombic force of attraction between the cation and the coordinated oxalate group increases.

VISIBLE AND ULTRA-VIOLET SPECTRA

EXPERIMENTAL

Most of the visible and ultra-violet spectra were obtained by means of a Unicam SP 500. This entailed measuring the optical density at selected wavelengths from 600 to 220 mμ and then converting these to the molar extinction coefficients, ϵ_m. Graphs were plotted of ϵ_m against wavelength and $\log \epsilon_m$ against wavelength to show at which wavelengths the peaks, indicating maximum absorption, occurred. Some of the later spectra were measured on a recording Unicam SP 700 when this was made available and this greatly facilitated measurements.

Compounds of the type $[Coen_2CO_3]X$

The visible spectra of these complexes in the solid state were obtained where X = chloride, bromide, iodide, nitrate, perchlorate, thiocyanate, dithionate and sulphate. These spectra of solids were measured by means of a reflectance unit using magnesium carbonate as a reference. In this case only the optical density and not the molar extinction coefficient could be obtained. These spectra were only measured from 600 to 350 mμ since the glass of the cells used absorbed at wavelengths below 350 mμ.

Compounds of the type $[Coen_2AA]X$

The visible and ultra-violet spectra were measured for complexes containing the dicarboxylate group AA = carbonate, oxalate, malonate and succinate and X = Br. Also the spectra were obtained for the complexes

where AA = malonate, X = the appropiate univalent malonate anion; and AA = succinate, X = perchlorate.

The spectra of all these complexes were obtained for the solid state and for solutions in water.

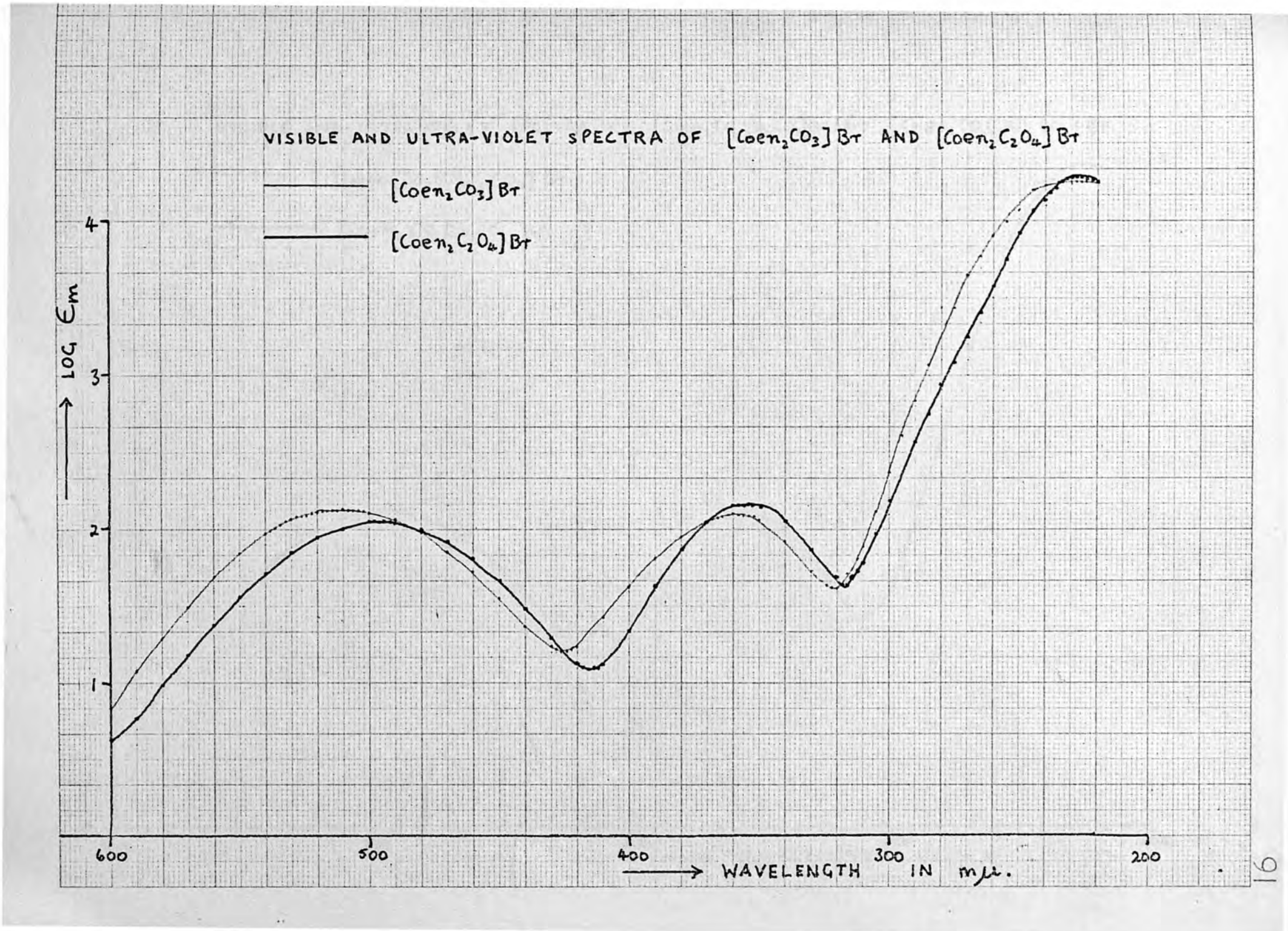
Action of Alkali on Carboxylate Ligands

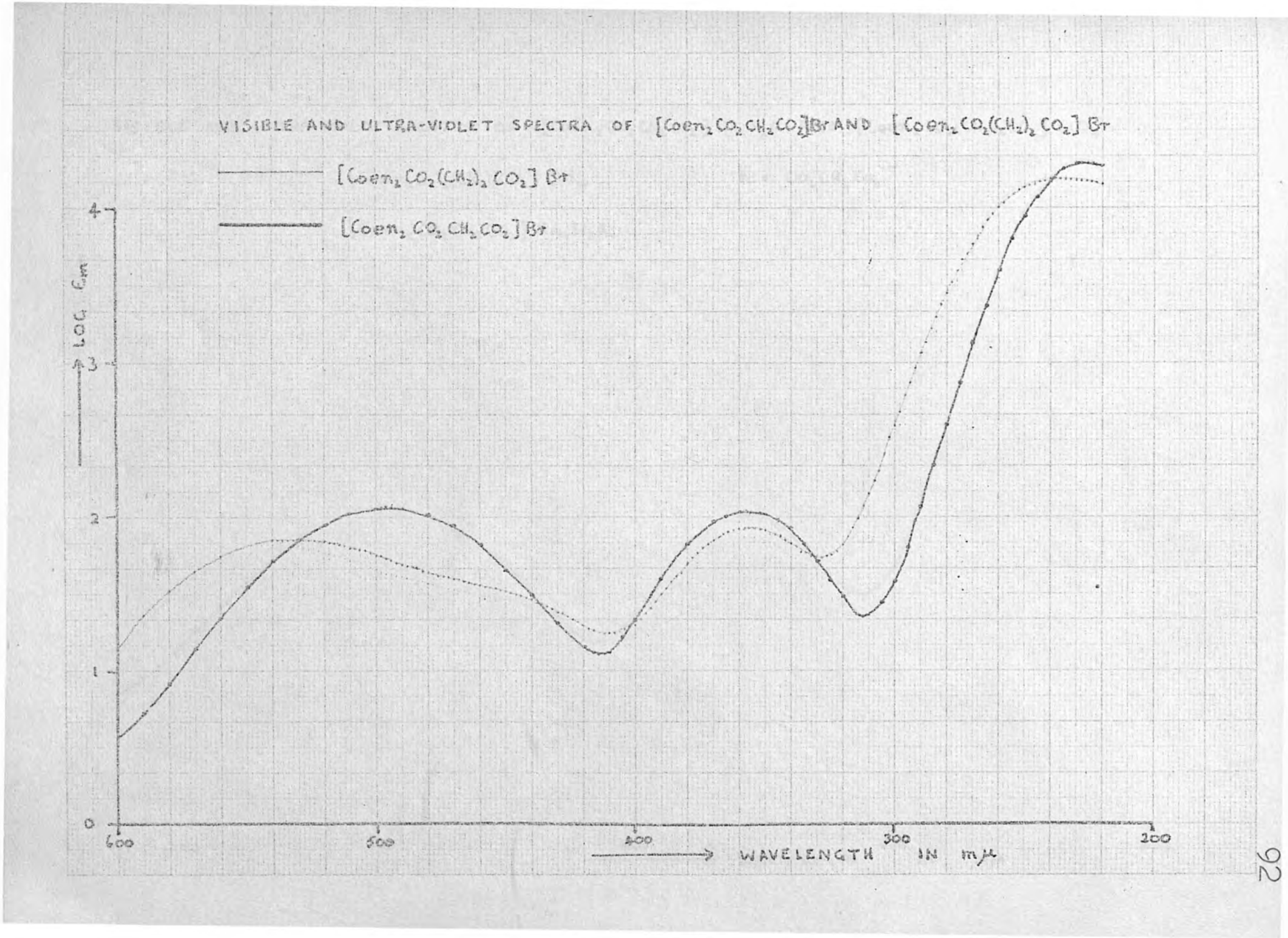
The action of sodium hydroxide solution on complexes of the type $[Coen_2AA]Br$, where AA = oxalate, malonate and succinate, was obtained by means of spectral measurements. A solution of 10^{-2} M complex was made up in ~1N sodium hydroxide and a series of three spectra were taken for each complex:- firstly the initial spectrum was measured, and then the spectrum after leaving the solution to stand for about three days, and then the solution was heated to ensure completion of reaction and a final spectrum was obtained. In each case the second and third spectra were found to be the same so that only the initial and final spectra have been recorded.

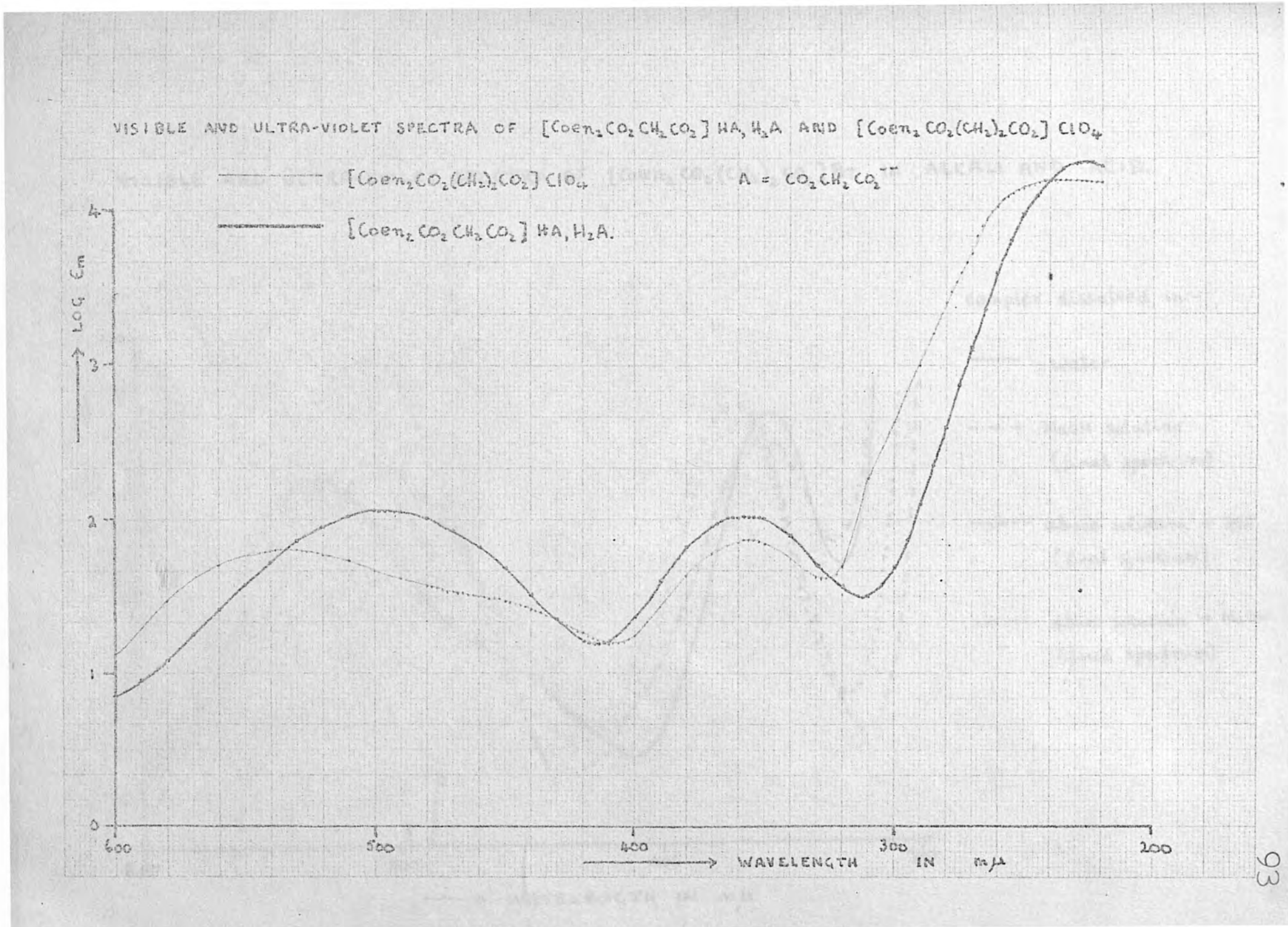
After these measurements had been made 3 ml. of ~1N hydrochloric acid were added to 3 ml. of the solution of complex in sodium hydroxide which had completed reaction and again initial and final spectra were obtained. In the case of the succinato complex to 4 ml. of this acidified solution was added 2 ml. of ~1N sodium hydroxide solution and the spectrum was measured.

Action of Acid on Carboxylate Ligands

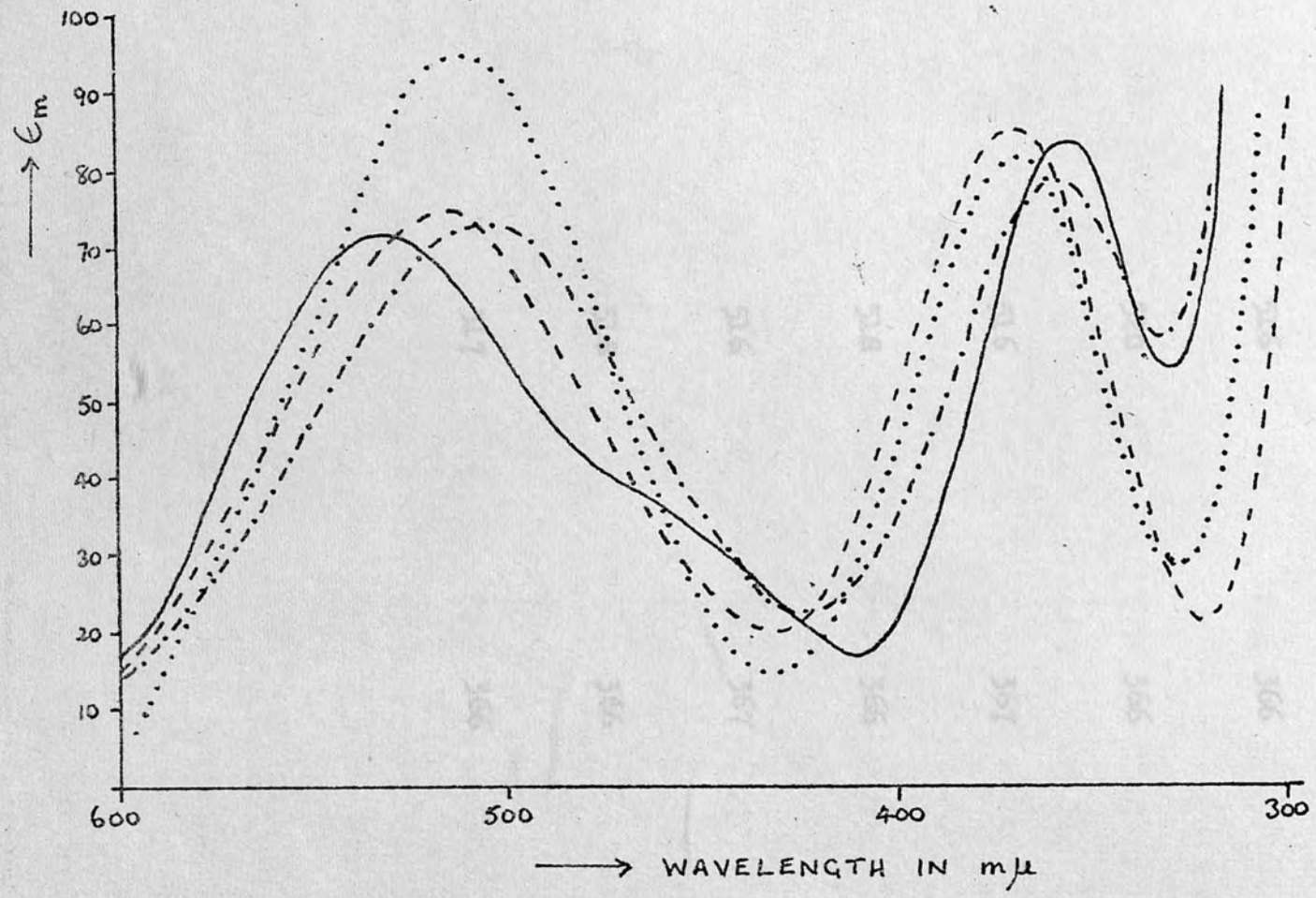
The action of solutions of perchloric acid of differing concentrations on the malonato and succinato complexes was obtained by spectral measurements made after successive timed intervals.


VISIBLE AND ULTRA-VIOLET SPECTRA OF [Coen$_2$CO$_3$]Br AND [Coen$_2$C$_2$O$_4$]Br
[Coen$_2$CO$_3$]Br
[Coen$_2$C$_2$O$_4$]Br
LOG ϵ_m
4
3
2
1
600
500
400
300
200
WAVELENGTH IN mμ.


VISIBLE AND ULTRA-VIOLET SPECTRA OF [Coen₂CO₂CH₂CO₂]Br AND [Coen₂CO₂(CH₂)₂CO₂]Br
[Coen₂CO₂(CH₂)₂CO₂]Br
[Coen₂CO₂CH₂CO₂]Br
LOG εm
4
3
2
1
0
600
500
400
300
200
WAVELENGTH IN mμ


VISIBLE AND ULTRA-VIOLET SPECTRA OF [Coen2CO2CH2CO2]HA, H2A AND [Coen2CO2(CH2)2CO2]ClO4
[Coen2CO2(CH2)2CO2]ClO4
A = CO2CH2CO2--
[Coen2CO2CH2CO2]HA, H2A.
Log ε
4
3
2
1
0
600
500
400
300
200
WAVELENGTH IN mμ

VISIBLE AND ULTRA-VIOLET SPECTRA OF $[Coen_2CO_2(CH_2)_2CO_2]Br$ IN ALKALI AND ACID.



complex dissolved in:-

——— water

– – – NaOH solution (final spectrum)

–·–·– above solution + HCl (final spectrum)

····· above solution + NaOH (final spectrum)

VISIBLE AND ULTRA-VIOLET SPECTRA OF COMPLEXES OF THE TYPE $[Coen_2CO_3]X$ IN THE SOLID STATE

X	Wavelengths at maximum optical densities, mμ	
Cl	518	364
Br	516	366
I	520	366
NO_3	516	367
ClO_4	518	366
SCN	516	367
$\frac{1}{2}S_2O_6$	518	366
$\frac{1}{2}SO_4$	517	366

VISIBLE AND ULTRA-VIOLET SPECTRA OF COMPLEXES OF THE TYPE $[Coen_2AA]X$

AA	Wavelengths at maximum optical densities, mμ				
X	Molar Extinction Coefficients, ϵ_m				
	solid		in water		
Carbonate	516	366	510	360	228
Bromide			135.0	126.6	17,950
Oxalate	498	353	496	355	227
Bromide			112.4	144.4	19,350
Malonate	502	356	496	356	227
Bromide			117.0	107.7	19,350
Malonate	504	359	496	356	227
Malonate anion			116.1	107.3	20,540
Succinate	532 shoulder at 450	356	534	356	246
Bromide			77.6	91.3	13,130
A different sample of same complex			71.8	85.0	15,350 (237)
Succinate			534	356	234
Perchlorate			63.6	73.4	15,450

VISIBLE AND ULTRA-VIOLET SPECTRA OF COMPLEXES OF THE TYPE $[Coen_2AA]Br$ IN SODIUM HYDROXIDE

AA			Wavelengths at maximum absorption mμ / Molar Extinction Coefficients ϵ_m	
Oxalate in NaOH		initial	500	359
10^{-2}M	1N		106.6	125.8
		final	518	372
			72.5	76.0
Malonate in NaOH		initial	500	358
10^{-2}M	1N		118.5	118.2
		final	516	370
			71.4	86.6
Malonate in NaOH + HCl		initial	496	354
$0.5x10^{-2}$M	0.5N 0.5N	and final	46.2	63.0
Succinate in NaOH		initial	518	370
10^{-2}M	0.1N	and final	75.2	86.4
Succinate in NaOH + HCl		initial	502	358
$0.5x10^{-2}$M	0.05N 0.05N	and final	74.2	80.4
Succinate in NaOH + HCl + NaOH		initial and final	512	368
$0.33x10^{-2}$M	.033N .033N .033N		95.7	82.5

VISIBLE AND ULTRA-VIOLET SPECTRA

DISCUSSION

The visible and ultra-violet absorption spectra of all the complexes studied show the same general pattern of two weak bands with molecular extinction coefficients of the order of 100 near 350 and 500 mμ and a strong band with a molecular extinction coefficient of the order 10,000 in the region 200-250 mμ.

Orgel[80] has shown that for the Co(III) ion in a strong field there are four transitions from the lower to the upper level of which only two are spin-allowed. These are the transitions fron the $^1A_{1g}$ ground state to the two upper singlet states $^1T_{1g}$ and $^1T_{2g}$ of which the latter is on a higher energy level so that the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ will give rise to an absorption band at a higher frequency (lower wavelength) than the transition $^1A_{1g} \rightarrow {}^1T_{1g}$. So that for the complexes studied, which all contain a bidentate carboxylate ligand (AA), the absorption bands correspond to the following transitions:-

wavelength	frequency	transition	
500 mμ	20,000 $cm.^{-1}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	colour of $[Coen_2AA]^+$ = red
350 mμ	28,600 $cm.^{-1}$	$^1A_{1g} \rightarrow {}^1T_{2g}$	

This can be compared with the spectrum of the spin-paired complex $[Coen_3]^{3+}$ [73] which also has two absorption bands:-

wavelength	frequency	transition	
467 mμ	21,400 $cm.^{-1}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	colour of $[Coen_3]^{3+}$ = yellow
338 mμ	29,600 $cm.^{-1}$	$^1A_{1g} \rightarrow {}^1T_{2g}$	

Thus on replacing one of the ethylenediamine ligands in $[Coen_3]^{3+}$ by a bidentate carboxylate ligand it is seen that the frequencies of the absorption bands are decreased so that the carboxylate ligands must exert a weaker ligand field as predicted from the spectrochemical series.

From the spectra of complexes of the type $[Coen_2AA]Br$, as set out on page 96, it is seen that in the solid state the visible and ultra-violet d-d bands vary in their position as shown by the following values for the visible bands in order of increasing wavelength:-

AA	oxalate	malonate	carbonate	succinate
wavelength, λ_{max}, mμ	498	502	516	532
frequency, $cm.^{-1}$	20,080	19,920	19,380	18,800

So that the strength of the ligand field produced by these carboxylate ligands decreases in the order of decreasing frequency:-

oxalate > malonate > carbonate > succinate

This decrease in the strength of the ligand field could be due in part to a decrease in covalent character of the metal-ligand bond, so that the above order indicates a decrease in covalent character of the cobalt-oxygen bond on going from left to right. Comparing this order with that obtained from the infrared spectra it is seen that the order is the same except that the malonato and carbonato have exchanged positions.

With regards to the spectra of the succinato complexes splitting of the visible band is observed in the form of a shoulder at about 450 mμ. This could suggest a trans type structure or that there is considerable strain and distortion in the molecule since this causes a splitting of the energy levels between which the transitions occur.

The bands near 250 mμ are assigned to transitions involving the carbonyl group in these complexes, as set out on page 96. The spectra of the carbonato, oxalato and malonato complexes all have a strong band at 227-228 mμ of similar intensity, ϵ_{max} = 18,000-20,500. But the spectrum of the succinato complex has a band at a higher wavelength with a lower intensity, λ_{max} = 246 mμ and ϵ_{max} = 13,130. Another preparation of the same complex gave λ_{max} = 237 mμ and ϵ_{max} = 15,350.

The ketonic carbonyl group exhibits an absorption maximum between 270 and 285 mμ.[77] The shift of this band to shorter wavelengths in the spectra of these complexes suggests that the carbonyl group in the complexes has some ionic character and hence that the cobalt-oxygen bond has some ionic character. The fact that the band in the spectrum of the succinato complex is at a longer wavelength than that in the other complexes suggests that a carbonyl group in the succinate ligand is more covalent than that in the other carboxylate ligands and hence that a cobalt-oxygen bond in the succinato complex is more covalent than that in the other complexes. This can be explained by assuming that the succinate group is present as a unidentate ligand so that the carboxylate group coordinated to the cobalt ion would be covalent and that on the other end of the succinate ligand would be ionic. This structure could explain the splitting of the visible band into the band at 532 mμ and the shoulder at about 450 mμ. The presence of the succinate ion as a unidentate ligand also agrees with the results of the infrared spectra as these also showed the presence of a covalently bound carboxylate group and an ionically bound group.

The change in the spectra of the complexes caused by the addition of alkali and acid is set out on page 97. In the case of the oxalato and malonato complexes the addition of alkali produced solutions whose final spectra were the same as that for $[Coen_2(OH)_2]^+$ as expected. When acid was then added to these solutions a spectrum was immediately obtained which corresponded to that for the $[Coen_2(H_2O)_2]^{3+}$.

The addition of alkali to the succinato complex immediately produced a spectrum which corresponded to that for the dihydroxy complex but on the addition of acid the spectrum obtained did not correspond to that for the diaquo complex and then on the addition of alkali to the acidified solution another different spectrum was obtained which was not the same as that for the dihydroxy species. None of these spectra had the shoulder in them as in the succinato complex. These spectra are on page 94.

BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$

INTRODUCTION

Base hydrolysis of Cobalt(III) Complexes.

In basic media the rate of hydrolysis is first order with respect to the concentration of both complex and hydroxide ion, so that the kinetics are second order:- rate = $k[complex][OH^-]$. In view of the great nucleophilic character of the hydroxide ion, Ingold, Nyholm and co-workers consider the mechanism of base hydrolysis to involve direct S_N2 attack of hydroxide ion on the complex:-

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [HO...Co(NH_3)_5...Cl]^+ \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$$

Transition state

Basolo, Pearson and co-workers, however, favour a dissociative process preceded by a rapid conjugate-base equilibrium (the S_N1CB mechanism) :-

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O \qquad K_a \quad \text{(fast)}$$

$$[Co(NH_3)_4(NH_2)Cl]^+ \rightleftharpoons [Co(NH_3)_4(NH_2)]^{2+} + Cl^- \qquad k_{CB} \quad \text{(slow)}$$

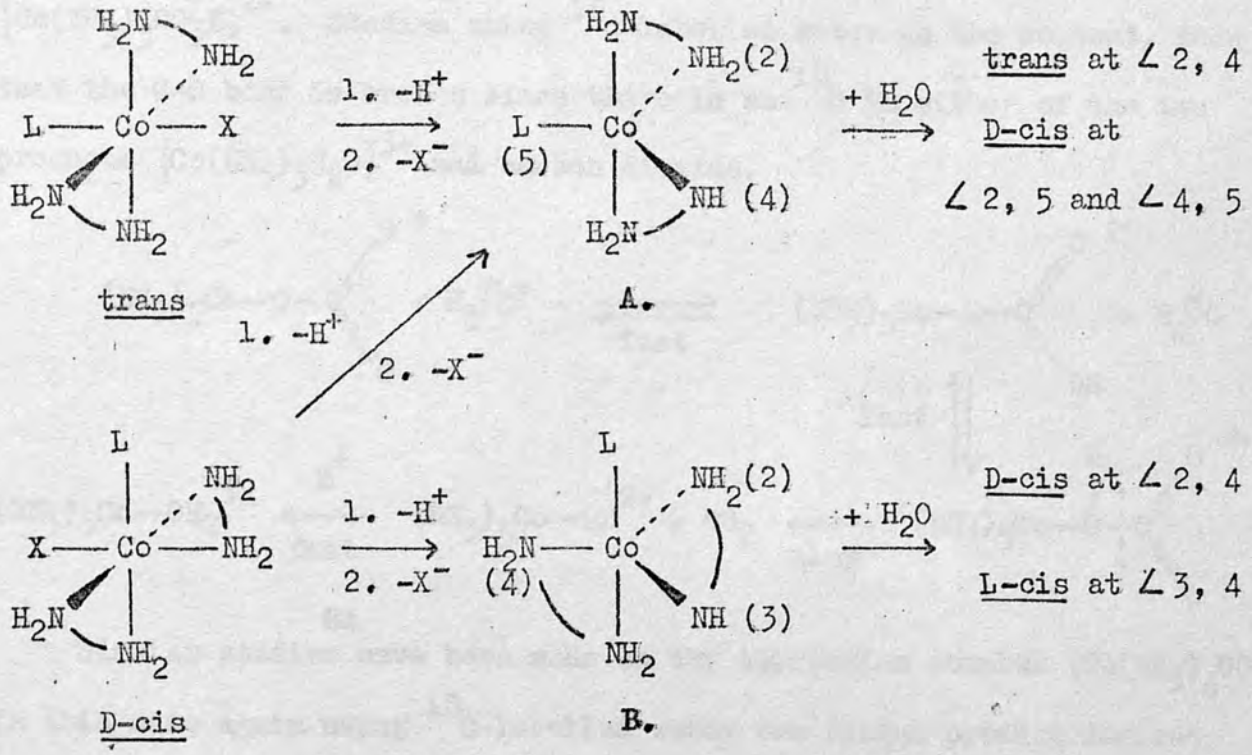
$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w \quad \text{(fast)}$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} \qquad \text{(fast)}$$

Hence $-d[Co(NH_3)_5Cl^{2+}]/dt = k_{CB}K_a/K_w.[OH^-][Co(NH_3)_5Cl^{2+}]$

so that the observed second-order rate constant $k' = k_{CB}K_a/K_w$.

The main evidence in support of the S_N1CB mechanism is that only OH^- acts as a nucleophilic reagent for Co(III) octahedral complexes. In all other cases of substitution by Y^- the mechanism has gone through



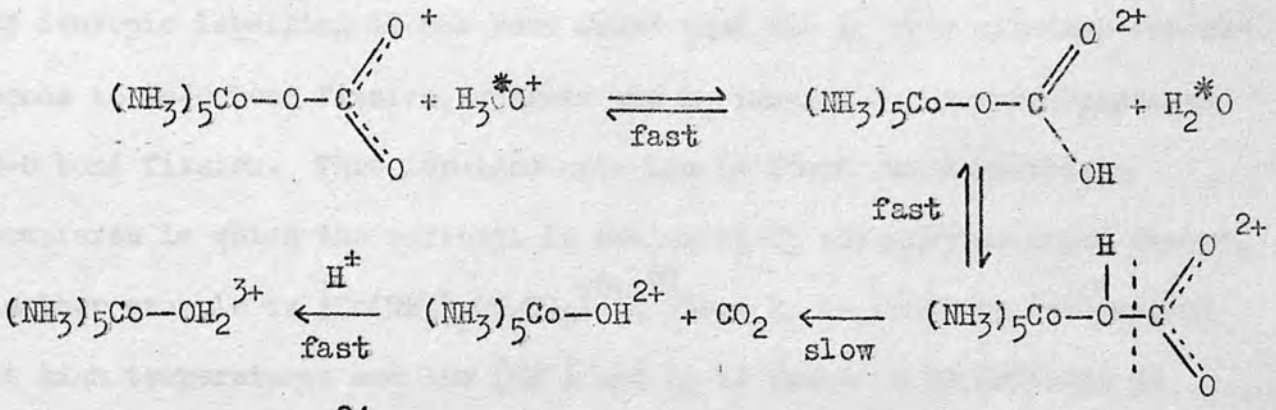
S_N1CB mechanism for the base hydrolysis of $[Coen_2LX]^{n+}$

the intermediate formation of an aquo complex. Also it is found that certain complexes which do not contain an acidic proton hydrolyse at a rate independent of pH over the alkaline range. For example the ion cis-$[Co(dipy)_2(OAc)_2]^+$ hydrolyses at the same rate at pH 11-12 as at pH 6-8.[81] The existence of a five-coordinated intermediate also gives support to the S_N1CB mechanism.

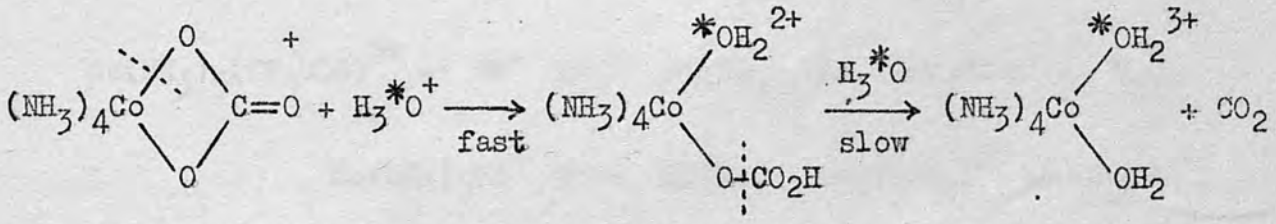
Substitution of Carboxylate Ligands

Substitution of carboxylate ligands can take place in one of two ways: either a Co-O or a C-O bond is broken. In the case of the acid hydrolysis of $[Co(NH_3)_5CO_3]^+$ the rate of this is exceptionally fast compared with the acid hydrolysis of most Co(III) complexes which are exceedingly slow.[82] Kinetic studies show that the reacting species is the bicarbonato complex,

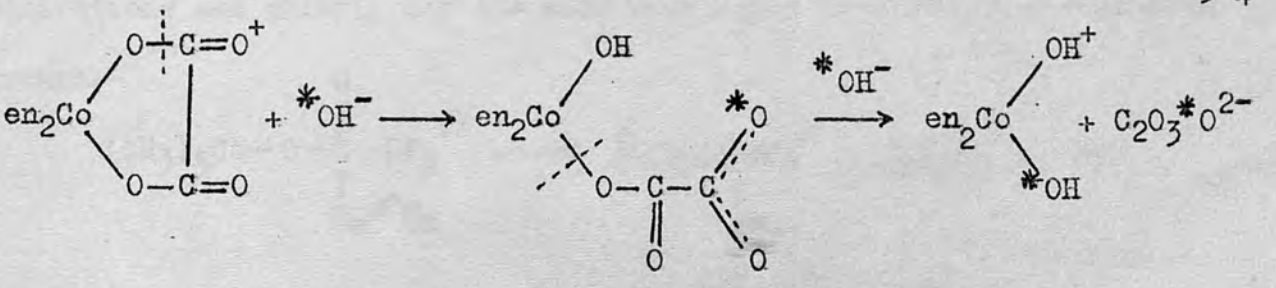
$[Co(NH_3)_5CO_3H]^{2+}$.[83] Studies using ^{18}O-labelled water as the solvent, show that the C-O bond is broken since there is no ^{18}O in either of the two products $[Co(NH_3)_5H_2O]^{3+}$ and carbon dioxide.



Similar studies have been made on the tetraamine complex $[Co(NH_3)_4CO_3]^+$.[84] In this case again using ^{18}O-labelled water the diaquo product derives half of its oxygen from the solvent. So the first step involves breaking of the Co-O bond, and the second step breaking of the C-O bond:-



In contrast to the carbonato complexes the oxalato complex $[Coen_2C_2O_4]^+$ has been found to be very stable to acid hydrolysis but readily hydrolysed in basic medium.[85] Using ^{18}O-labelled water it has been shown[86] that the first step is the breaking of the C-O bond followed by the removal of the oxalate ligand by Co-O fission. This is the reverse of the process for $[Co(NH_3)_4CO_3]^+$.



The oxalato-pentaamine-cobalt(III) complex $[Co(NH_3)_5C_2O_4]^+$ has been shown[87] to have a two-term rate law for base hydrolysis:-

$$\text{Rate} = \left(k_1[OH^-] + k_2[OH^-]^2\right)(\text{complex})$$

By isotopic labelling it has been found that the k_1 rate constant corresponds to Co-O bond fission, whereas the k_2 rate constant corresponds to C-O bond fission. This two-term rate law is found for carboxylato complexes in which the carboxyl is activated by strongly negative groups. Another example is $[Co(NH_3)_5CF_3CO_2]^{2+}$.[87] Here k_1 is found to be dominant at high temperatures and low $[OH^-]$ and k_2 is found to be dominant at low temperatures and high $[OH^-]$. These two reaction paths have also been found in the hydrolysis of $[Coen_2C_2O_4]^+$.[88]

The k_1 path of the hydrolysis of $[Co(NH_3)_5CF_3CO_2]^{2+}$ is thought to go through a conjugate base mechanism:-[89]

$$Co(NH_3)_5(CF_3COO)^{2+} + OH^- \rightleftharpoons Co(NH_3)_4(NH_2)(CF_3COO)^+ + H_2O$$

$$\downarrow$$

$$Co(NH_3)_5OH^{2+} \longleftarrow Co(NH_3)_4(NH_2)(OH_2)^{2+} + CF_3COO^-$$

A possible mechanism[89] for the k_2 path involves attack of an OH^- at the carbonyl carbon followed by a second OH^- removing a H^+ from the first, leading to C-O bond fission. This path leads to incorporation of ^{18}O into the carboxylate ion produced. The k_2 path occurs at high base concentrations and chiefly for the more negatively substituted carboxylate groups:-

$$(NH_3)_5Co-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \bar{O}H \leftarrow \bar{O}H}{\uparrow}}{C}}-CF_3^{2+} \longrightarrow [(NH_3)_5CoO]^+ + O_2C_2F_3^- + H_2O$$

$$\downarrow H_2O$$

$$(NH_3)_5CoOH^{2+} + OH^-$$

The base hydrolysis of $[Coen_2CO_3]^+$ has been carried out[90] and it has been shown that the reaction proceeds in two stages:-

(a) Initial de-chelation of the carbonate:-

$$Coen_2CO_3^+ + OH^- \longrightarrow Coen_2\begin{cases} OH^o \\ CO_3 \end{cases}$$

Co-O bond fission is postulated with an S_N1CB or S_N2 ion pair mechanism. At high base concentrations the de-chelation process proceeds by a mechanism first order in $[OH^-]$. At low base concentrations an acid catalysed reaction path is also present.

(b) Removal of carbonate:-

$$Coen_2CO_3OH^o + OH^- \longrightarrow Coen_2(OH)_2^+ + CO_3^{2-}$$

The rate of loss of carbonate was found to vary with the wavelength at which the loss was measured and loss of optical activity was shown to be slower than the decomposition. Several different species are undergoing decomposition, racemisation and isomerisation at different rates.

The base hydrolysis of $[Coen_2C_2O_4]^+$ also proceeds in two similar stages to the above and the presence of the intermediate $Coen_2C_2O_4.OH$ has been shown.[91] The initial de-chelation, which takes place by C-O bond fission, was found to be faster than that for the $[Coen_2CO_3]^+$ ion.[90] At high concentrations of base and low temperatures a term second order in $[OH^-]$ enters into the rate law and is consistent with the O^{18} results of Taube.[86]

BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$

EXPERIMENTAL

In preliminary experiments it was observed that on adding bench reagent sodium hydroxide solution to a solution of the malonato complex the latter gradually changed from its usual orange-red colour to a blue-red colour. So it seemed that the base hydrolysis of this complex could be followed spectrophotometrically. A 0.01M solution of the complex was made up in 1M sodium hydroxide and the spectrum was taken at timed intervals. Finally the mixture was heated to ensure completion of the reaction and the final spectrum that was taken was seen to be the same as that given by Bjerrum and Rasmussen[92] for the cis-trans equilibrium mixture of the dihydroxy species $[Coen_2(OH)_2]^+$. The observed change in colour was therefore due to the shift from the absorption peaks of the malonato complex to those of the dihydroxy complex which are at longer wavelengths. On acidification the mixture was seen to return to the orange-red colour and as expected the spectrum was seen to be the same as that given by Bjerrum and Rasmussen for the cis-trans equilibrium mixture of the diaquo ion $[Coen_2(H_2O)_2]^{3+}$.

Preliminary experiments were also carried out on the acid hydrolysis of the malonato complex using varying concentrations of perchloric acid from 0.8M - 9M and temperatures up to 94°. From these it was seen that the acid hydrolysis of the malonato complex is exceedingly slow. (Details are given later.)

From these preliminary experiments a programme was drawn up for the kinetic runs. It was decided to follow the base hydrolysis spectrophotometrically

by withdrawing samples of the reaction mixture at timed intervals and quenching the reaction with perchloric acid which would convert the $[Coen_2(OH)_2]^+$ that had been formed to an equivalent amount of $[Coen_2(H_2O)_2]^{3+}$ and yet would not cause any acid hydrolysis on unchanged malonato complex. The absorption spectrum should therefore change from that corresponding to the malonato complex to that for the diaquo complex. The practical details of the hydrolysis were as follows:-

5 ml. of a 0.1M solution of complex were pipetted into 45 ml. of varying quantities if 0.1M sodium hydroxide and 0.1M sodium perchlorate which were contained in a 250 ml. Pyrex flask in a thermostatted water bath. A stop clock was started when half the solution of the complex had been added. The flask was then stoppered and 4 ml. of solution were withdrawn at intervals and run into 4 ml. of 0.1M perchloric acid in ice.

Spectral measurements were made on these solutions using a Unicam SP 500. The measurements were made at selected wavelengths where the spectrophotometric curves corresponding to the initial and final reaction mixtures differed greatly and also at wavelengths where they both agreed so as to check that the concentration had not been changed by evaporation. For one of the kinetic runs spectral measurements were taken at wavelength intervals throughout the spectrum (see page 112).

The ionic strength was kept constant at 0.1M and the hydroxide concentration was varied at each of three different temperatures. The concentration of the malonato complex as the reaction proceeded was obtained from spectral measurements taken at 496 and 356 mμ since these correspond to the peaks of the malonato and the diaquo complexes. The molar extinction coefficients for the malonato complex at these two

wavelengths were taken as 117 and 107.7 respectively. The corresponding values for the diaquo complex were obtained from the infinity reading for each kinetic run.

A graph was plotted for each kinetic run relating the spectral measurement to the percentage of product formed. From this the concentration, x, of product in mole./litre could be obtained for each sample and this would be equal to the decrease in concentration of the malonato complex. Hence the concentration of the malonato complex, a-x, and the concentration of the hydroxide ion, b-2x, were determined for each time, t, where a and b are the initial concentrations of the malonato complex and sodium hydroxide respectively. These results were then plotted according to second order kinetics so that a graph of $\log\left(a(b-2x)/b(a-x)\right)$ against t should be linear.

The rate constant, k, for each kinetic run was calculated from the slope of each graph and hence an average value for the rate constant, k_{av}, was obtained for each temperature. A further graph of $\log k_{av}$ against $1/T$, where T is the corresponding absolute temperature, gave the energy of activation, E, for the process and the Arrhenius frequency factor, A, could then be calculated.

The ionic strength, μ, of the solutions was varied while keeping the hydroxide concentration and the temperature constant for one set of runs and a graph was plotted of log k against $\sqrt{\mu}$.

In addition a run was carried out in excess sodium hydroxide (1M) and the results were therefore plotted according to first order kinetics.

BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$

SUMMARY OF RESULTS

The overall chemical reaction between alkali hydroxide and the complex cation $[Coen_2CO_2CH_2CO_2]^+$ is represented by the equation:-

$$Coen_2CO_2CH_2CO_2^+ + 2OH^- \longrightarrow Coen_2(OH)_2^+ + C_2O_4^{2-}$$

This equation is concluded from the spectrophotometric observations. The dihydroxy species is considered to be in cis-trans equilibrium, since this occurs very rapidly at the temperature of the experiments.[92 93]

The rate of the reaction was found to be first order with respect to [complex] and first order with respect to $[OH^-]$ so that the kinetics are second order and the rate law is of the form:-

$$\text{Rate} = k(Coen_2CO_2CH_2CO_2^+)(OH^-)$$

The rate constants were obtained from the slope of the standard integrated form of the appropiate second-order equation:-

$$\log_{10} \frac{a(b - 2x)}{b(a - x)} = \frac{k_m(b - 2a)}{2.303} t$$

Where a and b represent the initial concentrations of complex and hydroxide respectively, and x is calculated from the optical density measurements at 360 and 500 mμ carried out initially and at time t.

The plots are reasonably linear, except that as the reaction nears completion there is a "tailing off" for the fastest reaction at each temperature, i.e. B 13 and B 19 ($t=38^\circ$), "tailing off" after 60% reaction; B 5 ($t=45^\circ$) and B 11/12 ($t=55^\circ$), "tailing off" after 80% reaction.

The rate constants k_m ($l.mole^{-1}min^{-1}$) were obtained at three different temperatures and were converted to k_s ($l.mole^{-1}sec^{-1}$). From the Arrhenius plot of $\log_{10} k_s$ against $1/T$ the following Arrhenius rate expression was obtained:-

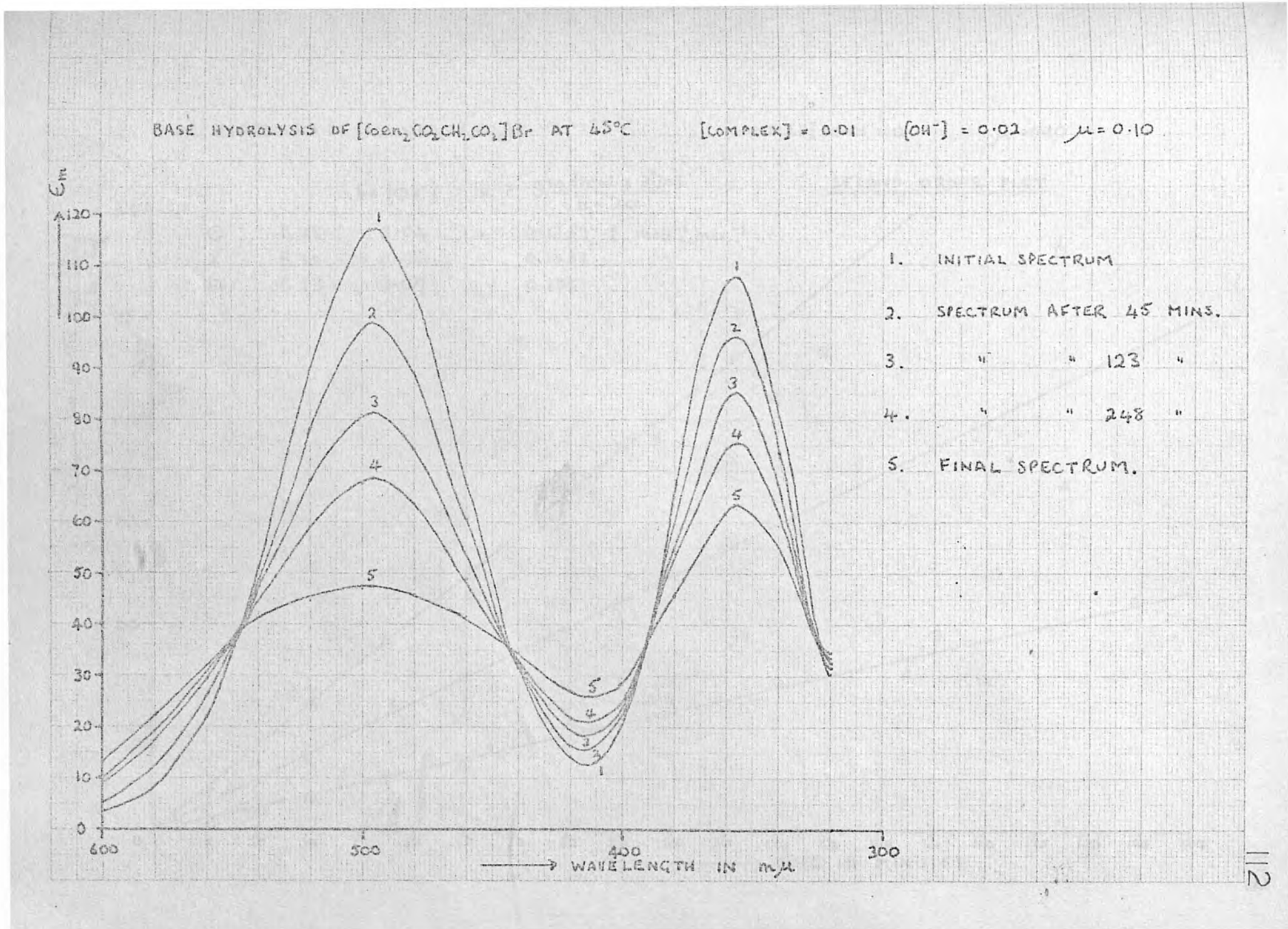
$$k_s = 8.7 \times 10^{17}\ e^{-29,000/RT}\ l.mole^{-1}sec^{-1}$$

From the kinetic runs for which the ionic strength only was varied, by using differing quantities of sodium perchlorate, a graph of $\log_{10} k_\mu$ against $\sqrt{\mu}$ gave a curve which tended towards a straight line for low values of μ. The maximum slope of this straight line is equal to -1. From the simple limiting form of the Debye-Huckel equation the rate of a reaction between ions of charge z_A and z_B varies with the ionic strength as follows:-

$$\log k_\mu = \log k_o + 1.02\ z_A z_B \sqrt{\mu}$$

where k_μ and k_o are the rate constants at ionic strength μ and 0. A graph of $\log k_\mu$ against $\sqrt{\mu}$ gives a line of slope $\simeq z_A z_B$, i.e. the product of the charges on the ions involved in the rate-determining step. In the present experiments $z_A z_B \sim -1$ so that the rate-determining step could involve OH^- and a unipositive complex cation, i.e. S_N2 mechanism. This is not conclusive evidence as the Debye-Huckel relationship only holds for dilute solutions ($\mu < 0.01$). But it can be concluded that the rate of the reaction decreases with increasing ionic strength.

The run carried out in higher base concentration (1M) at 37.3° gave a low value of $k_m = 0.047$, compared with that obtained for lower base concentrations ($\sim 0.1M$) at 38° for which $k_m = 0.14\ l.mole^{-1}min^{-1}$ This will be discussed later.

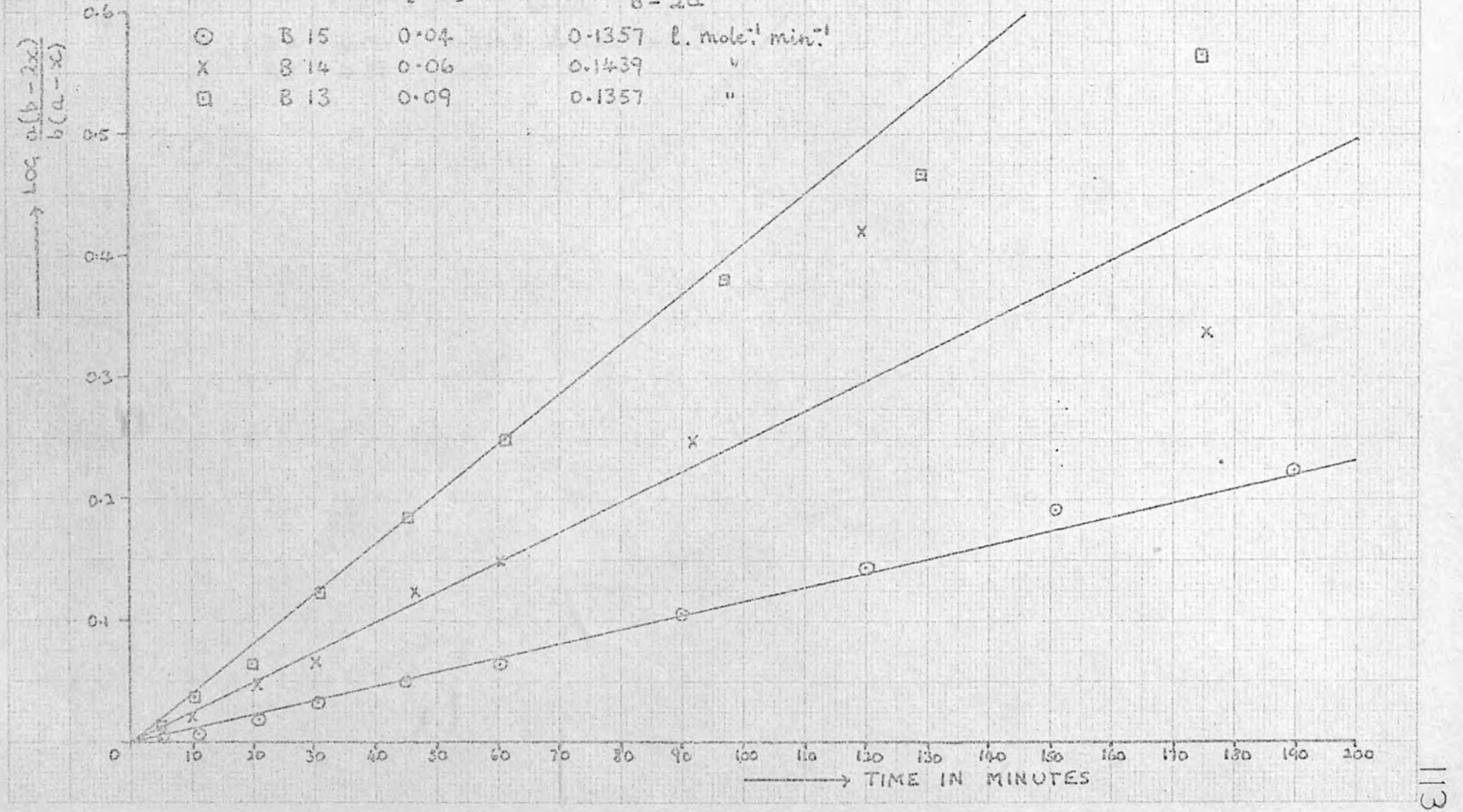

BASE HYDROLYSIS OF [Coen$_2$CO$_2$CH$_2$CO$_2$]Br AT 45°C
[COMPLEX] = 0·01
[OH⁻] = 0·02
μ = 0·10
ε
A
120
110
100
90
80
70
60
50
40
30
20
10
0
600
500
400
300
WAVELENGTH IN mμ
1. INITIAL SPECTRUM
2. SPECTRUM AFTER 45 MINS.
3. " " 123 "
4. " " 248 "
5. FINAL SPECTRUM.

BASE HYDROLYSIS OF $[Coen_2CO_3CH_2CO_2]Br$ AT 38°C. [COMPLEX] = 0·01 = a μ = 0·10

$b = [OH^-]$ $\quad k = \dfrac{\text{gradient} \times 2{\cdot}303}{b - 2a}$

SECOND ORDER PLOT

⊙	B 15	0·04	0·1357	l. mole^{-1} min^{-1}
X	B 14	0·06	0·1439	"
⊡	B 13	0·09	0·1357	"

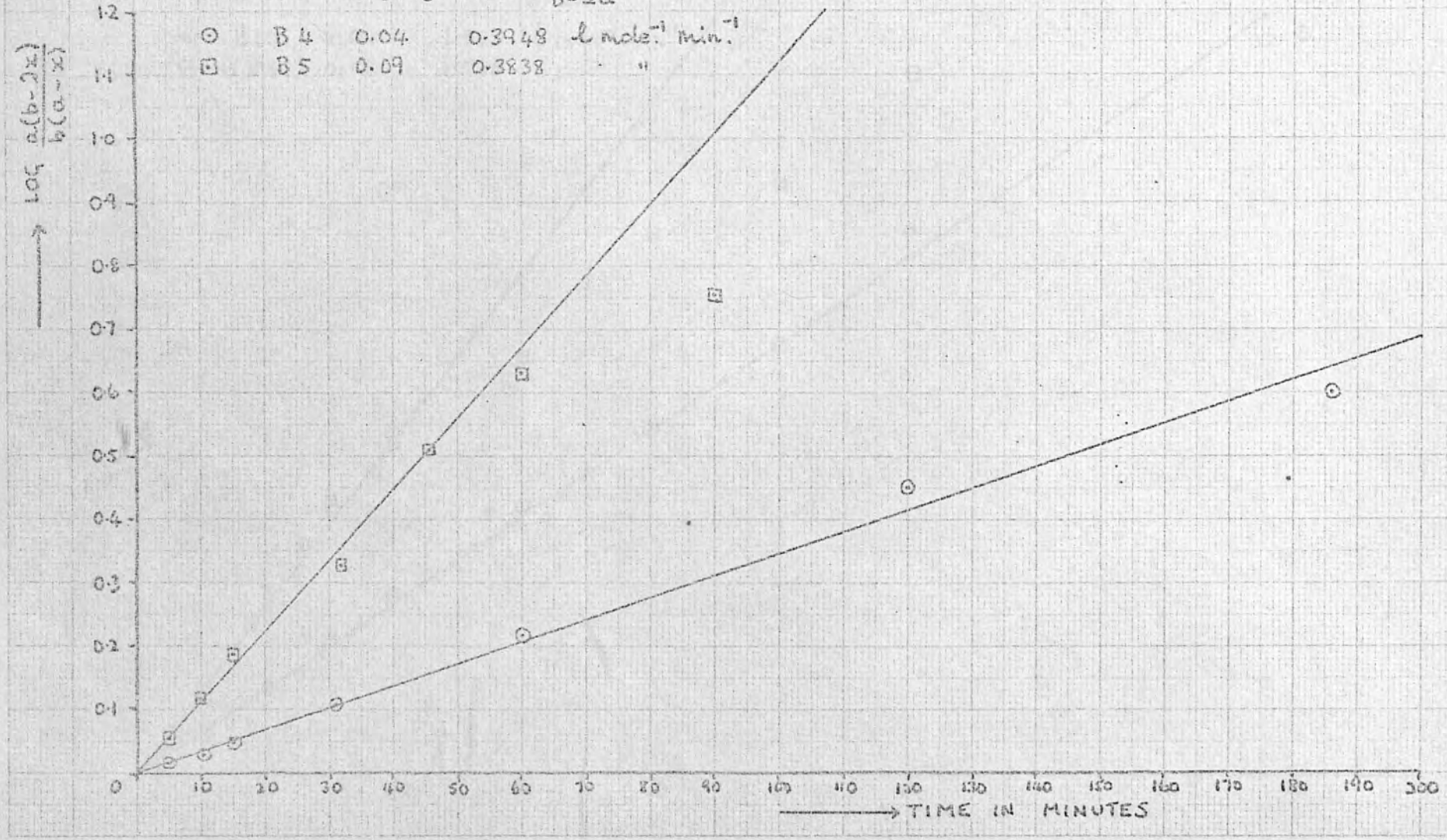


BASE HYDROLYSIS OF $[Coen_2CO_3CH_2CO_2]Br$ AT 45°C [COMPLEX] = 0.01 = a μ = 0.10

$b = [OH^-]$ $k = \frac{\text{gradient} \times 2.303}{b-2a}$

SECOND ORDER PLOT

⊙	B 4	0.04	0.3948	$l\ mole^{-1}\ min^{-1}$
⊡	B 5	0.09	0.3838	"

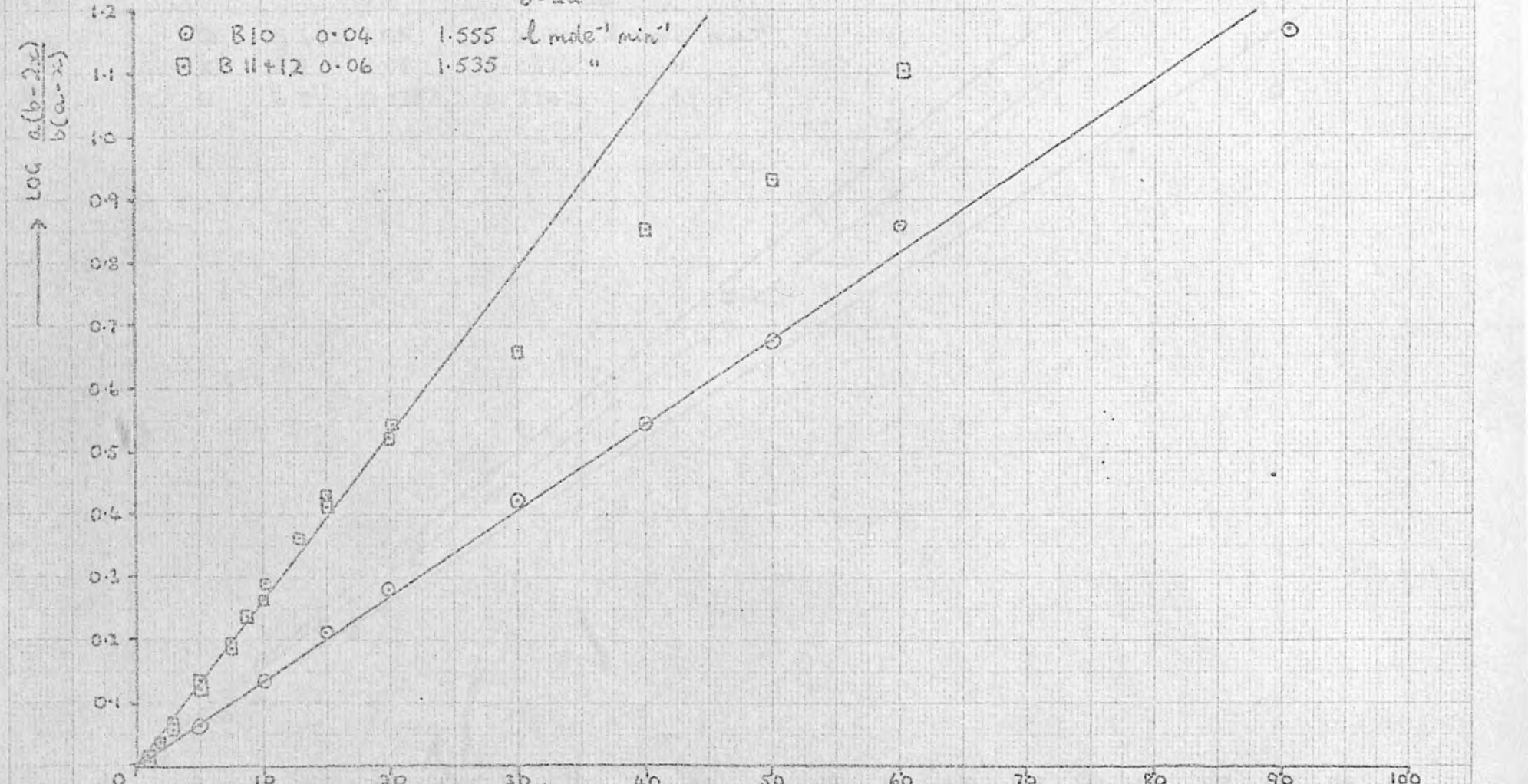


BASE HYDROLYSIS OF $[Coen_2CO_3CH_2CO_2]Br$ AT 55°C [COMPLEX] = 0·01 = a μ = 0·10

$b = [OH^-]$ $k = \frac{\text{gradient} \times 2{\cdot}303}{b - 2a}$

SECOND ORDER PLOT

⊙	B10	0·04	1·555 $l\ mole^{-1}\ min^{-1}$
⊡	B 11+12	0·06	1·535 "

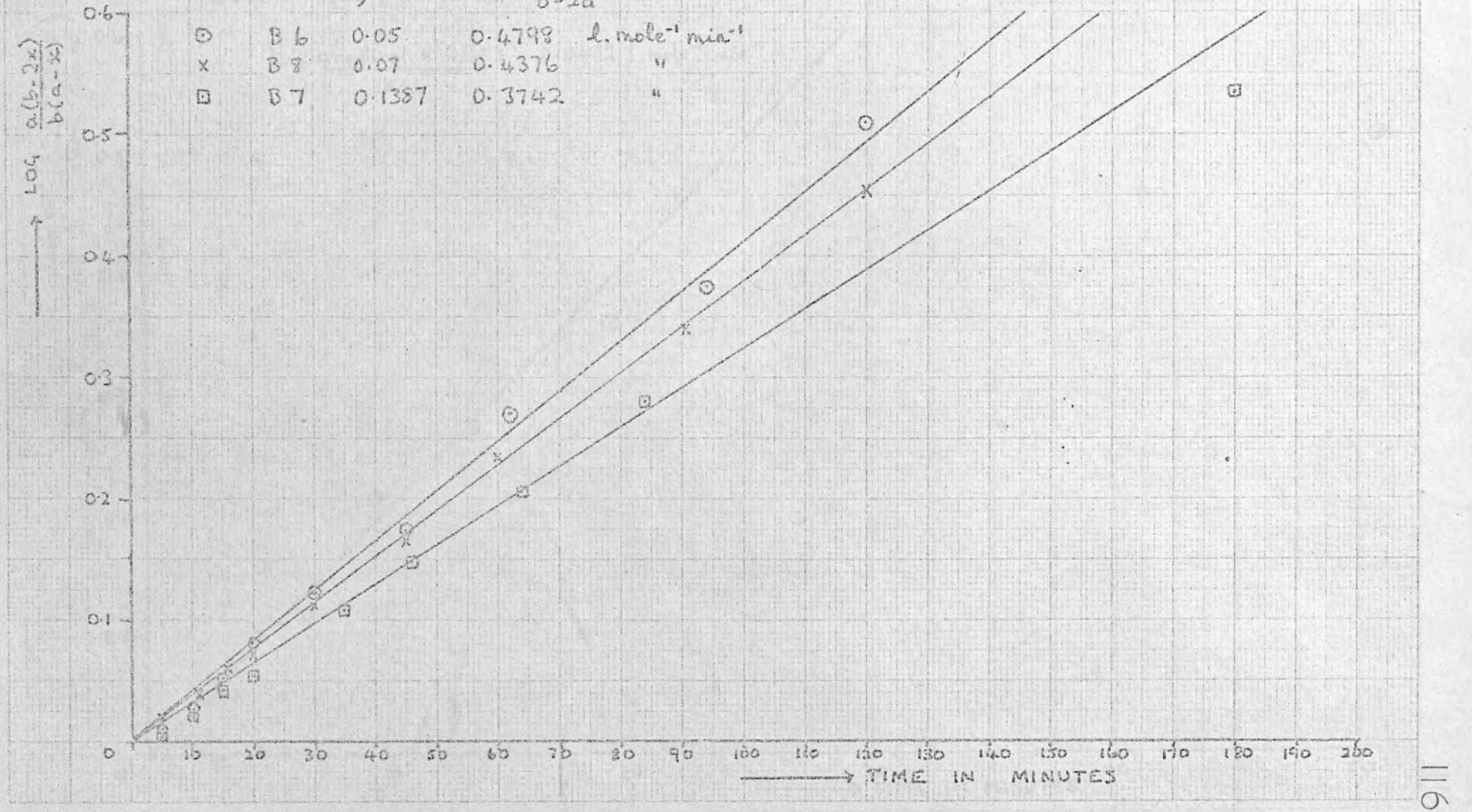


BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$ AT 45°C [COMPLEX] = 0·01 = a $[OH^-]$ = 0·04 = b

SECOND ORDER PLOT

$k = \frac{\text{gradient} \times 2{\cdot}303}{b-2a}$

		μ	k	
⊙	B 6	0·05	0·4798	$l.\,mole^{-1}\,min^{-1}$
×	B 8	0·07	0·4376	"
⊡	B 7	0·1387	0·3742	"

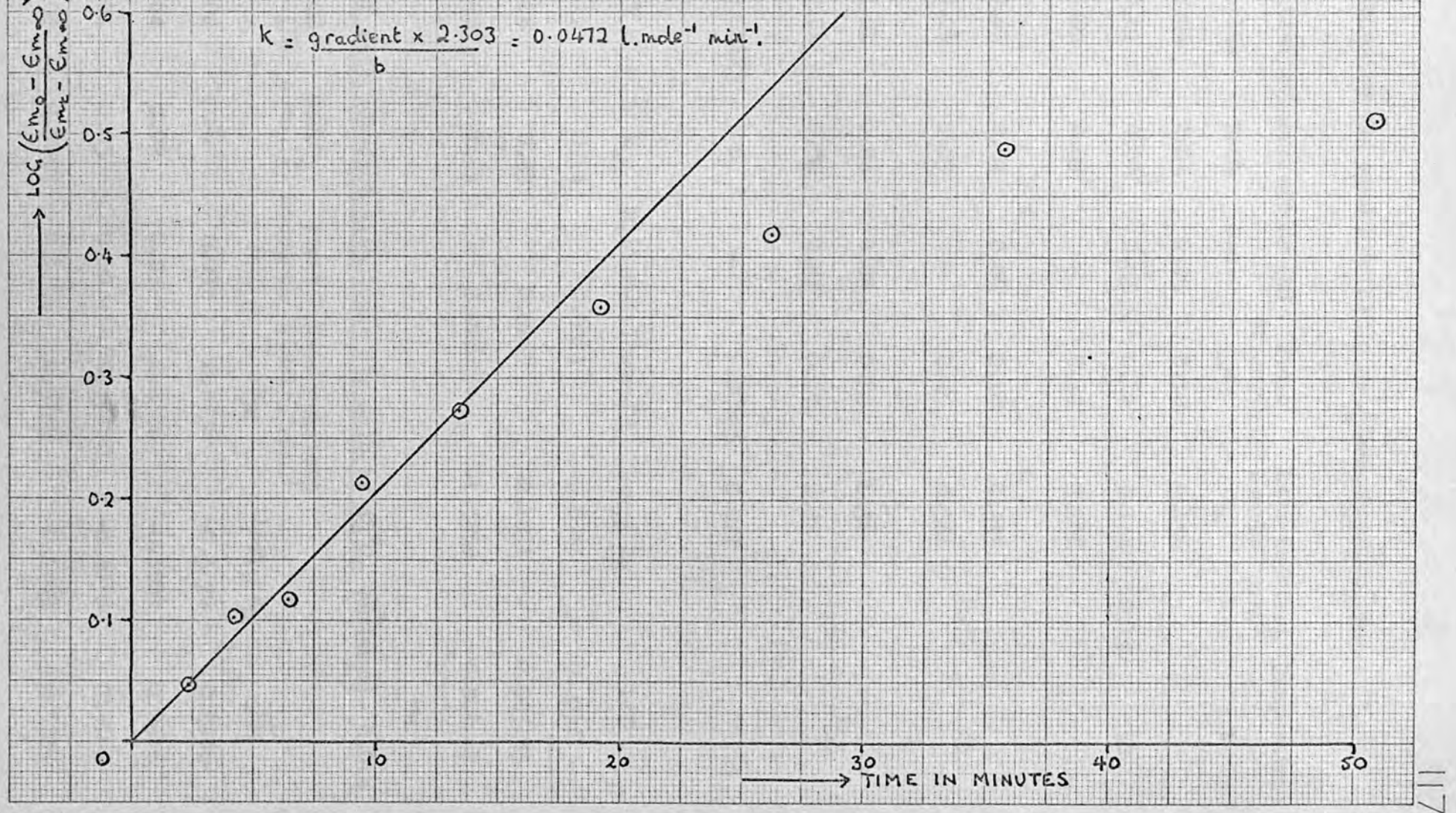


BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$ AT 37·3°C [COMPLEX] = 0·00625 = a . μ = 1·00625

B 19 $[OH^-]$ = 1·0 = b

FIRST ORDER PLOT

$$k = \frac{\text{gradient} \times 2{\cdot}303}{b} = 0{\cdot}0472 \text{ l.mole}^{-1} \text{ min}^{-1}.$$



KINETIC RESULTS ON THE BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$

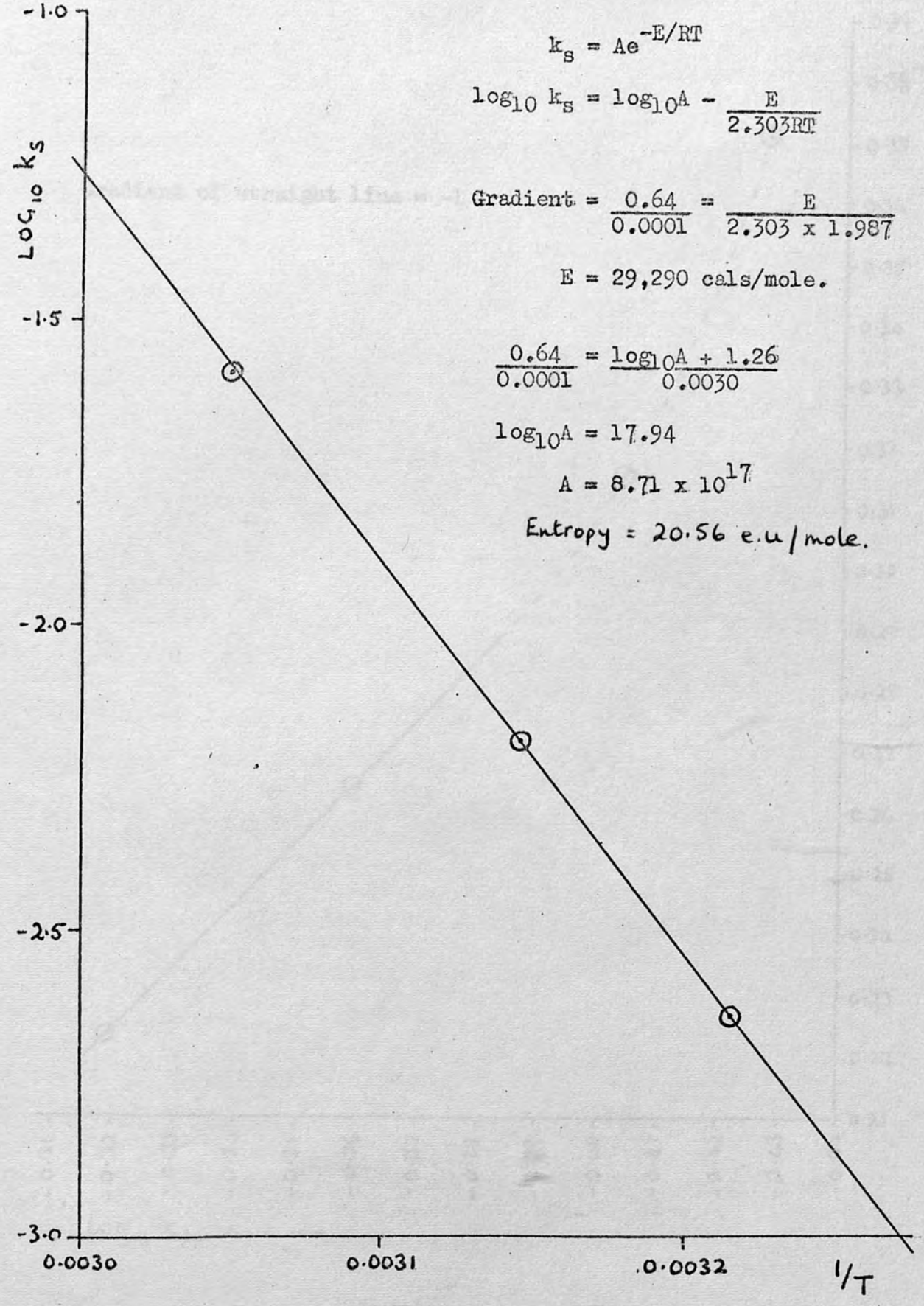
Expt. no.	Initial concentrations (M)			Ionic strength	Rate constant $l.mole^{-1}min^{-1}$		Temperature
	complex	NaOH	$NaClO_4$	μ	k_m	k_{av}	t
B 15	0.01	0.04	0.05	0.10	0.136		
B 14	0.01	0.06	0.03	0.10	0.144	0.14	38
B 13	0.01	0.09	--	0.10	0.136		
B 4	0.01	0.04	0.05	0.10	0.395		
B 5	0.01	0.09	--	0.10	0.384	0.39	45
B 10	0.01	0.04	0.05	0.10	1.56		
B 11/12	0.01	0.06	0.03	0.10	1.54	1.55	55
B 19	0.00625	1.0	--	1.00625	0.047		37.3

t	T	k_{av}	$k_s(l.mole^{-1}sec^{-1})$	$\log_{10} k_s$	1/T
38	311	0.14	0.0023	-2.6383	0.003215
45	318	0.39	0.0065	-2.1871	0.003145
55	328	1.55	0.026	-1.5850	0.003049

Variation of Rate Constant with Ionic Strength at 45°C. [complex] = 0.01M

Expt. no.	NaOH conc.(M)	$NaClO_4$ conc.(M)	Ionic strength μ	Rate constant $l.mole^{-1}min^{-1}$ k_μ	$\log_{10} k_\mu$	$\sqrt{\mu}$
B 6	0.04	--	0.05	0.4798	-0.3190	0.2236
B 8	0.04	0.02	0.07	0.4376	-0.3589	0.2646
B 4	0.04	0.05	0.10	0.3942	-0.4036	0.3162
B 7	0.04	0.0887	0.1387	0.3742	-0.4269	0.3725

ARRHENIUS PLOT FOR THE BASE HYDROLYSIS OF $[Coen_2CO_2CH_2CO_2]Br$



$$k_s = Ae^{-E/RT}$$

$$\log_{10} k_s = \log_{10} A - \frac{E}{2.303RT}$$

$$\text{Gradient} = \frac{0.64}{0.0001} = \frac{E}{2.303 \times 1.987}$$

$$E = 29{,}290 \text{ cals/mole.}$$

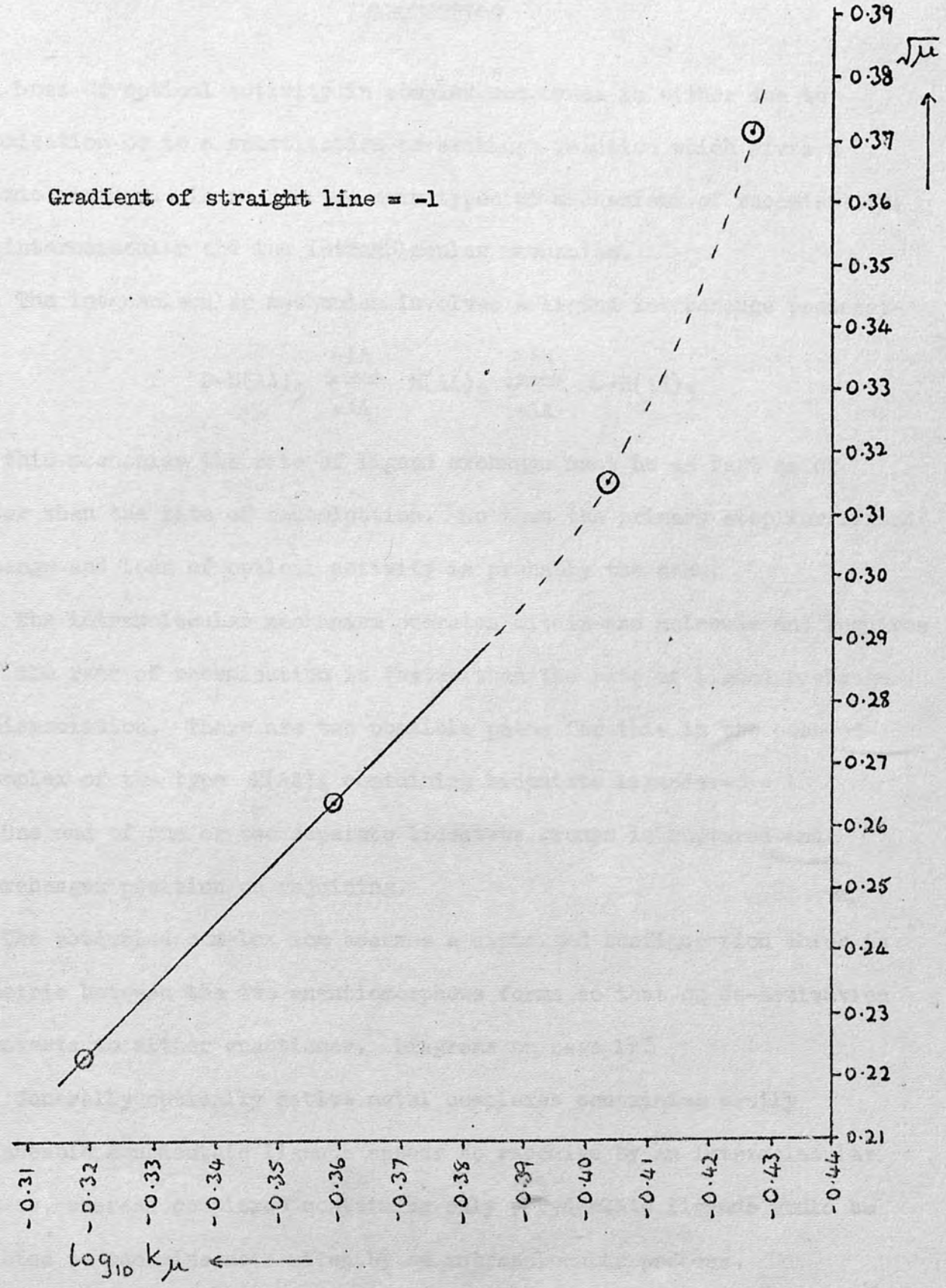
$$\frac{0.64}{0.0001} = \frac{\log_{10} A + 1.26}{0.0030}$$

$$\log_{10} A = 17.94$$

$$A = 8.71 \times 10^{17}$$

Entropy = 20.56 e.u/mole.

VARIATION OF RATE CONSTANTS WITH IONIC STRENGTH



LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

INTRODUCTION

Loss of optical activity in complex compounds is either due to racemisation or to a substitution or exchange reaction which gives a racemic mixture. There are two main types of mechanisms of racemisation; the intermolecular and the intramolecular mechanism.

The intermolecular mechanism involves a ligand interchange process:-

$$D\text{-}M(AA)_3 \underset{+AA}{\overset{-AA}{\rightleftharpoons}} M(AA)_2 \underset{-AA}{\overset{+AA}{\rightleftharpoons}} L\text{-}M(AA)_3$$

For this mechanism the rate of ligand exchange must be as fast as or faster than the rate of racemisation. So that the primary step for ligand exchange and loss of optical activity is probably the same.

The intramolecular mechanism operates within the molecule and requires that the rate of racemisation is faster than the rate of ligand exchange or dissociation. There are two possible paths for this in the case of a complex of the type $M(AA)_3$ containing bidentate ligands:-

a) One end of one or two separate bidentate groups is ruptured and interchanges position on rejoining.

b) The activated complex ion assumes a distorted configuration which is symmetric between the two enantiomorphous forms so that on de-activation it reverts to either enantiomer. Diagrams on page 123

Generally optically active metal complexes containing easily replaceable monodentate ligands appear to racemise by an intermolecular process, whereas complexes containing only polydentate ligands would be expected to racemise more often by an intramolecular process.

The complexes d-$[Ni(o\text{-}phen)_3]^{2+}$ and d-$[Ni(dipy)_3]^{2+}$ however are exceptions to this since the rate constants for dissociation and racemisation are the same over considerable ranges of temperature and acidity suggesting that these complexes racemise by an intermolecular process.[94]

Several complexes of the type $[M(AA)_2X_2]^+$ have been found to racemise by an intermolecular mechanism. For example the complexes:- l-cis-$[Coen_2Cl_2]^+$,[95] l-cis-$[Cren_2Cl_2]^+$[96] and d-cis-$[Coen_2F_2]^+$[97] have been found to have an initial optical rotation change the rate of which is close to the rate of acid hydrolysis, i.e.:-

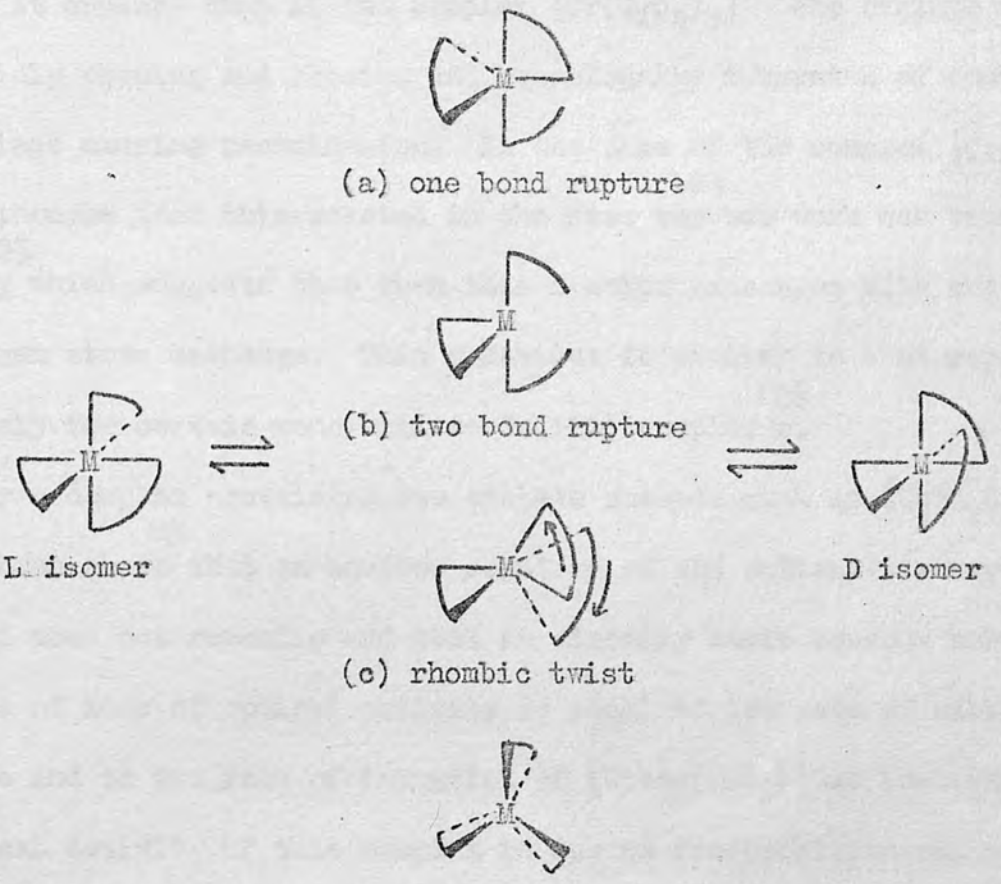
$$\text{cis-}[M(AA)_2X_2]^+ + H_2O \longrightarrow \text{cis-}[M(AA)_2(H_2O)X]^{2+} + X^-$$

The aqua ion produced then racemises more slowly, but at a much faster rate, than it loses further X^-.

Optical forms of the complex $[Coen_3]^{3+}$ are extremely stable and [illegible] solutions show no racemisation in one day at 90°, but with added decolourising charcoal the optical activity is completely lost in 2 min.[98] Here racemisation occurs by an intramolecular process and it is considered that this is due to an electron transfer process[99] between the $[Coen_3]^{3+}$ and catalytic amounts of the labile $[Coen_3]^{2+}$ produced by reduction of $[Coen_3]^{3+}$ by the charcoal.

In the case of the complex $[Coen_2CO_3]Cl$ it was shown by Holden and Harris[100] that the exchange of $H^{14}CO_3^-$ occurred at a faster rate than the racemisation showing that the dissociation of a bidentate ligand does not necessarily produce racemisation.

The complexes d-$[Co(C_2O_4)_3]^{3-}$ and d-$[Cr(C_2O_4)_3]^{3-}$ appear to racemise by an intramolecular mechanism since the rate of oxalate exchange with ^{13}C-oxalate is much slower than the rate of racemisation.[101] Also no oxalate



Intramolecular mechanism showing formation of activated complex

ions can be detected in aqueous solutions of the complexes[102] and the racemisation takes place in the solid state.[103] So the racemisation involves a bond rupture or a twisting process as shown above. It has been found that the mechanism is one of bond rupture (path a) by investigations of ^{18}O exchange between the solvent water and the complex.[104] It has been seen that the rate of acid-catalysed oxygen exchange in the system $[Cr(C_2O_4)_3]^{3-} - H_2{}^{18}O$ is slightly slower than the rate of racemisation of the complex but much faster than its exchange with $^{13}C_2O_4{}^{2-}$. Also all twelve oxygen atoms in the complex $[Cr(C_2O_4)_3]^{3-}$ were found to exchange at the same rate, requiring that the chelate ring open and close.

So it appears that in the complex $[Cr(C_2O_4)_3]^{3-}$ the oxalato rings are rapidly opening and closing and occasionally inversion of configuration takes place causing racemisation. In the case of the complex $[Co(C_2O_4)_3]^{3-}$ it was thought that this reacted in the same way but work has been done recently[104] which suggests that when this complex exchanges with water only six oxygen atoms exchange.[105] This behaviour is similar to that reported previously for certain mono-oxalato Co(III) complexes.[106]

For a complex containing one oxalato chelate such as $[Coen_2C_2O_4]^+$ it has been shown[85] that an aqueous solution of the optically active compound does not racemise and that in strongly basic aqueous solution the rate of loss of optical activity is equal to its rate of oxalate ion exchange and to its rate of formation of $[Coen_2(OH)_2]^+$ so that the loss of optical activity of this complex is due to decomposition rather than racemisation.

LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

EXPERIMENTAL

Preliminary experiments showed that the optically active form of the complex $[Coen_2CO_2CH_2CO_2]I$, although stable in aqueous solution, lost its optical activity at a measureable rate in basic media. So it was decided to examine the kinetics of the optical activity loss of this complex in sodium hydroxide solution and compare it with the base hydrolysis of the complex $[Coen_2CO_2CH_2CO_2]Br$.

The kinetic runs were carried out on a Hilger Standard Polarimeter with a thermostatted polarimeter tube. The practical details were:- 1 ml. of a 0.0125 M solution of the complex and 9 ml. of a mixture of varying quantities of 0.1094 M sodium hydroxide and 0.1094 M sodium perchlorate solutions were put separately in a thermostat until they reached the required temperature. Then the 9 ml. of NaOH and $NaClO_4$ mixture were added to the complex solution and the stop-clock was started when half had been added. The mixture was put in the polarimeter tube (10 cm.) and the angle of rotation α_t was read at intervals on the yellow wave.

The kinetic runs were carried out at three different temperatures and for each temperature runs were made using varying concentrations of hydroxide ion. The ionic strength was kept constant at approximately 0.1 so as to keep it in line with the base hydrolysis kinetic runs.

For each kinetic run the hydroxide concentration was in the region of 35 - 80 times the concentration of the complex and hence the results were plotted according to first order kinetics so that a graph of

$\log\left((\alpha_o - \alpha_\infty)/(\alpha_t - \alpha_\infty)\right)$ against time should be linear. α_o, the optical rotation of the complex solution before the reaction had begun, was obtained from the specific rotation of a solution of the complex in water. α_∞, the infinity reading, was taken as the zero reading on the polarimeter.

The rate constant, k, for each kinetic run was calculated from the slope of each graph and hence an average value, k_{av}, was obtained for each temperature. A further graph of log k_{av} against 1/T gave the energy of activation, E, for the reaction and the Arrhenius frequency factor, A, was then calculated.

In addition a kinetic run was carried out with the ionic strength increased by ten-fold to 1.0, by increasing the sodium hydroxide concentration, to examine the overall effect that an increase in ionic strength, and increase in hydroxide concentration had on the reaction.

LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

SUMMARY OF RESULTS

The optical activity of the malonato complex is not lost in neutral solution but decreases at a measureable rate in basic solution. The optical activity loss was therefore treated not as a racemisation but as a result of the following chemical reaction:-

$$Coen_2CO_2CH_2CO_2^+ + 2OH^- \longrightarrow Coen_2(OH)_2^+ + C_2O_4^{2-}$$

The rate of the reaction was found to be first order with respect to $[OH^-]$ and first order with respect to [complex] so that the kinetics are second order and the rate law is of the form:-

$$\text{Rate} = k(Coen_2CO_2CH_2CO_2^+)(OH^-)$$

The kinetic runs were carried out in excess alkali hydroxide so that the results were plotted according to first order kinetics and the rate constants were obtained from the slope of the integrated form of the appropiate first-order equation:-

$$\log_{10} \frac{(\alpha_o - \alpha_\infty)}{(\alpha_t - \alpha_\infty)} = k_m \frac{b}{2.303} t$$

Where α_t represents the optical rotation of the solution at time t, α_o and α_∞ represent the initial and final optical rotation of the solution respectively, and b is the concentration of the sodium hydroxide. k_m is the rate constant ($l.mole^{-1}min^{-1}$).

The plots were reasonably linear and the rate constants, k_m,

which were obtained at three different temperatures were converted to k_s ($l.mole^{-1}sec^{-1}$). From the Arrhenius plot of $\log_{10} k_s$ against $1/T$ the following Arrhenius rate expression was obtained:-

$$k_s = 9.1 \times 10^{17} e^{-29,000/RT} \; l.mole^{-1}sec^{-1}$$

This expression is seen to be identical with that obtained for the base hydrolysis of $[Coen_2CO_2CH_2CO_2]Br$, indicating that the loss of optical activity in this complex is due to decomposition rather than racemisation. This will be discussed later.

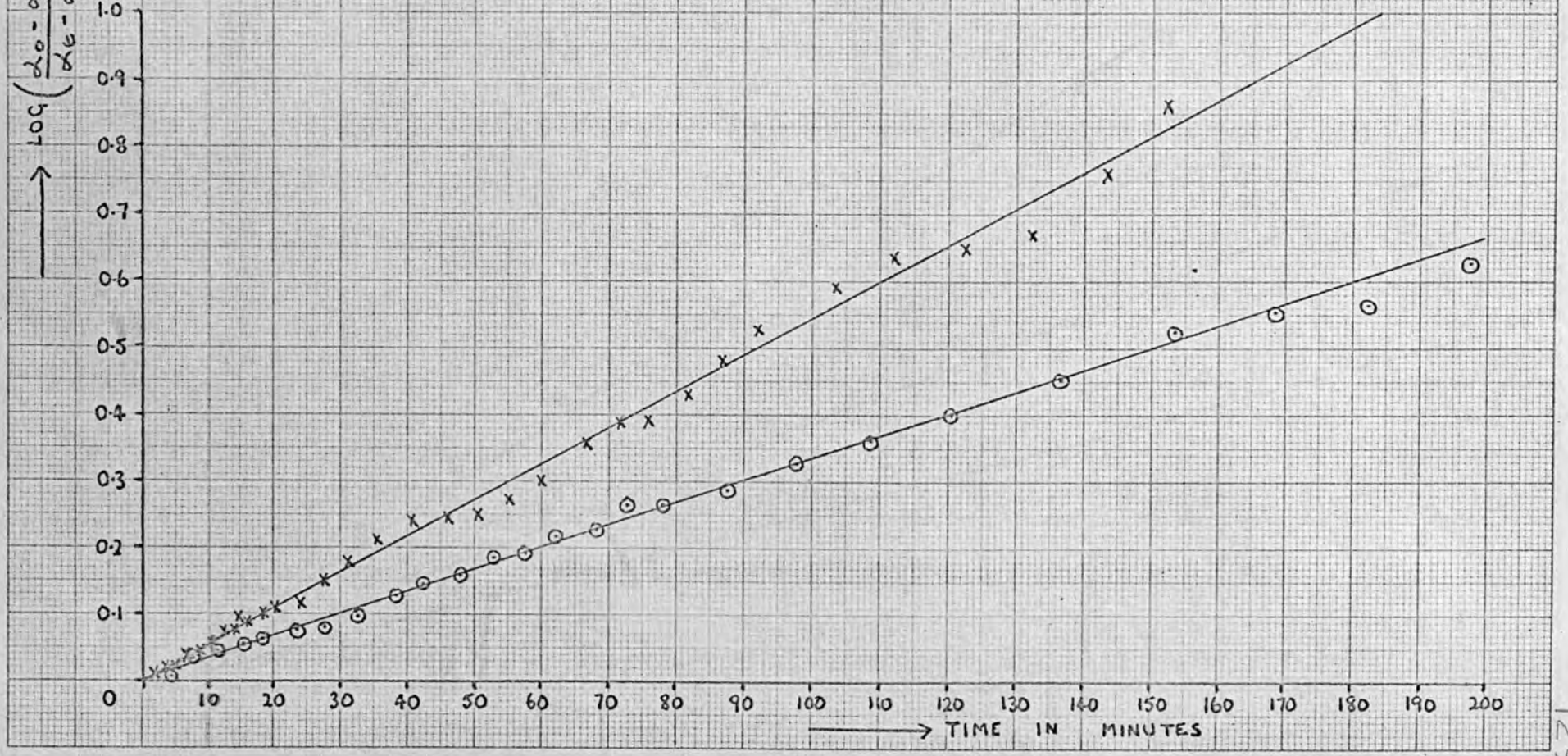
The run carried out in higher base concentration (1M) at 37.3° gave a value of $k_m = 0.0495$ $l.mole^{-1}min^{-1}$ which is the same as that obtained for the base hydrolysis under the same conditions. But, as with the base hydrolysis, this value of k_m for the loss of optical activity is lower than that obtained at lower base concentrations (~0.1M) at 37.3° for which $k_m = 0.12$ $l.mole^{-1}min^{-1}$

LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_3CH_2CO_2]I$ AT 37·3°C. [COMPLEX] = 0·00125 = a μ = 0·09971

$[OH^-] = b$ $k = \frac{\text{gradient} \times 2.303}{b}$

FIRST ORDER PLOT

⊙	R10	0·06564	0·1169	L. mole^{-1} min^{-1}.
×	R8	0·09846	0·1286	"

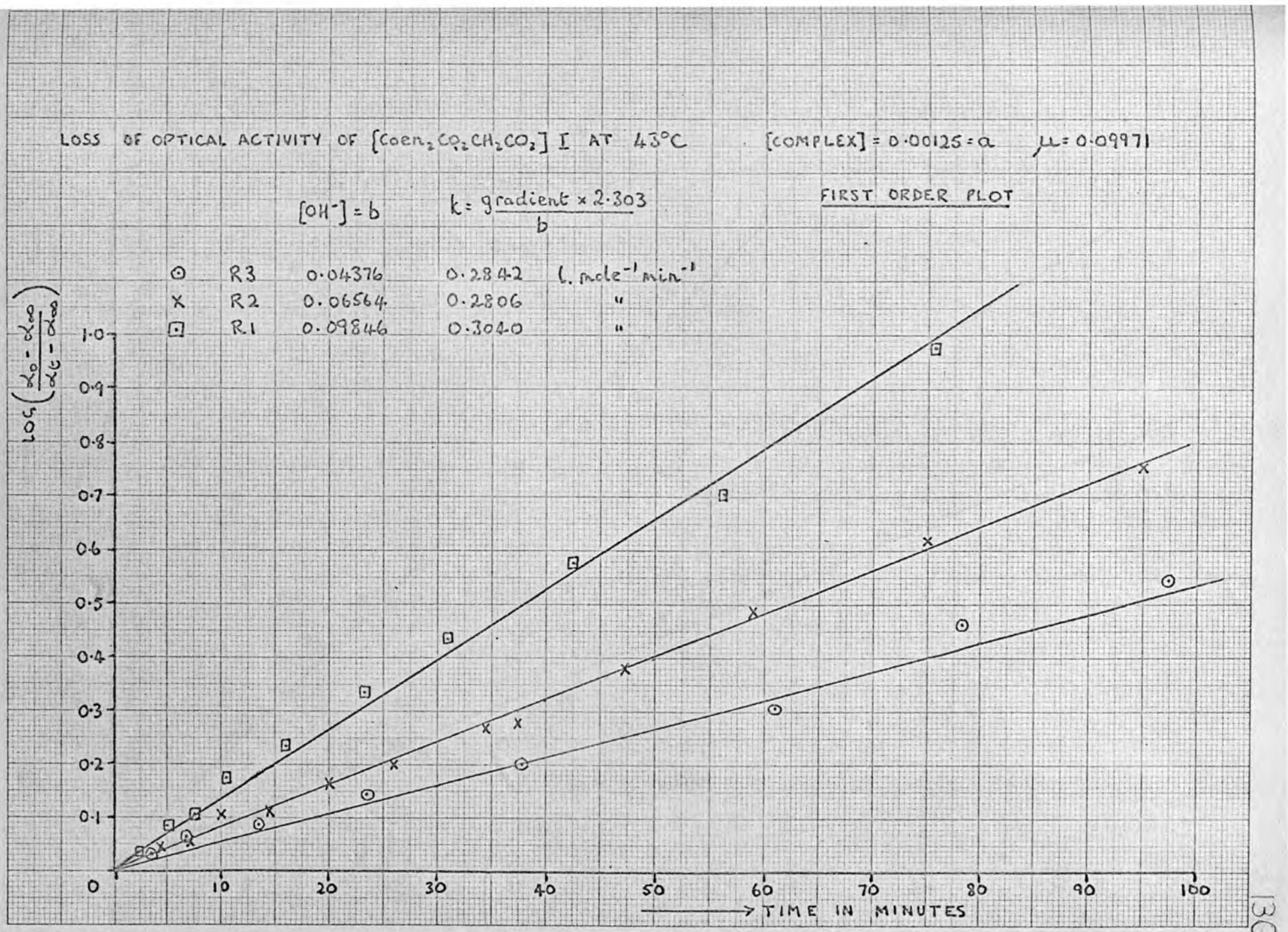


LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_3CH_2CO_2]$ I AT 43°C [COMPLEX] = 0·00125 = a μ = 0·09971

$[OH^-] = b$ $k = \frac{\text{gradient} \times 2{\cdot}303}{b}$

FIRST ORDER PLOT

⊙	R3	0·04376	0·2842	l. mole^{-1} min^{-1}
×	R2	0·06564	0·2806	"
⊡	R1	0·09846	0·3040	"

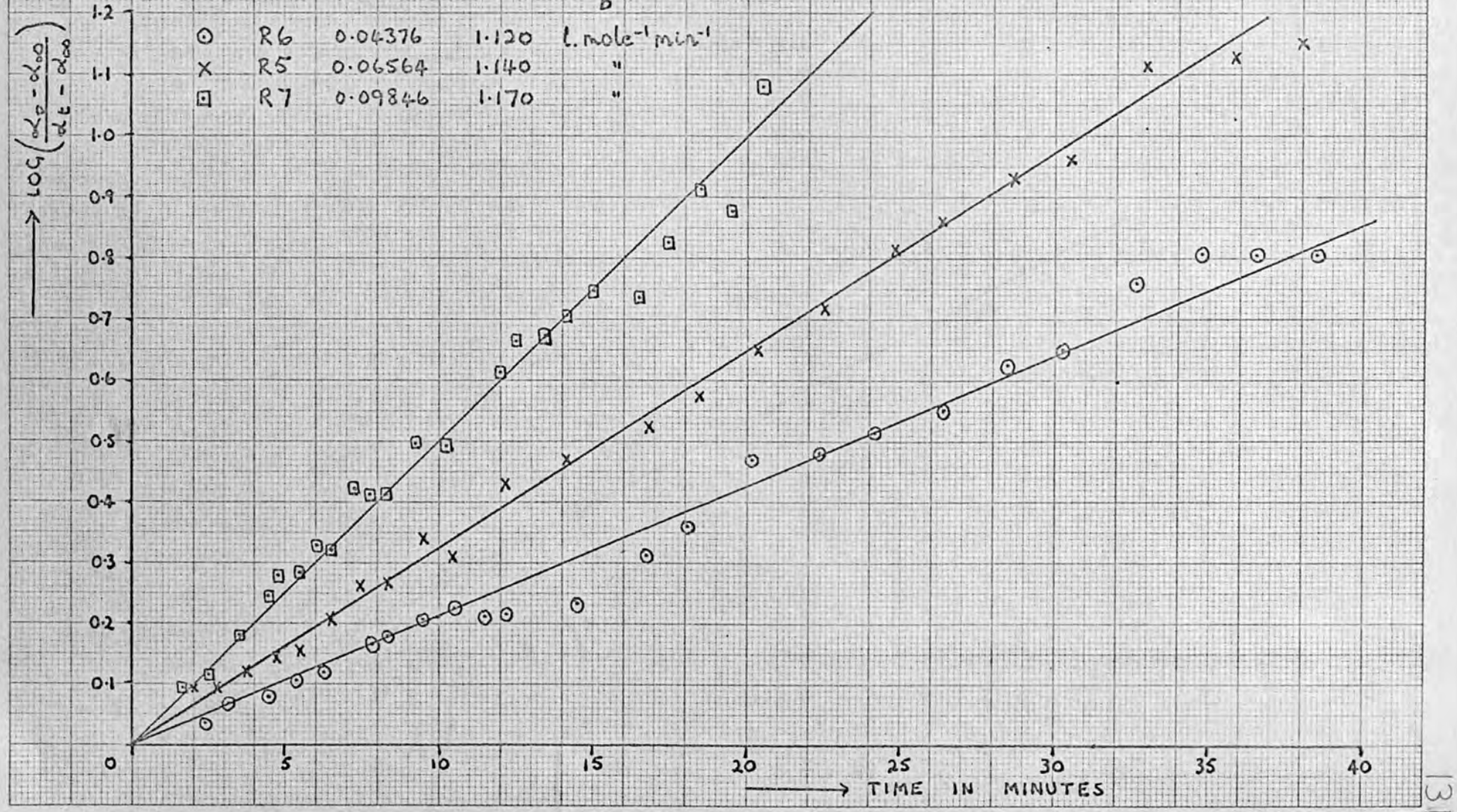


LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$ AT 52°C. [COMPLEX] = 0.00125 = a μ = 0.09971

$[OH^-] = b$ $\quad k = \frac{\text{gradient} \times 2.303}{b}$

FIRST ORDER PLOT

		$[OH^-] = b$	k
⊙	R6	0.04376	1.120 l. mole^{-1} min^{-1}
×	R5	0.06564	1.140 "
⊡	R7	0.09846	1.170 "

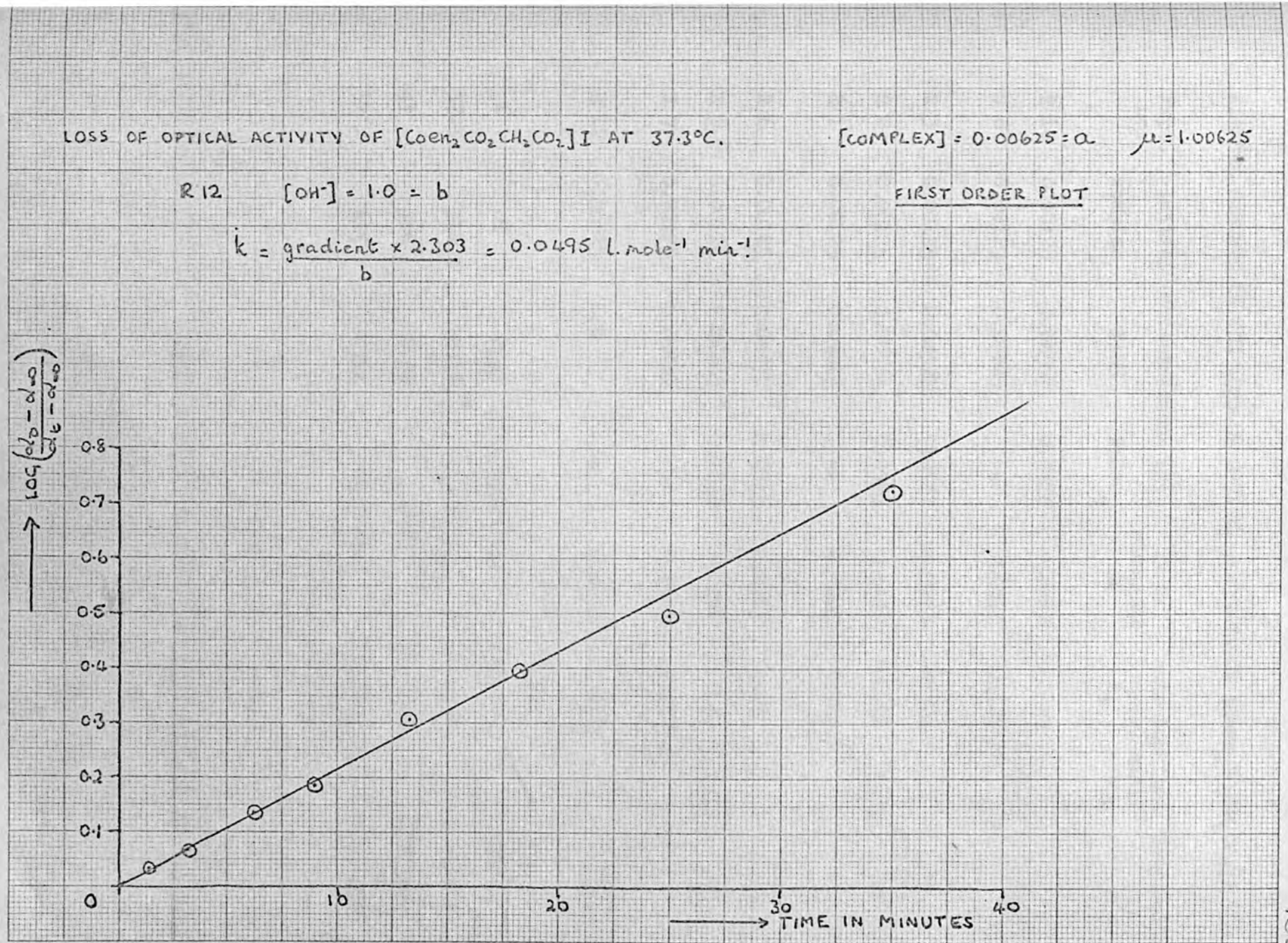


LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$ AT 37.3°C. [COMPLEX] = 0·00625 = a μ = 1·00625

R 12 $[OH^-]$ = 1·0 = b

FIRST ORDER PLOT

$$k = \frac{\text{gradient} \times 2.303}{b} = 0.0495 \text{ l. mole}^{-1} \text{ min}^{-1}$$

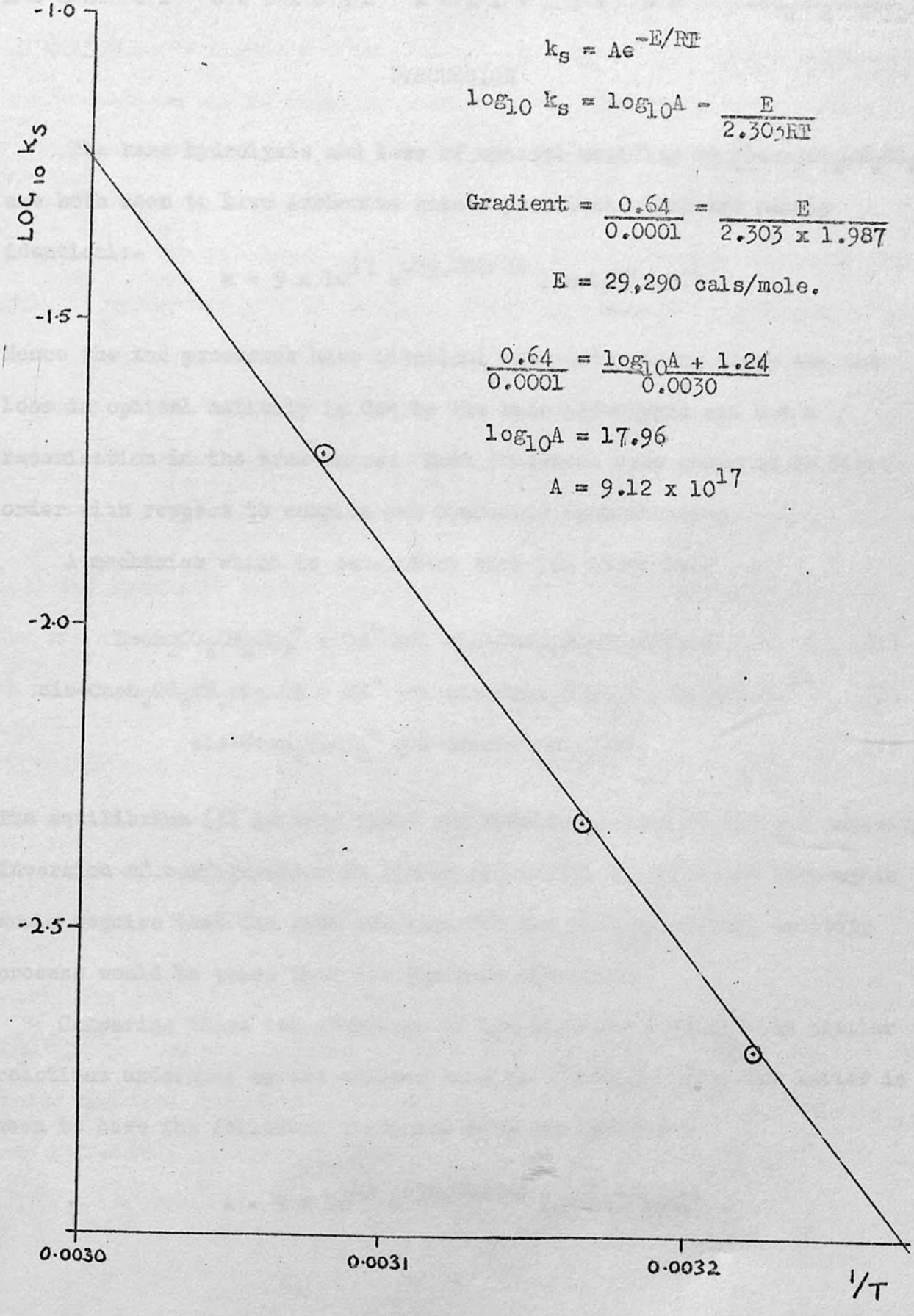


KINETIC RESULTS ON THE LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$

Expt. no.	Initial concentrations (M)			Ionic strength	Rate constant $l.mole.^{-1}min.^{-1}$		Temperature
	complex	NaOH	$NaClO_4$	μ	k_m	k_{av}	t
R 10	0.00125	0.06565	0.0328	0.0997	0.117	0.12	37.3
R 8	0.00125	0.09845	--	0.0997	0.129		
R 3	0.00125	0.04375	0.0547	0.0997	0.284	0.29	43
R 2	0.00125	0.06565	0.0328	0.0997	0.281		
R 1	0.00125	0.09845	--	0.0997	0.304		
R 6	0.00125	0.04375	0.0547	0.0997	1.12	1.14	52
R 5	0.00125	0.06565	0.0328	0.0997	1.14		
R 7	0.00125	0.09845	--	0.0997	1.17		
R 12	0.00625	1.0	--	1.00625	0.0495		37.3

t	T	k_{av}	$k_s(l.mole.^{-1}sec.^{-1})$	$\log_{10} k_s$	1/T
37.3	310.3	0.12	0.0020	-2.6990	0.003223
43	316	0.29	0.0048	-2.3188	0.003165
52	325	1.14	0.0190	-1.7212	0.003077

ARRHENIUS PLOT FOR THE LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]I$



$$k_s = Ae^{-E/RT}$$

$$\log_{10} k_s = \log_{10} A - \frac{E}{2.303RT}$$

$$\text{Gradient} = \frac{0.64}{0.0001} = \frac{E}{2.303 \times 1.987}$$

$$E = 29{,}290 \text{ cals/mole.}$$

$$\frac{0.64}{0.0001} = \frac{\log_{10} A + 1.24}{0.0030}$$

$$\log_{10} A = 17.96$$

$$A = 9.12 \times 10^{17}$$

KINETICS OF THE BASE HYDROLYSIS AND LOSS OF OPTICAL ACTIVITY OF $[Coen_2CO_2CH_2CO_2]^+$

DISCUSSION

The base hydrolysis and loss of optical activity of $[Coen_2CO_2CH_2CO_2]^+$ are both seen to have Arrhenius rate expressions which are nearly identical:-

$$k = 9 \times 10^{17}\ e^{-29,000/RT}\ l.mole.^{-1}sec.^{-1}$$

Hence the two processes have identical rate-determining steps and the loss in optical activity is due to the base hydrolysis and not a racemisation in the true sense. Both processes were shown to be first order with respect to complex and hydroxide concentration.

A mechanism which is consistent with the above is:-

$$Coen_2CO_2CH_2CO_2^+ + OH^- \rightleftharpoons cis\text{-}Coen_2CO_2CH_2CO_2.OH \qquad (1)$$

$$cis\text{-}Coen_2CO_2CH_2CO_2.OH + OH^- \longrightarrow cis\text{-}Coen_2(OH)_2^+ + CO_2CH_2CO_2^{2-} \qquad (2)$$

$$cis\text{-}Coen_2(OH)_2^+ \rightleftharpoons trans\text{-}Coen_2(OH)_2 \qquad (3)$$

The equilibrium (3) is very rapid and results in loss of optical activity. Inversion of configuration in either (1) or (2) is ruled out since this would require that the rate constant for the loss in optical activity process would be twice that for the base hydrolysis.

Comparing these two processes of the malonato complex with similar reactions undergone by the oxalato complex, $[Coen_2C_2O_4]Cl$, the latter is seen to have the following Arrhenius rate expression:-[85]

$$k = 9 \times 10^{19}\ e^{-34,000/RT}\ l.mole.^{-1}sec.^{-1}$$

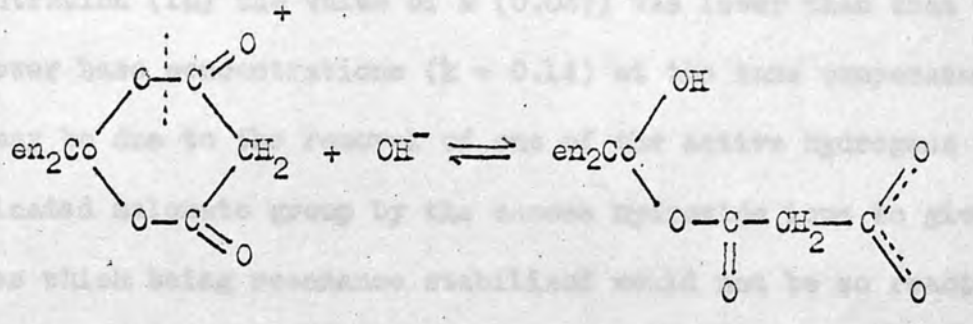
Hence the reactions of the malonato complex are faster than those of the oxalato complex which is as expected due to the strain and distortion in the malonato ligand and the greater ionic character in the cobalt-oxygen bond in the malonato complex. But the Arrhenius rate expression for the malonato complex is of a similar order to that for the oxalato complex and this similarity is greater than that between the malonato complex and the corresponding bidentate carbonato complex, $[Coen_2CO_3]^+$. Thus it is assumed that the mechanisms of the reactions undergone by the malonato complex are similar to those of the oxalato complex rather than to those of the carbonato complex. Further support for this assumption that the malonato complex is similar in its reactions to the oxalato complex and not the carbonato complex comes from the following observations:-

(i) The carbonato complex is very sensitive to acid decomposition[84] but the oxalato and malonato complexes are stable in acid for long periods at elevated temperatures.

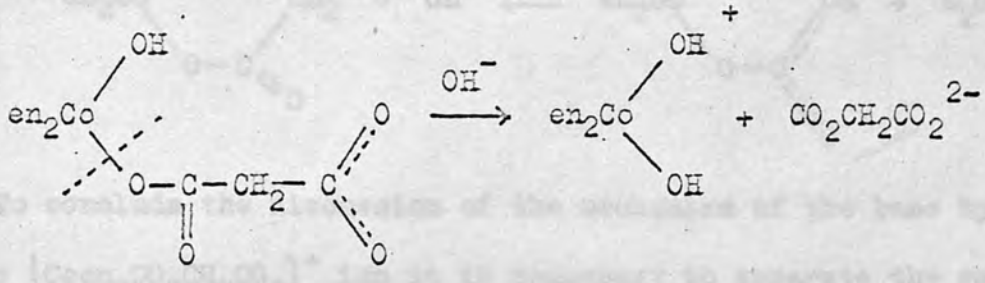
(ii) The base hydrolysis of $[Coen_2CO_3]^+$ is slower[90] than that of the oxalato and malonato complexes and ring opening in the carbonato complex takes place by Co-O bond fission whereas in the oxalato complex it takes place by C-O fission.

(iii) The rate of loss of optical activity of $[Coen_2CO_3]^+$ is much slower[100] than the rate of CO_3 exchange whereas for the oxalato and malonato complexes the rate of loss of optical activity is equated with the rate of base hydrolysis so that for both these complexes the loss of optical activity is not a true racemisation.

Hence, working on this assumption that the reactions undergone by the malonato complex have mechanisms which are similar to those of the oxalato complex, the first step in the base hydrolysis of the malonato complex would be the breaking of the C-O bond followed by the removal of the malonato ligand by Co-O fission. Reaction (1), as on page **135**, would therefore be the step in which the C-O bond is broken:-



Reaction (2) is the step in which the Co-O bond is broken:-

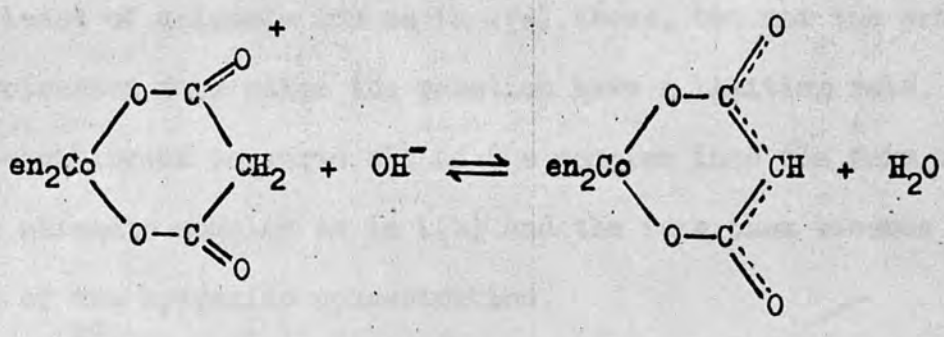


Comparing these reactions with those of the oxalato complex, reaction (2) is expected to be the rate-determining step for those kinetic runs conducted at low base concentrations and high temperatures.

The mechanism of this rate-determining step could be S_N2 or S_N1CB. The likelihood of the S_N1CB mechanism occurring is considerable since the malonato complex is seen to contain not only "acidic" protons in the ammine groups of the ethylenediamine rings but also two active protons in the malonate group.

The fact that these hydrogens are active in the chelated malonate group has been shown by the P. M. R. spectra of $[Coen_2CO_2CH_2CO_2]NO_3$ in D_2O.[68] It was seen that the intensity of the CH_2 signal of the malonate group decreased with time and disappeared overnight due to replacement of the CH_2 protons by deuterium.

Also it has been noted that in the run carried out at higher base concentration (1M) the value of k (0.047) was lower than that obtained for lower base concentrations (k = 0.14) at the same temperature. This may be due to the removal of one of the active hydrogens from the coordinated malonate group by the excess hydroxide ions to give a species which being resonance stabilised would not be so reactive.

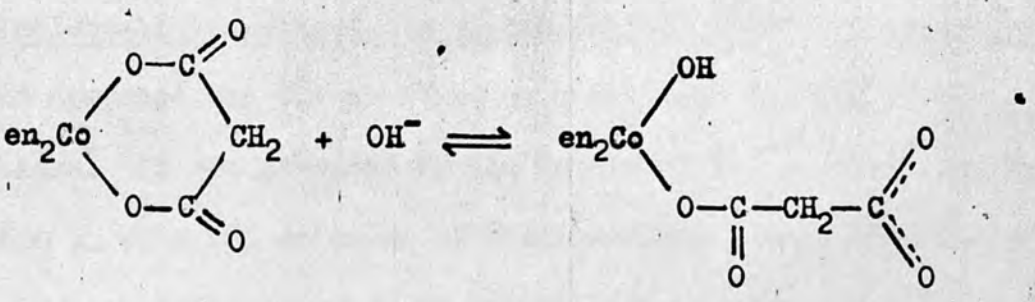


To conclude the discussion of the mechanism of the base hydrolysis of the $[Coen_2CO_2CH_2CO_2]^+$ ion it is necessary to separate the reactions into those that take place in low base and those that take place in high base concentrations.

1. Reactions at low base concentration. Here the polarimetric and spectrophotometric rates are the same and there are two possibilities:-

(a) Second order ring opening is rate determining followed by the fast release of malonate ion, which is independent of hydroxide concentration, thus giving rise to a second order rate constant.

(b) A fast pre-equilibrium between the chelated and the ring opened form



This would be an S_N1CB mechanism and the release of malonate ion from the hydroxo malonato complex would be independent of base.

2. Reactions at high base concentration. Here there is a limiting rate and again there are two possibilities:-

(a) The ring opening is still the rate determining step followed by the fast release of malonate ion as in 1(a) above, but now the presence of the deprotonated form makes the reaction have a limiting rate.

(b) A pre-equilibrium converts all of the complex into the form of the hydroxo malonato complex as in 1(b) and the rate then becomes independent of the hydroxide concentration.

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Recent work on ethyl malonato and benzyl malonato complexes shows that the ring opening and loss of malonate in these substituted malonato complexes are both second order and not first order which seems to rule out mechanism (a). But P. M. R. spectra indicates that the methylene group is active and so mechanism (a) is probably dominant at high base concentrations whereas the mechanism (b) is probably dominant at low base concentrations.

PREPARATION OF COMPOUNDS

Trans-Dichloro-bis(ethylenediamine)-cobalt(III) chloride, trans-$[Coen_2Cl_2]Cl$

This compound was the starting material used for the other preparations. It was prepared by the method of Bailar[107] which consists of adding 600 g. of a 10% solution of ethylenediamine to a solution of 160 g. of hydrated cobaltous chloride in 500 ml. of water in a two litre flask. Air was then vigorously drawn through the solution for ten hours. After this 350 ml. of concentrated hydrochloric acid were added and the solution was evaporated on a steam bath until a crust formed. Then the mixture was left to stand overnight after which it was filtered to collect the green crystalline trans-$[Coen_2Cl_2]Cl,HCl$. This was washed with alcohol and ether and then dried at 110° in an oven to give the green trans-$[Coen_2Cl_2]Cl$. If the solution was evaporated too long on the steam bath then some of the orange tris(ethylenediamine)-cobalt(III) chloride was formed but this can be removed from the final product by addition of a little dilute nitric acid to dissolve it out.

Cis-Dichloro-bis(ethylenediamine)-cobalt(III) chloride, cis-$[Coen_2Cl_2]Cl$

The trans- form was converted to the cis- form again using the method of Bailar.[107] A solution of the trans-$[Coen_2Cl_2]Cl$ was evaporated to dryness on a steam bath to give the violet cis-$[Coen_2Cl_2]Cl$. Any unchanged trans- material was either washed out with a little cold water or the transformation was completed by repeating the evaporation. But, according to Bailar, the evaporation must not be repeated more than two or three times as some decomposition occurs.

Conversion of cis- to trans-$[Coen_2Cl_2]Cl$

In order to convert the cis- to the trans- form it is only necessary to add acid to a solution of the cis- form since for any complex of the type $[Coen_2Cl_2]X$ a neutral solution goes to the cis-form and an acid solution to the trans- form.

Carbonato-bis(ethylenediamine)-cobalt(III) salts, $[Coen_2CO_3]X$

(a) Chloride

This was prepared from the trans-$[Coen_2Cl_2]Cl$ using the two methods of Werner.[108 109] The second method was preferred since it gave a better yield in a much shorter time.[109]

$$\text{trans-}[Coen_2Cl_2]Cl + K_2CO_3 \longrightarrow [Coen_2CO_3]Cl + 2KCl$$

Following this second method, firstly the trans-$[Coen_2Cl_2]Cl$ was ground together with the calculated amount of potassium carbonate as determined by the above equation. This was then mixed with water in the proportion complex : water = 2 : 1 and put on a steam bath until the mixture changed from green to red. This took about two minutes. The mixture was then quickly put into an ice-salt bath and stirred with a platinum spatula. The red crystalline powder was filtered off and washed with alcohol and ether. It was purified by recrystallisation from hot water when dark red, well developed, flaky crystals with a strong sheen were obtained. These crystals contain one molecule of water of crystallisation which is lost on standing to give a blue-red powder.

(b) Bromide

This was prepared from the chloride using the method of Werner.[108]

To a solution of 5 g. of $[Coen_2CO_3]Cl$ in 150 ml. of water was added the calculated amount (2 g.) of solid potassium bromide. The $[Coen_2CO_3]Br$ came down as a shining blue-red crystalline precipitate which could be purified by recrystallisation from warm water. Usually two distinct crystalline forms were obtained. One form was easily seen to appear as large, dark red, glistening, hexagonal crystals which were found to contain one molecule of water of crystallisation which they lost on standing to give a blue-red powder. The other form was seen as smaller crystals which were joined together in a brown-red crust. On closer examination using a polarising microscope they were seen to be cubic crystals and were found to be anhydrous.

(c) Iodide

This was prepared[108] from $[Coen_2CO_3]Cl$ by dissolving 5 g. of it in 200 ml. of water and then adding the equivalent amount (3 g.) of potassium iodide. The $[Coen_2CO_3]I$ came down immediately as a micro-crystalline blue-red powder. It was recrystallised from hot water to give glistening, dark red, prismatic crystals which were found to be anhydrous.

(d) Nitrate

This was prepared[108] from $[Coen_2CO_3]Br$, 5 g. of which were dissolved in hot water and the equivalent amount (3 g.) of silver nitrate was added. The precipitated silver bromide was filtered off, the filtrate was evaporated to half its original volume on a steam bath and then left overnight when dark red, strongly glistening, flaky crystals were obtained. These were dried in an oven.

(e) Perchlorate

The preparation of this compound was not found in the literature. It was prepared using two different methods. The first method followed was the normal procedure[108] of adding the equivalent amount (2.5 g.) of sodium perchlorate to 5 g. of $[Coen_2CO_3]Cl$ in 50 ml. of water. A red, finely crystalline precipitate was formed almost immediately, which was recrystallised from hot water. This method was repeated using the bromide. The second method was similar to that used for preparing $[Coen_2CO_3]Cl$ from trans-$[Coen_2Cl_2]Cl$[109]. The calculated amounts of trans-$[Coen_2Cl_2]ClO_4$ and sodium carbonate were ground together into a paste with a little water. The mixture was heated on a water bath and a red crystalline powder was obtained which was washed with alcohol and ether. Each method produced fine crystals which were anhydrous.

(f) Thiocyanate

This was prepared[108] from $[Coen_2CO_3]Cl$, 5 g. of which were dissolved in water to give a concentrated solution and then the calculated amount (2 g.) of potassium thiocyanate was added. A purple-red micro-crystalline powder was obtained which was recrystallised from hot water to give red, hexagonal prisms which crumbled on standing. Red needles were also obtained from the mother-liquor. The crystals were dried in an oven.

(g) Dithionate

This compound was prepared[108] from a dilute solution of $[Coen_2CO_3]Cl$ made by dissolving 5 g. of it in 300 ml. of water and then the calculated amount (2 g.) of sodium dithionate was added. A red crystalline precipitate

was obtained which was slightly soluble in water. This was recrystallised from hot water to give long, dark red needles which were dried in an oven at 100°.

(h) Sulphate

This was prepared from $[Coen_2CO_3]I$[108] 5 g. of which were dissolved in enough water to give a cold saturated solution. This solution was then treated with concentrated, aqueous silver sulphate solution until no more precipitation occurred. The silver iodide precipitate was filtered off and the filtrate was then cooled and the fairly insoluble sulphate was obtained as long, banded, red-black, flaky, prismatic crystals. These were found to contain ten molecules of water. They were dried at 100° to give the anhydrous salt.

Deuterated Compounds of the type $[Co(enD)_2CO_3]X$

The hydrogen atoms attached to the donor nitrogen atoms in the ethylenediamine ligands will undergo exchange with deuterium atoms so that the NH_2 groups are replaced by ND_2.

Deuterated compounds were prepared by dissolving the complexes in D_2O and then leaving the solution to stand in a desiccator over P_2O_5. The crystals that were formed were filtered off.

In addition the deuterated iodide was prepared from $[Coen_2CO_3]Cl$ by dissolving this in deuterium oxide, allowing it to stand and then potassium iodide was added to precipitate the $[Co(enD)_2CO_3]I$ which was filtered off.

Oxalato-bis(ethylenediamine)-cobalt(III) bromide, $[Coen_2C_2O_4]Br$

This compound was prepared from carbonato-bis(ethylenediamine)-cobalt(III) bromide using the method of Price and Brazier[110]. 2.5 g. of $[Coen_2CO_3]Br$ were dissolved in 70 ml. of water and to this was added 1 g. of oxalic acid in 20 ml. of water. The resulting solution was evaporated to small bulk and the crystals obtained were recrystallised from hot water to give dark red leaflets which were found to contain one molecule of water of crystallisation.

Malonato-bis(ethylenediamine)-cobalt(III) bromide, $[Coen_2C_3H_2O_4]Br$

This compound was prepared using the method of Price and Duff[111] which was adapted from the preparation by Price and Brazier[110] of cis-sulphonyldiacetato-bis(ethylenediamine)-cobalt(III) bromide. 5 g. of $[Coen_2CO_3]Br$ were dissolved in 80 ml. of warm water and the solution was filtered and cooled after which 1.7 g. of malonic acid were added and the solution was then left overnight in a vacuum desiccator containing soda-lime to absorb all the carbon dioxide. The solution was then evaporated on a steam-bath to small bulk and left to stand when crystals were obtained which were recrystallised from warm water to give dark red leaflets which were anhydrous.

Malonato-bis(ethylenediamine)-cobalt(III) malonate, $[Coen_2C_3H_2O_4]C_3H_3O_4$

The malonate was prepared according to the method of Werner[108]. 1 g. of $[Coen_2CO_3]Br$ was dissolved in a little water and to this solution was added 0.55 g. of freshly precipitated silver oxide and the mixture was shaken. The silver bromide was filtered off and the filtrate was

treated with malonic acid so that the molecular proportions of base to acid were one to two. The resulting solution was concentrated by evaporation on a water-bath and a red salt was obtained which was recrystallised from hot water and dried over calcium chloride to give the anhydrous salt.

Optically active malonato-bis(ethylenediamine)-cobalt(III) salts

The resolution of $[Coen_2CO_2CH_2CO_2]Br$ was attempted through the optical isomers of α-bromocamphor-Π-sulphonate but it was unsuccessful. The optical isomers of the ethylenediaminetetraacetato cobaltate (III) ion were then tried and this proved successful giving the optically active iodide but not the bromide. The resolution was carried out in the following three stages.

(1) Preparation of potassium ethylenediaminetetraacetato cobaltate(III)

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K[CoEDTA] was prepared using the method of Dwyer, Gyarfas and Mellor. 24 g. of hydrated cobaltous chloride, 60 g. of potassium acetate and 30 g. of ethylenediaminetetra-acetic acid were dissolved in 180 ml. of water. The solution was heated to nearly boiling and then 90 ml. of 30% hydrogen peroxide were added gradually. The solution was then cooled and alcohol was added and the K[CoEDTA] came down immediately. It was filtered off and washed with methanol and ether and dried in a vacuum desiccator.

(2) Resolution of potassium ethylenediaminetetraacetato cobaltate(III)

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K[CoEDTA] was resolved using the standard procedure by means of the optical isomer l-cis-dinitro-bis(ethylenediamine)-cobalt(III) iodide.

20.6 g. of l-cis-$[Coen_2(NO_2)_2]I$ and 262.5 ml. of water were placed in a one litre conical flask. 45 g. of freshly precipitated silver chloride were added, the mixture was heated to 50-60° and the flask was stoppered and shaken for 4-5 minutes, while being kept at 50-60°. The silver iodide was filtered off and washed with some warm water (37.5 ml.). 30 g. of K[CoEDTA] were added to the filtrate, the mixture was then cooled in ice and the sides of the vessel were scratched to give a precipitate of the diastereoisomer $[l\text{-}Coen_2(NO_2)_2][CoEDTA]3H_2O$. This was filtered off, washed with cold 50% ethanol, ethanol and acetone and air dried at room temperature.

15 g. of the diastereoisomer were mixed with 112.5 ml. of water in a mortar. 30 g. of potassium iodide were added and the mixture was ground for 4-5 minutes to give a precipitate of l-cis-$[Coen_2(NO_2)_2]I$. This was filtered off, 135 ml. of ethanol were slowly added to the filtrate and the sides of the vessel scratched to give d-$K[CoEDTA]2H_2O$ as violet plates. The solution was allowed to stand for 3-4 minutes and then more ethanol was added (165 ml.). The crystals were washed with cold ethanol.

(3) Resolution of malonato-bis(ethylenediamine)-cobalt(III) salts

This resolution was carried out by adapting the method used by Dwyer, Reid and Garvan[114] for the resolution of the $[Coen_2C_2O_4]^+$ ion. 8 g. of $[Coen_2CO_2CH_2CO_2]Br$ in 40 ml. of water at 65° were shaken in a conical flask with 3.2 g. of silver acetate for 10 minutes. The silver bromide was filtered off and washed with a little hot water. The filtrate was heated to 60° and 4.22 g. of d-$K[CoEDTA]2H_2O$ were added and

dissolved by shaking. The diastereoisomer d-[$Coen_2CO_2CH_2CO_2$]-d-[CoEDTA] commenced to separate and the mixture was allowed to cool to room temperature. The diastereoisomer was collected, washed with ice-water and then ethanol and then ground with 33.5 ml. of water containing 6.7 g. of potassium iodide to give an orange precipitate of d-[$Coen_2CO_2CH_2CO_2$]I. Sometimes the solution had to be concentrated before the precipitate was obtained. The resolving agent was recovered from the filtrate by adding alcohol.

The other optical isomer was obtained by treating the filtrate from the separation of the diastereoisomer at 60° with 10 ml. of a 50% aqueous solution of ammonium bromide giving the bromide which was filtered off, washed and dried.

Trans-Dichloro-bis(ethylenediamine)-cobalt(III) salts

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The malonate was prepared by the method of Price and Brazier. 3 g. of trans-[$Coen_2Cl_2$]Cl were dissolved in 10 ml. of water and then 4 g. of malonic acid were added which immediately gave a dark green crystalline precipitate which was washed with water and then alcohol. The formula of this salt is of the type trans-[$Coen_2Cl_2$]$HAA,H_2AA,2H_2O$, where AA = $CO_2CH_2CO_2^{2-}$.

The oxalate and succinate were prepared and given by Dr. Farago. These are also green crystalline compounds which have formulas of the type trans-[$Coen_2Cl_2$]HAA, where AA = $C_2O_4^{2-}$ and $CO_2(CH_2)_2CO_2^{2-}$.

Succinato-bis(ethylenediamine)-cobalt(III) salts, $[Coen_2CO_2(CH_2)_2CO_2]X$

(a) Bromide

This compound was prepared using the method described by Duff.[116] 5 g. of $[Coen_2CO_3]Br$ were dissolved in 100 ml. of water and the solution was boiled. 1.6 g. of succinic anhydride were then added and the mixture was boiled for two minutes after which it was concentrated to small bulk on a water-bath and then left to crystallise. But a crystalline product was not obtained from any of the preparations carried out. Either a gel was formed which set to a hard resin, or, if it was precipitated by some other agent, then a gelatinous precipitate was obtained. So that all the measurements have been made on this gelatinous precipitate, after washing and drying it.

(b) Nitrate and Iodide

These compounds were prepared using the same method as for the bromide. But again only gels were obtained.

Preparation of the nitrate was also attempted by the method of Duff.[116] 1.24 g. of silver nitrate were added to 3 g. of $[Coen_2CO_2(CH_2)_2CO_2]Br$ in water and the silver bromide precipitate was filtered off. The filtrate was then concentrated to small bulk on a water-bath but again a gel was obtained.

(c) Succinate

The preparation of this compound was attempted by the method of Duff.[116] 6 g. of $[Coen_2CO_3]Br$ were dissolved in 120 ml. of water and 4 g. of freshly prepared moist silver oxide were added to give the carbonato base.

The silver bromide was filtered off and the filtrate was boiled, after which 4.44 g. of succinic anhydride were added and the mixture was boiled for five minutes. It was then evaporated to small bulk after which a little alcohol was stirred in giving a gelatinous precipitate.

(d) Perchlorate

This compound was obtained by the addition of perchloric acid to an aqueous solution of $[Coen_2CO_2(CH_2)_2CO_2]Br$ giving a gelatinous precipitate which was only moderately soluble in water and was then recrystallised from water to give again a gelatinous precipitate. Some measurements were made on this precipitate.

The perchlorate was also prepared by adding the equivalent amount of succinic anhydride to 5 g. of $[Coen_2CO_3]ClO_4$ in 100 ml. of water and then evaporating to low bulk after which it was left to crystallise but again a gelatinous precipitate was obtained.

(e) Bromide + NaOH

An interesting compound was obtained from $[Coen_2CO_2(CH_2)_2CO_2]Br$ dissolved in sodium hydroxide solution. It was precipitated by the addition of methyl alcohol, acetone and ether. The precipitate was redissolved in hot M/10 sodium hydroxide and reprecipitated by the addition of methyl alcohol, acetone and ether. It was a palle pink powder and its infrared and visible and ultra-violet absorption spectra were different from those of $[Coen_2CO_2(CH_2)_2CO_2]^+$ and $[Coen_2(OH)_2]^+$.

ANALYSES

		% Carbon	% Hydrogen	% Halogen
$[Coen_2CO_3]Cl$	Calcd:	21.98	5.87	12.91
	Found:	22.14	5.97	12.78
$[Coen_2CO_3]Br$	Calcd:	18.82	5.05	25.04
	Found:	18.83	5.25	24.42
$[Coen_2CO_3]Br,H_2O$	Calcd:	17.82	5.31	23.71
	Found:	17.55	5.39	22.60
$[Coen_2CO_3]I$	Calcd:	16.41	4.41	34.66
	Found:	16.41	4.74	36.79
$[Coen_2CO_3]NO_3$	Calcd:	19.94	5.36	23.1 (Nitrogen)
	Found:	20.72	5.56	21.0
$[Coen_2CO_3]ClO_4$	Calcd:	17.74	4.76	10.47
	Found:	17.30	4.73	10.14
$[Coen_2CO_3]SCN$	Calcd:	24.24	5.43	10.78 (Sulphur)
	Found:	24.48	5.13	10.64
$[Coen_2CO_3]_2S_2O_6$	Calcd:	18.81	5.05	10.02 (Sulphur)
	Found:	18.26	5.35	
$[Coen_2CO_3]_2S_2O_6,2H_2O$	Calcd:	17.80	5.38	9.54 (Sulphur)
	Found:	17.51	5.34	9.71
$[Coen_2CO_3]_2SO_4,10H_2O$	Calcd:	15.92	6.95	4.18 (Sulphur)
	Found:	15.53	6.85	3.90
$[Coen_2C_2O_4]Br,H_2O$	Calcd:	19.73	4.97	21.89
	Found:	20.30	5.24	19.42
$[Coen_2C_3H_2O_4]Br$	Calcd:	23.29	5.02	22.13
	Found:	23.38	5.09	21.58
$[Coen_2C_3H_2O_4]C_3H_3O_4$	Calcd:	31.26	5.51	
	Found:	31.27	5.99	
$[Coen_2C_4H_4O_4]Br,H_2O$	Calcd:	24.45	5.64	20.32
	Found:	24.47	6.25	20.00
trans-$[Coen_2Cl_2]C_6H_7O_8,2H_2O$	Calcd:	24.35	5.52	14.37
	Found:	25.61	5.52	16.5

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20.6 g. of l-cis-$[Coen_2(NO_2)_2]I$ and 262.5 ml. of water were placed in a one litre conical flask. 45 g. of freshly precipitated silver chloride were added, the mixture was heated to 50-60° and the flask was stoppered and shaken for 4-5 minutes, while being kept at 50-60°. The silver iodide was filtered off and washed with some warm water (37.5 ml.). 30 g. of K[CoEDTA] were added to the filtrate, the mixture was then cooled in ice and the sides of the vessel were scratched to give a precipitate of the diastereoisomer $[l\text{-}Coen_2(NO_2)_2][CoEDTA]3H_2O$. This was filtered off, washed with cold 50% ethanol, ethanol and acetone and air dried at room temperature.

15 g. of the diastereoisomer were mixed with 112.5 ml. of water in a mortar. 30 g. of potassium iodide were added and the mixture was ground for 4-5 minutes to give a precipitate of l-cis-$[Coen_2(NO_2)_2]I$. This was filtered off, 135 ml. of ethanol were slowly added to the filtrate and the sides of the vessel scratched to give d-$K[CoEDTA]2H_2O$ as violet plates. The solution was allowed to stand for 3-4 minutes and then more ethanol was added (165 ml.). The crystals were washed with cold ethanol.

(3) Resolution of malonato-bis(ethylenediamine)-cobalt(III) salts

This resolution was carried out by adapting the method used by Dwyer, Reid and Garvan[114] for the resolution of the $[Coen_2C_2O_4]^+$ ion. 8 g. of $[Coen_2CO_2CH_2CO_2]Br$ in 40 ml. of water at 65° were shaken in a conical flask with 3.2 g. of silver acetate for 10 minutes. The silver bromide was filtered off and washed with a little hot water. The filtrate was heated to 60° and 4.22 g. of d-$K[CoEDTA]2H_2O$ were added and

dissolved by shaking. The diastereoisomer d-[$Coen_2CO_2CH_2CO_2$]-d-[CoEDTA] commenced to separate and the mixture was allowed to cool to room temperature. The diastereoisomer was collected, washed with ice-water and then ethanol and then ground with 33.5 ml. of water containing 6.7 g. of potassium iodide to give an orange precipitate of d-[$Coen_2CO_2CH_2CO_2$]I. Sometimes the solution had to be concentrated before the precipitate was obtained. The resolving agent was recovered from the filtrate by adding alcohol.

The other optical isomer was obtained by treating the filtrate from the separation of the diastereoisomer at 60° with 10 ml. of a 50% aqueous solution of ammonium bromide giving the bromide which was filtered off, washed and dried.

Trans-Dichloro-bis(ethylenediamine)-cobalt(III) salts

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The malonate was prepared by the method of Price and Brazier. 3 g. of trans-[$Coen_2Cl_2$]Cl were dissolved in 10 ml. of water and then 4 g. of malonic acid were added which immediately gave a dark green crystalline precipitate which was washed with water and then alcohol. The formula of this salt is of the type trans-[$Coen_2Cl_2$]$HAA,H_2AA,2H_2O$, where AA = $CO_2CH_2CO_2^{2-}$.

The oxalate and succinate were prepared and given by Dr. Farago. These are also green crystalline compounds which have formulas of the type trans-[$Coen_2Cl_2$]HAA, where AA = $C_2O_4^{2-}$ and $CO_2(CH_2)_2CO_2^{2-}$.

Succinato-bis(ethylenediamine)-cobalt(III) salts, $[Coen_2CO_2(CH_2)_2CO_2]X$

(a) Bromide

This compound was prepared using the method described by Duff.[116] 5 g. of $[Coen_2CO_3]Br$ were dissolved in 100 ml. of water and the solution was boiled. 1.6 g. of succinic anhydride were then added and the mixture was boiled for two minutes after which it was concentrated to small bulk on a water-bath and then left to crystallise. But a crystalline product was not obtained from any of the preparations carried out. Either a gel was formed which set to a hard resin, or, if it was precipitated by some other agent, then a gelatinous precipitate was obtained. So that all the measurements have been made on this gelatinous precipitate, after washing and drying it.

(b) Nitrate and Iodide

These compounds were prepared using the same method as for the bromide. But again only gels were obtained.

Preparation of the nitrate was also attempted by the method of Duff.[116] 1.24 g. of silver nitrate were added to 3 g. of $[Coen_2CO_2(CH_2)_2CO_2]Br$ in water and the silver bromide precipitate was filtered off. The filtrate was then concentrated to small bulk on a water-bath but again a gel was obtained.

(c) Succinate

The preparation of this compound was attempted by the method of Duff.[116] 6 g. of $[Coen_2CO_3]Br$ were dissolved in 120 ml. of water and 4 g. of freshly prepared moist silver oxide were added to give the carbonato base.

The silver bromide was filtered off and the filtrate was boiled, after which 4.44 g. of succinic anhydride were added and the mixture was boiled for five minutes. It was then evaporated to small bulk after which a little alcohol was stirred in giving a gelatinous precipitate.

(d) Perchlorate

This compound was obtained by the addition of perchloric acid to an aqueous solution of $[Coen_2CO_2(CH_2)_2CO_2]Br$ giving a gelatinous precipitate which was only moderately soluble in water and was then recrystallised from water to give again a gelatinous precipitate. Some measurements were made on this precipitate.

The perchlorate was also prepared by adding the equivalent amount of succinic anhydride to 5 g. of $[Coen_2CO_3]ClO_4$ in 100 ml. of water and then evaporating to low bulk after which it was left to crystallise but again a gelatinous precipitate was obtained.

(e) Bromide + NaOH

An interesting compound was obtained from $[Coen_2CO_2(CH_2)_2CO_2]Br$ dissolved in sodium hydroxide solution. It was precipitated by the addition of methyl alcohol, acetone and ether. The precipitate was redissolved in hot M/10 sodium hydroxide and reprecipitated by the addition of methyl alcohol, acetone and ether. It was a pale pink powder and its infrared and visible and ultra-violet absorption spectra were different from those of $[Coen_2CO_2(CH_2)_2CO_2]^+$ and $[Coen_2(OH)_2]^+$.

ANALYSES

		% Carbon	% Hydrogen	% Halogen
$[Coen_2CO_3]Cl$	Calcd:	21.98	5.87	12.91
	Found:	22.14	5.97	12.78
$[Coen_2CO_3]Br$	Calcd:	18.82	5.05	25.04
	Found:	18.83	5.25	24.42
$[Coen_2CO_3]Br,H_2O$	Calcd:	17.82	5.31	23.71
	Found:	17.55	5.39	22.60
$[Coen_2CO_3]I$	Calcd:	16.41	4.41	34.66
	Found:	16.41	4.74	36.79
$[Coen_2CO_3]NO_3$	Calcd:	19.94	5.36	23.1 (Nitrogen)
	Found:	20.72	5.56	21.0
$[Coen_2CO_3]ClO_4$	Calcd:	17.74	4.76	10.47
	Found:	17.30	4.73	10.14
$[Coen_2CO_3]SCN$	Calcd:	24.24	5.43	10.78 (Sulphur)
	Found:	24.48	5.13	10.64
$[Coen_2CO_3]_2S_2O_6$	Calcd:	18.81	5.05	10.02 (Sulphur)
	Found:	18.26	5.35	
$[Coen_2CO_3]_2S_2O_6,2H_2O$	Calcd:	17.80	5.38	9.54 (Sulphur)
	Found:	17.51	5.34	9.71
$[Coen_2CO_3]_2SO_4,10H_2O$	Calcd:	15.92	6.95	4.18 (Sulphur)
	Found:	15.53	6.85	3.90
$[Coen_2C_2O_4]Br,H_2O$	Calcd:	19.73	4.97	21.89
	Found:	20.30	5.24	19.42
$[Coen_2C_3H_2O_4]Br$	Calcd:	23.29	5.02	22.13
	Found:	23.38	5.09	21.58
$[Coen_2C_3H_2O_4]C_3H_3O_4$	Calcd:	31.26	5.51	
	Found:	31.27	5.99	
$[Coen_2C_4H_4O_4]Br,H_2O$	Calcd:	24.45	5.64	20.32
	Found:	24.47	6.25	20.00
trans-$[Coen_2Cl_2]C_6H_7O_8,2H_2O$	Calcd:	24.35	5.52	14.37
	Found:	25.61	5.52	16.5

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