

Complexes of cobalt (II) halides with aromatic amines

Author:

Rooney, Michael Lawrence

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COMPLEXES OF COBALT(II) HALIDES

WITH AROMATIC AMINES

A Thesis

submitted for the Degree of

Master of Science

in the

University of New South Wales

by

M. L. Rooney, B.Sc.

October, 1970

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I hereby declare that the work described in this thesis has not been submitted, in part or in full, to any other University or Institution for any degree whatsoever.

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LIST OF ABBREVIATIONS

The following abbreviations appear in Tables and Figures:

<u>Compound</u>	<u>Abbreviation</u>
p-acetamidooaniline	p-acetamidooan
p-acetylaniline	p-acetylan
p-anisidine	p-anis
p-bromoaniline	p-bran
p-chloroaniline	p-clan
p-fluoroaniline	p-flan
p-nitroaniline	p-nitran
p-toluidine	p-tol
o-anisidine	^o / _p -anis
o-toluidine	o-tol

SUMMARY

The complexes of cobalt(II) halides and cobalt(II) thiocyanate with several aromatic amines have been prepared. The stereochemistry of the metal in each complex in the solid-state has been assigned. These assignments have been made using evidence from absorption spectra, magnetic moments, infra-red spectra and thermogravimetric analysis (in one instance). The complexes of the halides are all tetrahedral monomers while those of the thiocyanate are octahedral polymers. Ethanol and water adducts have been isolated in some instances.

The solution chemistry of the complexes has been investigated using electrical conductance measurements and absorption spectroscopy. Stereochemical equilibria have been considered in some detail. Evidence has been found for extensive dissociation of the complexes in the more polar solvents.

Some evidence has been found for variation in ligand field strength depending upon the substituent in the para position of the amine. Such variation appears to be very small.

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INTRODUCTION

1. Stereochemistry of Cobalt(II) Compounds in the Solid State

Bivalent cobalt forms a wide variety of compounds, both simple and complex. The stereochemical environment of the cobalt may be one of several types depending upon the nature of the atoms or ions which make up that environment. The most common stereochemistries are octahedral and tetrahedral⁽¹⁾. These are found when cobalt(II) is in the spin-free state.

Cobalt(II) forms more tetrahedral complexes than any other transition metal^(2a). Jorgensen and Bjerrum using simple ligand field theory^(2b) have shown that of all bivalent first row transition metal ions, cobalt(II) is most likely to form tetrahedral complexes. Such complexes are usually formed with unidentate anionic ligands. Thus the tetrahalo complex ions are all tetrahedral, e.g. $\left[\text{CoCl}_4\right]^{2-}$. Tetrahedral complexes are also formed when the ligands consist of two unidentate anions plus two neutral molecules⁽²⁾. However there are exceptions. Bidentate monoanions which are bulky, such as N-alkylsalicylaldiminato anions also form tetrahedral complexes. When the ligands of this type are less hindered sterically, higher co-ordination numbers are involved. In the case of the acetylacetonate, the co-ordination number is six⁽³⁾.

Octahedral stereochemistry is normally found when the ligands exert a fairly weak field, as is the case with the fluoride ion, water and ammonia⁽⁴⁾. Thus the hexammine complexes of cobalt chloride and iodide have been shown by Stoll⁽⁵⁾, using X-ray crystallography, to have six ammonia molecules at the points of a regular octahedron.

The other stereochemistries which are less commonly found are square planar, trigonal bipyramidal and tetragonal. Square planar complexes have been found with several bidentate singly charged anions such as dimethylglyoxime⁽⁶⁾. Several neutral bidentate ligands also form square planar complexes. Quadridentate ligands such as porphyrins also form square planar complexes⁽⁶⁾. An example of a trigonal bipyramidal complex of cobalt(II) is found in bis (N-methylsalicylaldiminato) cobalt(II)⁽⁷⁾. The tetragonal complexes are formed with such donor atoms as sulphur, phosphorus or arsenic. Alderman and Owston⁽⁸⁾ have used X-ray diffraction to show that the structure of the nitrosyl derivative of bis (N,N-dimethyldithiocarbamate) cobalt(II) is a tetragonal pyramid. Five co-ordinate complexes may be either high or low-spin. The square planar complexes so far examined have all been low-spin⁽⁹⁾.

This thesis is concerned with the stereochemistry of certain high-spin complexes of cobalt(II) involving nitrogen donors. The background to such complexes is now considered in greater detail.

2. Structural Background to this Investigation

The isolation of a compound formed by reaction of a cobalt(II) halide with an aromatic amine was first reported by Leeds⁽¹⁰⁾. He reacted cobalt(II) chloride with aniline. Since that time preparations of a variety of compounds of cobalt(II) halides or pseudohalides with ring substituted anilines have been described in the literature⁽¹⁰⁻¹⁶⁾. Two ligands, o-anisidine and o-aminobenzenethiol have been found to chelate in complexes with cobalt halides^(17,18). Recently one other amine, m-chloroaniline, has been reported to form a complex of the type CoX_2B_4 ⁽¹⁹⁾. The rest of the complexes have all had the empirical formula CoX_2B_2 where X represents Cl, Br, I or NCS and B stands for aniline or one of its ring substituted analogues. Ablov et al⁽¹³⁾ reported preparation of compounds of the type CoX_2B_2 with the following ligands; B = aniline, o- and p-toluidine, o- and p-anisidine, o-, m- and p-chloroaniline, o-, m- and p-bromoaniline and p-iodoaniline, X = Cl, Br, and I. The chloro and bromo complexes were blue and the iodo complexes green. Preparation of the o-, m- and p-bromoaniline complexes of cobalt iodide was not reported. In each case analysis for inorganic constituents and macroscopic crystal form were the only information about the complexes reported.

Sarju Prasad et al⁽¹¹⁾ also reported preparation of some of the above complexes with cobalt chloride and included as ligands benzidine, ethylaniline and a phenylenediamine. The compounds were described as

FIGURE 1

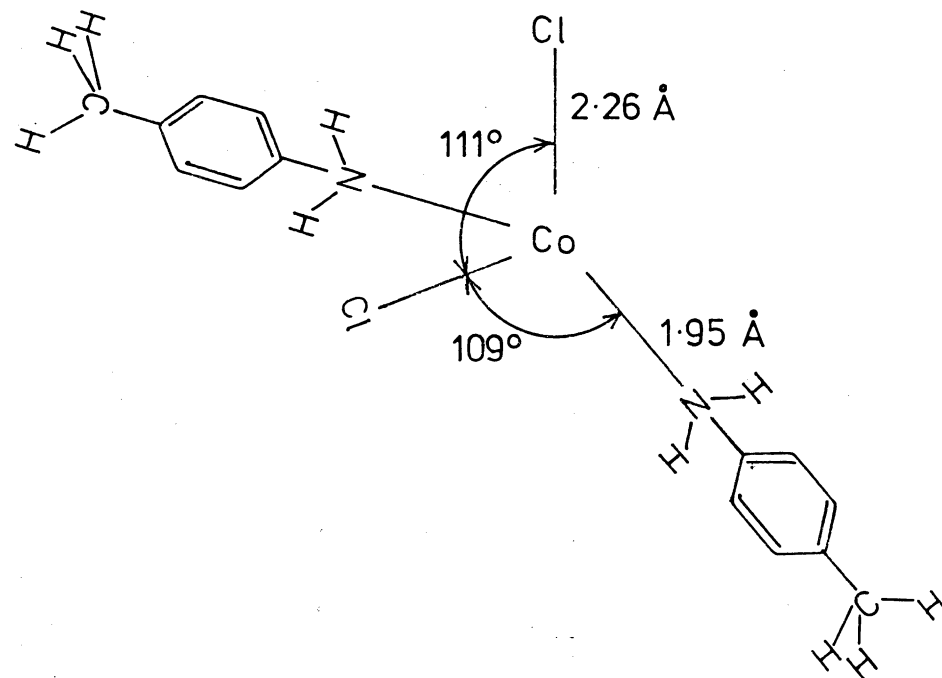


FIGURE 1.

CRYSTAL STRUCTURE OF $\text{CoCl}_2 \cdot \text{p-TOLUIDINE}_2$

being blue, green, violet or even grey or black.

Ahuya et al⁽¹⁵⁾ investigated some of the spectroscopic properties of complexes of the type CoX_2B_2 where B = aniline, o-, m- and p-toluidine and 2,5- and 3,4-xylidines.

It was not until 1956 that some of these compounds were investigated by means of X-ray diffraction. Malinovskii^(14,16,21) investigated the structures of $\text{CoCl}_2\text{p-toluidine}_2$ and $\text{CoI}_2\text{p-toluidine}_2$ by single crystal X-ray crystallography. In a preliminary investigation he found that $\text{CoCl}_2\text{p-iodoaniline}_2$ and $\text{CoI}_2\text{aniline}_2$ were isomorphous with both the former two complexes.

The structure of bis (p-toluidine) cobalt(II) chloride is shown in Figure 1. The cobalt atom is in an environment which is tetrahedral within experimental error. The angles N-Co-N and Cl-Co-Cl are all 111° and the angles Cl-Co-N are 109° , respectively. (The tetrahedral angle is $109^\circ 5'$ ⁽²²⁾.) However, all the cobalt-donor atom bond lengths are not equal. The Co-Cl distances are both 2.26\AA while the Co-N distances are 1.95\AA .

In the case of $\text{CoI}_2\text{p-toluidine}_2$ only the heavy atoms were located. The structure (tetrahedral) appears similar to that in Figure 1 except that the I-Co-I angle is 110° and the Co-I distance 2.63\AA . The structures of these complexes are stable and only one case of polymerisation has been reported in cobalt halide complexes with aromatic amines. This was reported very recently by Beech et al⁽²³⁾ who suggest that

FIGURE 2

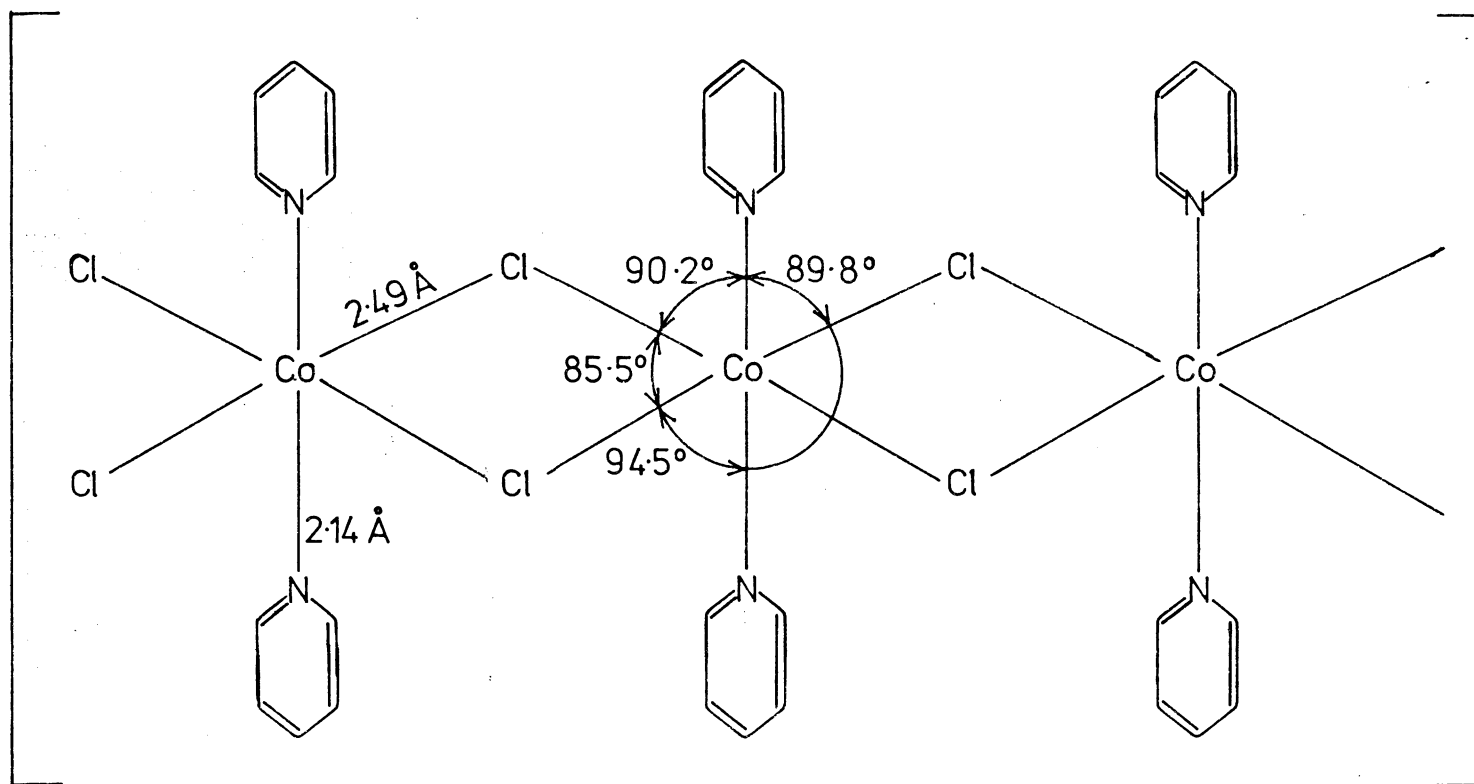


FIGURE 2.

CRYSTAL STRUCTURE OF VIOLET POLYMERIC FORM OF $\text{CoCl}_2 \cdot \text{PYRIDINE}_2$.

$\text{CoCl}_2\text{p-fluoroaniline}_2$ is an octahedral polymer. In view of the wide knowledge available concerning heterocyclic base complexes with cobalt(II) halides, discussion of these compounds will provide the most convenient source of comparative data for this introduction.

The stereochemistry of the cobalt atom in aromatic amine complexes with cobalt chloride is quite different from that of the stable violet polymeric form of $\text{CoCl}_2\text{pyridine}_2$. In the latter compound the cobalt atom is in an octahedral environment⁽²⁴⁾, consisting of four chlorine atoms and two pyridine molecules. The four chlorine atoms are located at the corners of a square as shown in Figure 2. Thus the molecule consists of a polymer in which all four chlorine atoms are bridging to adjacent cobalt atoms. The Co-Cl distance is 2.49\AA . The nitrogen atoms of the pyridines complete the octahedron and the Co-N distance was shown to be 2.14\AA in each case. There is an unstable (blue) isomer of this compound which has been shown^(25,26) to have a tetrahedral structure as in $\text{CoCl}_2\text{p-toluidine}_2$. Recently⁽²⁷⁾ a partial structure of $\text{CoCl}_2(\text{p-vinylpyridine})_2$ has been reported. It is tetrahedral with the Co-Cl distances 2.22\AA and the Co-N distances are 2.01\AA . The Cl-Co-Cl angle is 117° but the other angles at the cobalt are almost exactly tetrahedral. With the exception of compounds of o-anisidine and o-aminobenzenethiol and $\text{CoBr}_2\text{m-chloroaniline}_4$, all the compounds formed between cobalt halides with aromatic amines reported to date have had the stoichiometry CoX_2B_2 . However, when the organic base is not an aromatic amine but pyridine or one of its

ring substituted analogues, compounds of the type CoX_2B_4 are frequently formed^(28,29). In the case of $\text{CoCl}_2\text{pyridine}_4$ X-ray crystal structure determination⁽³⁰⁾ has revealed an octahedral ligand cage about the cobalt atom. In this compound the cobalt atom is surrounded by four nitrogen donor atoms and two chlorine atoms. The bond lengths are 2.32Å for Co-Cl and 1.99Å for Co-N. In several instances the chloride complexes of heterocyclic bases have been shown to be isostructural with the corresponding bromide and iodide complexes⁽³¹⁾.

Finally, consideration should be given to compounds of cobalt pseudohalides of the type $\text{Co(NCS)}_2\text{aniline}_2$ and $\text{Co(NCS)}_2\text{pyridine}_2$. The properties of these complexes may be considered conveniently with those of the corresponding halide complexes as other workers^(29,26) and subsequent discussions show. There has been no crystallographic study of $\text{Co(NCS)}_2\text{aniline}_2$ reported. However, Nyholm⁽³³⁾ has suggested that this complex is in fact an octahedral polymer. The related pyridine complex $\text{Co(NCS)}_2\text{pyridine}_2$ has not been investigated crystallographically but Nyholm et al⁽³⁴⁾ conclude that it is an octahedral polymer on the basis of its magnetic properties.

3. Physical Properties of the Complexes in the Solid State

There are three physical ^{MEASUREMENTS}~~properties~~ of solid cobalt(II) complexes which provide evidence as to their stereochemistry. These ^{MEASUREMENTS}~~properties~~ are diffuse reflectance spectra in the visible region^(29,35-38),

magnetic moments^(29,34,39,40) and infra-red spectra^(28,29,32). The first two ^{MEASUREMENTS USEFULLY STUDIED IN} ~~properties are applicable to~~ all cobalt(II) compounds but the last is ^{(CONSIDERED IN THE} ~~used~~ mainly ^{for} investigation of the mode of bonding of thiocyanate groups to the cobalt atoms. The use of far infra-red ^{SPECTRA} ~~spectroscopy~~ has been reported recently^(41,42) but this is not used to the same extent as the other ^{PROPERTIES MEASUREMENT OF} ~~techniques~~. While ^{PROPERTIES SINGLY} ~~none of these tech-~~ ^{niques} provides unequivocal evidence as to stereochemistry, when they ^{MEASURED} ~~are used~~ in combination a reliable assignment may usually be made^(43,44).

(a) Diffuse Reflectance Spectra in the Visible Region:

Examination of the solid state reflectance spectra of a large number of known octahedrally co-ordinated cobalt(II) compounds has revealed that these compounds have an absorption band in the region 500-600nm⁽²⁹⁾. Known tetrahedrally co-ordinated compounds have a much more intense absorption band in the region 600-700nm⁽²⁹⁾. The bands exhibited by the two stereochemical species are mutually exclusive unless there are occupied octahedral sites in a tetrahedral lattice and vice versa, and in the case of contamination. (Owing to its intensity of colour, two per cent of tetrahedral species in an octahedral matrix is enough to make the mixture appear blue instead of the pinkish shade of the octahedral species.)

The origin of these bands is generally agreed to lie in d-d trans-

itions although there has been at least one author⁽⁴⁵⁾ who has doubted this. These transitions are believed to result from the fact that the energy separating sets of non-degenerate 3d orbitals in cobalt(II) compounds is of the same order as that of visible light. The Ligand Field Theory provides a satisfactory explanation for the observed light absorption behaviour. This theory is an extension of the Crystal Field Theory⁽⁴⁷⁻⁵⁰⁾ which considers the effect of point charges on the energy of a central ion. The Ligand Field Theory is thus an electrostatic approach and is used here to consider the effect of the approach of ligand donor atoms (Lewis bases) towards the cobalt(II) ion. The outermost shell of the cobalt(II) ion is the 3d shell and this contains seven electrons. The shapes of the five 3d orbitals consist⁽⁵¹⁾ essentially of two sets of lobes (regions of high probability of finding an electron when occupied by one). One set has its regions of highest electron density pointing along the x, y and z axes. The other set points between these axes thus giving overall spherical symmetry to the filled 3d shell of d^5 or d^{10} ions as in the manganese(II) and the zinc(II) ions. However, in the presence of an electrostatic field these two sets of orbitals may be split in several ways depending on the stereochemical environment.

By far the two most common fields provided by donor atoms of ligands in cobalt(II) compounds are tetrahedrally or octahedrally

directed fields. An octahedral field produced by six ligands approaching a cobalt(II) ion symmetrically along the x,y and z axes will raise the energy of those orbitals with high electron density along these axes. These orbitals are the d_{z^2} and the $d_{x^2-y^2}$ which are termed d_{γ} . Since ligands are not point charges, repulsion will be experienced by electrons in the orbitals pointing between the axes, but the energy of these orbitals will be raised to a lesser extent. In the case of four ligands approaching in a symmetrical fashion between the axes (a tetrahedral field), the orbitals pointing between the axes will be strongly raised in energy. These orbitals are the d_{xy} , d_{xz} and d_{yz} (d_{ϵ}). Once again the other 3d orbitals, the d_{γ} , will be raised in energy to a lesser extent. Thus the apparent degeneracy of the five 3d orbitals is removed and differing energy levels are exhibited by 3d electrons in the presence of a ligand field. These effects are illustrated in Figure 3. Fields of other symmetry are possible, viz. square planar. However these are less common and have not been found in the type of complexes under consideration.

When an electron in the lower energy set of d orbitals absorbs a quantum of light in the visible region, the electron is promoted to the higher energy set of orbitals and it is this absorption which is detected in the visible reflectance spectrum. Cotton and Holm⁽⁴⁰⁾ have discussed this further and have shown

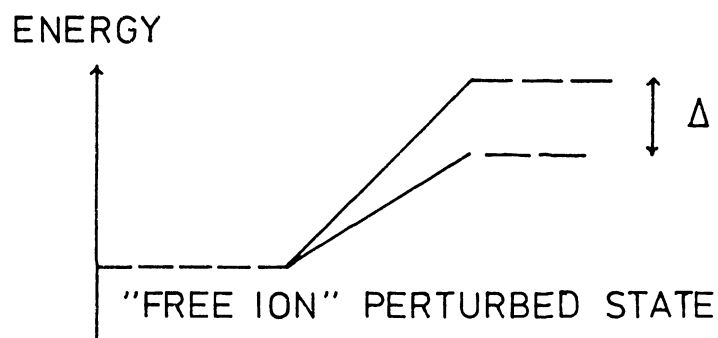
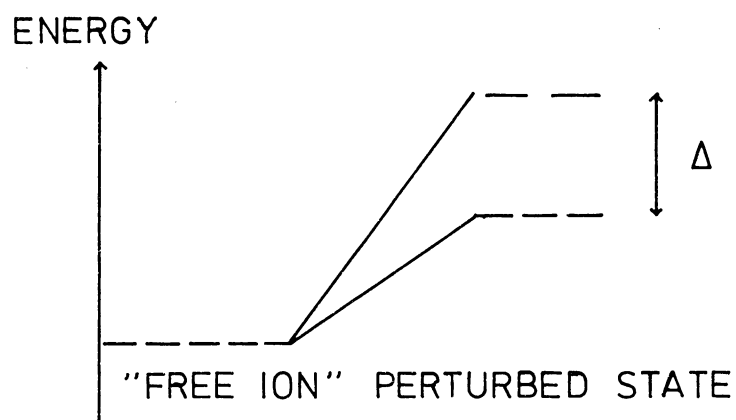


FIGURE 3.
SIMPLEST SPLITTING OF d ORBITALS IN THE PRESENCE
OF (a) AN OCTAHEDRAL LIGAND FIELD.
(b) A TETRAHEDRAL LIGAND FIELD.

that a further absorption band predicted from the Ligand Field Theory to be around 3,500nm for tetrahedral cobalt(II) compounds is in fact observed as a low intensity band.

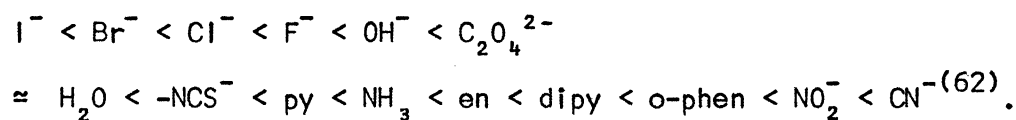
From the foregoing simplified picture, it would be assumed that a single quantum of energy separates the d_{ϵ} and d_{γ} orbitals. However, the spectra of both octahedral and tetrahedral cobalt(II) compounds are found to consist of broad bands. The broad peak has been shown⁽⁵²⁾ in the case of $[\text{CoCl}_4]^{2-}$ to consist of as many as 6 overlapping bands. There has been considerable discussion as to the assignment of bands in cobalt(II) complexes^(40,53-55). A convenient criterion, however, for comparison of reflectance spectra of different complexes lies in the wavelengths of their centres of gravity⁽⁴⁰⁾ or of their half widths⁽²⁸⁾.

There is a complication which may be observed in the spectra of cobalt(II) complexes. This is the presence of an intense charge transfer band. This band just short of the low wavelength extremity of the visible region may interfere with the usual profile of the broad, low intensity peak found in the spectra of octahedrally co-ordinated compounds. This charge transfer band results from the comparatively low energy charge transfer process when sulphur, iodine or even bromine (the more polarisable donor atoms) are co-ordinated to the cobalt atom. Thus the extent of the shift of this band into the visible region increases with decrease in energy of the charge transfer process. Hence a very large

shoulder is noted for SCN^- (when sulphur is a donor) and I^- . The shoulder is less significant in the case of Br^- and very small for Cl^- . Jørgensen has suggested that this band in thiocyanate and selenocyanate compounds may be of internal ligand origin⁽⁵⁶⁾. In general, this shoulder does not interfere with the typical profile of spectra of tetrahedral compounds. In the case of thiocyanate compounds, the position of this band is diagnostic of the mode of bonding of the thiocyanate to the metal (57,58). If the thiocyanate group is unidentate with bonding to the cobalt only through the nitrogen atom, there is no charge transfer between the sulphur and the cobalt indicated in the visible spectrum. However, if the thiocyanate is bridging two cobalt atoms by a Co-N bond and a Co-S bond, there is charge transfer and the absorption appears in the UV with a significant shoulder extending beyond 400nm. This aspect will be discussed further under *infra-red spectroscopy*.

As mentioned above, ligand field bands in the visible region are the result of d-d transitions. By changing the ligands coordinated to the cobalt atom it is possible to change the strength of the ligand field and thus to vary the extent of splitting between the d_e and the d_γ . If ligands are listed in order of the extent of their ability to split the 3d orbitals into d_e and d_γ , a series showing the relative magnitudes of their ligand fields is obtained. Several ligands have been placed in such a series⁽⁵⁹⁾.

This series, the Spectrochemical Series, was originally derived experimentally^(60,61) on the basis of the wavelength of the absorption bands for similar types of stereochemistry of complexes involving the ligands concerned. Thus ligands, which result in an absorption at shorter wavelengths, produce a larger separation between the d_e and d_γ orbitals. The gradation in "orbital separation energy" is thus revealed by an abbreviated Spectrochemical Series shown below:



(b) *Magnetic Moments:*

As mentioned above the 3d shell of the cobalt atom in cobalt(II) compounds is occupied by seven electrons. Generally, cobalt(II) complexes are found with the 3d electrons of the metal atom in the high-spin state, i.e. four electrons paired and three unpaired. It is only in the case of complexes with ligands capable of exerting strong ligand fields that spin pairing is enforced, whereby two of the unpaired electrons are forced to pair spins, as the spin pairing energy is then less than the orbital separation energy. (The ligands investigated in this and related work should not exert such high fields.)

On the basis of three unpaired electrons, the "spin only" value

for the magnetic moment of cobalt(II) is 3.88 B.M. However it is found in practice that both tetrahedral and octahedral cobalt(II) compounds have magnetic moments well above this value (28,39,40). Tetrahedral compounds usually have moments in the range 4.4 - 4.8 B.M. while octahedral complexes have moments lying between 4.5 - 5.2 B.M. (63,64,65,66). The origin of this enhancement of the value of the magnetic moments above the "spin only" value of 3.88 B.M. has been explained by Schlapp and Penney (67) for the case of Co(II) in particular. They explained this enhancement as a result of a contribution from spin-orbit coupling. The amount by which the value of μ_{eff} for tetrahedrally co-ordinated cobalt(II) is enhanced is by a factor of

$$\frac{1 + 4\lambda'}{\Delta}$$

where λ' is the effective spin-orbit coupling constant and Δ is the energy of separation between the d_{γ} and d_{ϵ} sets of orbitals. The value of λ' is sensitive to the nature of the ligands to a lesser extent than is that of Δ . Thus it may be seen that by varying ligands, and hence ligand field strength, changes in the magnetic moment should be effected. This will be elaborated later.

Penney and Schlapp accounted for the introduction of some orbital angular momentum into the ground state of the ion as a result of mixing of energy levels. Spin-orbit coupling results in decompos-

ition of some degenerate excited states into several energy levels, of which two have the same symmetry as the ground state of the cobalt(II) ion. When there is a mixing of these energy levels some orbital angular momentum is introduced into the ground state. The phenomenon is in fact even more complex than this owing to the fact that there are seven electrons involved, not just one.

Cotton and Holm investigated the effect of ligand field strength on the value of μ_{eff} of several cobalt(II) complexes. Examination⁽⁴⁰⁾ of the complex tetrahalo ions of the form $[\text{CoX}_4]^{2-}$ showed that the value of μ_{eff} did in fact increase as X was varied from Cl to I, i.e. as the ligand field strength (and hence Δ) decreased. Their investigation was extended⁽³⁹⁾ to compounds of the type CoX_2L_2 where L was p-toluidine and triphenylphosphine. Once again the change in μ_{eff} with halogen was observed with each ligand. This result leads to consideration of the "average value" concept of ligand field strength which is to be used later. If two ligands L' and L'' are selected and used to form the complex $\text{CoL}'_2\text{L}''_2$ the ligand field lies between those of CoL'_4 and CoL''_4 . Accordingly, magnetic moments and visible spectra lie between the extremes of those of $[\text{CoL}'_4]^{n-}$ and $[\text{CoL}''_4]^{n-}$, where $n > 0$ ^(15,68,69).

(c) *Infra-red Spectroscopy:*

Extensive use has been made of infra-red spectroscopy as a means of determining the mode of bonding of the NCS^- group to the cobalt atom in complexes of the type $\text{Co}(\text{NCS})_2\text{B}_n$ where $n = 2$ or 4 , B = heterocyclic base^(28,29,70,72). There are three modes of bonding of the NCS^- ion to a metal atom. These are N-donor, S-donor and N and S both donors (but to different metal atoms). Since infra-red spectra are the consequence of intra-molecular vibrations, it would be expected that removal of charge from the $\text{N}=\text{C}=\text{S}^-$ system would affect the strengths and hence the force constants of the interatomic bonds. There are two vibrations which have been used in assignment of stereochemistry of thiocyanate complexes⁽⁷²⁾. These are the symmetric stretch and the asymmetric stretch. These are detected by absorption around 800cm^{-1} and 2000cm^{-1} , respectively. Examination of visible reflectance spectra of compounds of the type $\text{Co}(\text{NCS})_2\text{B}_2$ where B (included some para substituted pyridine complexes) reveals that the absorption band is at too short a wavelength to be the result of bonding of the thiocyanate through the sulphur alone⁽²⁹⁾. This is concluded by noting the positions of SCN^- and NCS^- (S and N donors respectively), in the Spectrochemical Series. However there is extensive evidence for bonding through the nitrogen alone⁽²⁹⁾ and through both nitrogen and sulphur (in polymers)^(29,71). It is generally found that when nitrogen is the sole donor atom

the thiocyanate asymmetric stretch occurs at frequencies lower than 2100cm^{-1} , whereas in the case of bridging thiocyanates this absorption is found at 2100cm^{-1} or slightly higher frequencies⁽⁷³⁾. Good supporting evidence for thiocyanate bridging is found in the shift of the charge transfer band towards the visible region in UV/visible spectra. Normally it is only a shoulder of this band which extends beyond 400nm but even at this wavelength the intensity of absorption is much greater than the intensity of the band due to octahedrally co-ordinated cobalt(II).

4. Behaviour of the Complexes in Solution

Although compounds of the type CoX_2B_n ($n = 2$ or 4) ($X = \text{halogen}$, $B = \text{heterocyclic base}$) have been found to adopt either octahedral or tetrahedral stereochemistry in the solid state, the same stereochemistry is not always adopted in solution. Examination of these compounds in solution has thus been fruitful in revealing the behaviour of the systems outside the confines of a crystal lattice. The behaviour, both expected and found, will be discussed below, but consideration should be given first to the methods of examination used.

As with the study of complexes in the solid state visible absorption spectroscopy^(28,29,32,72) and magnetic properties^(34,74) have been used with considerable success. In addition to these techniques, conductivity measurements^(28,29,32,72) and molecular weight determination⁽³⁴⁾ have been shown to provide useful evidence. These techniques will

now be considered in more detail.

Physical Properties of Complexes in Solution

(a) Visible Absorption Spectra:

What has been said concerning diffuse reflectance spectroscopy above applies generally to absorption spectra of solutions. However in the case of solution spectra there is an added means of distinction between tetrahedral and octahedral species. This criterion is the intensity of the absorption band measured in terms of the molar extinction coefficient, ϵ . It has been found that the absorption band at $\approx 500\text{nm}$ for octahedral species has very low intensity, $\epsilon < 30^{(28)}$. In the case of tetrahedral species, however, the intensity is at least ten times that of octahedral species, ϵ being 300-2000⁽²⁸⁾. Thus, even when an absorption band may lie at a wavelength between the extremes normally associated with tetrahedral and octahedral species the intensity of the band may be used as a sound guide to stereochemistry.

It has been found in several cases that solution spectra may be modified in profile by varying the solvent⁽⁷⁵⁻⁷⁷⁾. In general, the profile of the absorption envelope of solution spectra is slightly more resolved than in the solid state.

(b) *Magnetic Moments:*

Magnetic moment measurements on solutions have been less widely used than on the solid state. However Nyholm et al⁽³⁴⁾ used solution magnetic moments to support the theory that the violet form of $\text{CoCl}_2\text{pyridine}_2$ was octahedral (known now to be octahedral polymer) and dissociated to give the tetrahedral species in nitrobenzene. Similarly $\text{Co(NCS)}_2\text{pyridine}_2$ has a solid state moment of 5.10B.M. but in solution the moment is 4.50B.M., typical of tetrahedral cobalt(II).

(c) *Electrical Conductivity:*

Electrical conductivity, usually reported as Molar Conductance, has been used extensively as a criterion of dissociation of complexes to produce ionic species in solution. Furthermore, when a neutral complex forms a conducting solution, it is evident that dissociation has led to formation of ionic species. This distinguishes between complexes which dissociate to give neutral groups from those which dissociate into ions. Thus stable complexes give conductances of no more than about 3 mho. as 10^{-3} M solutions in chloroform. In nitromethane a uni-univalent electrolyte has a conductance of approximately 80 mho. while a stable complex should have a very small conductivity.

(d) *Molecular Weight:*

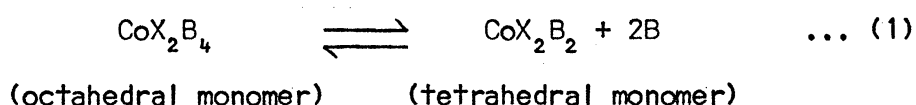
Molecular weight determinations by such methods as cryoscopy and osmometry are rather tedious but have provided valuable information concerning the behaviour of polymeric compound $\text{CoCl}_2\text{pyridine}_2$ when dissolved in nitrobenzene, chloroform⁽⁷⁸⁾ and bromoform⁽⁷⁹⁾.

Behaviour of Compounds of the Type CoX_2B_2 and CoX_2B_4 in Solution

When compounds of this type are dissolved the reactions (if any) which occur are dependent on the nature of the solvent. The solvents commonly used may be broadly classified either as co-ordinating or non-co-ordinating. The former group includes such solvents as low molecular weight alcohols, nitromethane, dimethyl formamide and possibly nitrobenzene. The latter group would include benzene, toluene, chloroform, dichloroethane, etc. A general classification of the type of reactions which these compounds may undergo in solution is set out below, where X = halogen, B = base.

(i) *Dissociation to form non-ionic species:*

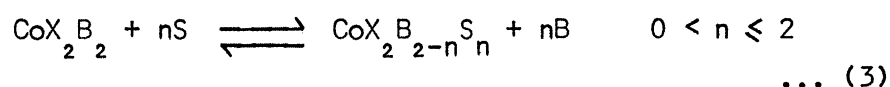
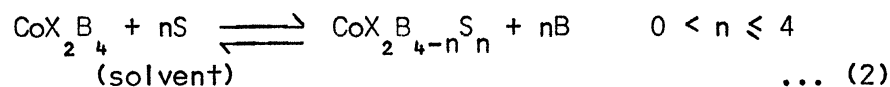
1. Dissociation of hexaco-ordinate compounds by loss of two base molecules -



Dissociation of tetraco-ordinate compounds by loss of two base molecules -

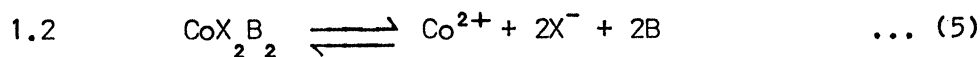
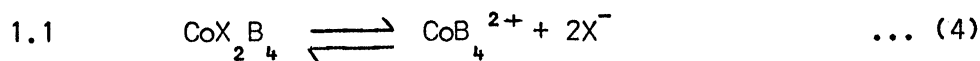


2. Solvolytic dissociation resulting in displacement of base -

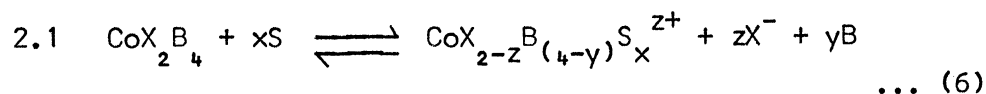


(II) Dissociation to form ionic species:

1. Dissociation by loss of halide ions -



2. Solvolytic displacement of halide ions -



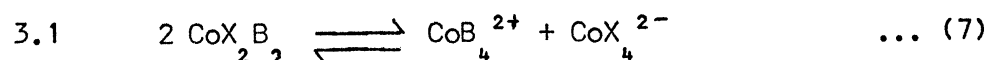
$$y \leq 4 > 0$$

$$x \leq 6 > 0$$

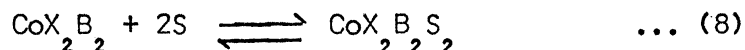
$$z \leq 2 > 0$$

$$4 \leq x-y-z+6 \leq 6$$

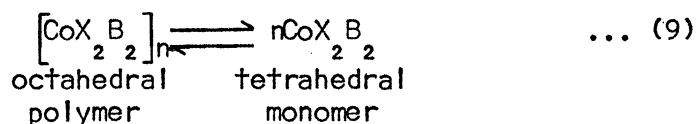
3. Bimolecular disproportionation -



(iii) Co-ordination of solvent molecules to increase the co-ordination number:

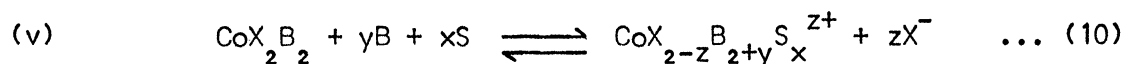


(iv) Dissociation of polymers into tetrahedral monomers:



Solutions Involving Free Base as a Component of a Solvent Mixture

Introduction of the base B as a component of the solvent mixture would be expected to affect many of the above reactions markedly. Those equilibria involving dissociation to liberate the ligand B would be expected to be moved in the reverse direction. A further equilibrium, however, may be set up as shown below,



$$x+y-z = 2$$

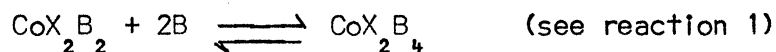
$$0 \leq y \leq 4$$

$$0 \leq z \leq 2$$

$$x \leq 4$$

Thus the result would be replacement of halide ion in the complex by either an increased number of base molecules or by solvent molecules dependent upon the nature and proportions of B and S in the system.

However by far the most important effect of dissolving the tetrahedral or octahedral polymer complexes in mixtures containing the base is the following equilibrium:



This equilibrium, the tetrahedral-octahedral equilibrium, is studied conveniently by varying the concentration of free ligand B and determining the relative concentrations of CoX_2B_2 and CoX_2B_4 . In the event of the tetrahedral species CoX_2B_2 being partly dissociated, addition of the free ligand would initially result in reversal of the dissociation reaction. Subsequent additions of free ligand would result in change in the position of equilibrium of reaction 1 above. The significance of the small dissociation of complexes of the type $\text{CoX}_2\text{mepy}_2$ (where mepy is 2-methylpyridine or 4-methylpyridine) in nitrobenzene was discussed by Graddon and Watton⁽²⁸⁾. Subsequently de O'Cabral et al⁽⁷²⁾ also investigated this dissociation of complexes of CoX_2B_2 in nitromethane/heterocyclic base mixtures. In their investigation B was pyridines with substituents as follows: 3-methyl-, 4-methyl-, 3-ethyl-, 4-ethyl- and 3-5-dimethyl- and 3-4-dimethyl-.

The behaviour of complexes of cobalt(II) halides with heterocyclic bases in solution has been investigated by means of conductivity measurements and absorption spectroscopy. A very useful contribution of Nelson et al⁽⁷²⁾ has been to divide complexes of this type into two classes based on their behaviour in solution. Class 1 compounds (10^{-3}M in chloroform or nitromethane) show very little dissociation.

This dissociation was detected spectrophotometrically by comparing spectra of the compound in pure solvent and in solvent plus increasing amounts of added base. The extinction of the band due to the tetrahedral species at approximately 600 nm increased with small additions of base as reaction 1a, $\text{CoX}_2\text{B}_2 \rightleftharpoons \text{CoX}_2 + 2\text{B}$ was reversed. Subsequent additions of base resulted in a decrease in extinction with formation of octahedral species as shown in reaction 1, $\text{CoX}_2\text{B}_2 + 2\text{B} \rightleftharpoons \text{CoX}_2\text{B}_4$. The increase in extinction was less than 5% for class I compounds and was more marked in nitromethane solutions than in those in chloroform. These solutions obeyed Beer's Law. Conductances of such solutions in nitromethane remained constant or decreased with increasing amounts of base. The authors did not consider molar conductances of as much as 39 mho. significant dissociation even when the ratio of base/complex was 300. This does seem questionable. However their evidence from spectra of such solutions and solid-state spectra of corresponding compounds of the type CoX_2B_2 indicated formation of the octahedral species as per reaction 1 above rather than reaction 10, $\text{CoX}_2\text{B}_2 + y\text{B} + x\text{S} \rightleftharpoons \text{CoX}_{2-z}\text{B}_{2+y} + z\text{X}^-$. This behaviour of partial dissociation was noted previously by Graddon et al⁽²⁸⁾, and by Nelson in an earlier publication⁽³²⁾.

Class II complexes included all of the iodo and bromo complexes and these behaved markedly differently from class I compounds. Class II complexes did not obey Beer's Law and increasing concentrations of added base resulted in an increase in apparent extinction around 500 nm. Furthermore, increasing base concentration resulted in higher conduct-

ances of as much as 93 mho. Clearly, this is very strong evidence for a reaction of the type shown as reaction 10 above in nitromethane. In Figure 4 the diffuse reflectance spectrum and solution spectra of $\text{CoBr}_2(4\text{-methylpyridine})_4$ in chloroform/base and nitromethane/base solutions are shown. The chloroform/base solution and the solid-state spectra show good agreement but the nitromethane/base solution spectrum shows formation of a different species altogether. The shift of the absorption to shorter wavelength indicates that ligands higher in the Spectrochemical Series have replaced the halide or base. Conductance measurements indicate displacement of halide ion. Oxygen and nitrogen donors such as base and nitromethane molecules would account for this behaviour in the absorption spectrum.

This classification into two classes by Nelson⁽⁷²⁾ appears rather arbitrary particularly in view of the high conductances obtained in nitromethane solution. None of the complexes he investigated gave molar conductances of less than 15 mho. as 10^{-3}M solutions. Such a conductance must surely indicate a large degree of lability of the halide ion and this would surely influence equilibrium constant determinations based on the existence of one reaction alone, viz. $\text{CoX}_2\text{B}_2 + 2\text{B} \rightleftharpoons \text{CoX}_2\text{B}_4$. Admittedly, most of the constants reported were measured in chloroform solution.

Attention has been drawn to this type of dissociation and to the weakness of Nelson's method of determining the concentration of octahedral species present (to be discussed later in the experimental

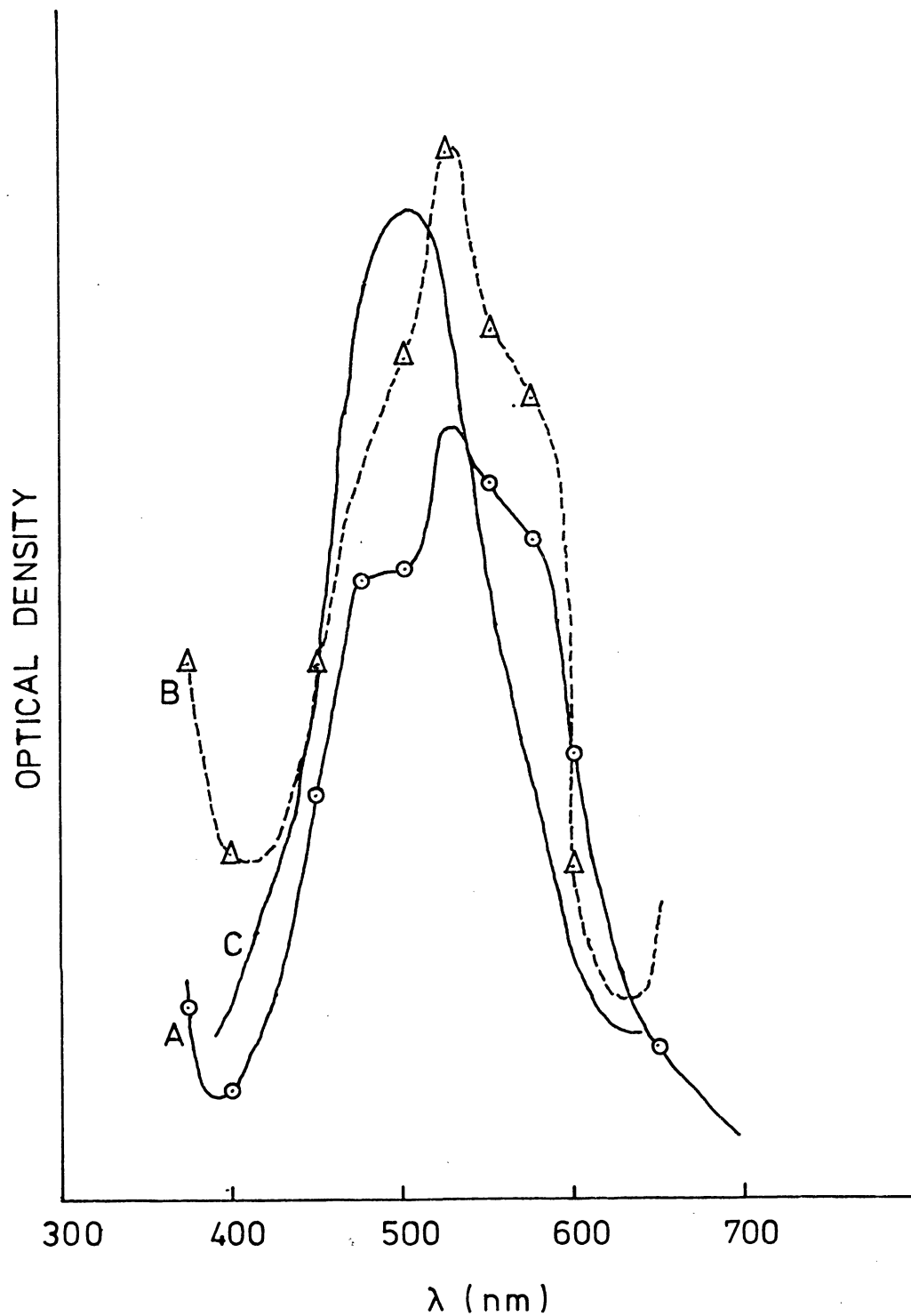


FIGURE 4.

VISIBLE SPECTRA OF $\text{CoBr}_2(4\text{-METHYLPYRIDINE})_4$.

A. Diffuse reflectance of solid.

B. Complex in 9 : 1 chloroform-4-methylpyridine solution.

C. Complex in 9 : 1 nitromethane-4-methylpyridine solution.

section). Graddon and Watton⁽²⁸⁾ noted that (with one exception) complexes of cobalt(II) halides with pyridine and its 2-methyl and 4-methyl derivatives dissociated beyond the CoX_2B_2 form in chloroform solution. This exception was $\text{Co}(\text{NCS})_2(4\text{-methylpyridine})_4$. Spectra of solutions of this compound with small amounts of added base showed no increase in extinction around 600 nm thus indicating that reaction 5 $\text{CoX}_2\text{B}_2 \rightleftharpoons \text{Co}^{2+} + 2\text{X}^- + 2\text{B}$ was not occurring but rather that reaction 1, $\text{CoX}_2\text{B}_2 + 2\text{B} \rightleftharpoons \text{CoX}_2\text{B}_4$ occurred immediately free base was added. The dissociation of the rest of the pyridine and picoline complexes examined was noted to occur even in benzene solution. The ligand replacement type reaction of the type of reaction 10, $\text{CoX}_2\text{B}_2 + y\text{B} + x\text{S} \rightleftharpoons \text{CoX}_{2-z}\text{B}_{2+y}\text{S}_x^{\text{Z}+} + z\text{X}^-$ (and that previously described by Dunn and Buffagni⁽⁸⁰⁾) and invoked by Nelson for class II complexes are unlikely to occur in benzene. Thus, there are in fact at least two different types of reaction occurring in these solvents. The behaviour in chloroform inferred by Nelson to be that in nitromethane is now dubious.

The "ortho effect" i.e. the effect of the methyl group in the 2-position of the pyridine ring has been found to be quite significant in the case of $\text{Co}(\text{NCS})_2(2\text{-methylpyridine})_2$. Whereas the 4-methylpyridine complex showed no sign of dissociation in chloroform, the 2-methylpyridine analogue dissociated to a greater extent than $\text{Co}(\text{NCS})_2\text{pyridine}_2$ ⁽²⁸⁾. In fact $\text{Co}(\text{NCS})_2(2\text{-methylpyridine})_2$ gave the same extinction in pure base as it did in the solvent plus base. Furthermore the extinction was always low even with large amounts of added base, indicating continuing partial dissociation as was found by Nelson for

other compounds.

A recent paper⁽²⁹⁾ described complexes with eight heterocyclic bases, the conductances of which as $10^{-3}M$ solutions in nitrobenzene did not exceed 8.5 mho (even for iodo complexes). Absorption wavelengths for solution spectra were similar to those of the corresponding diffuse reflectance spectra. Thus in nitrobenzene also, ionisation was quite small and ligand replacement undetectable in the visible spectra. Billing and Underhill⁽⁸¹⁾ found that $\text{CoI}_2(3\text{-bromopyridine})_2$ gave a solution spectrum in chloroform which agreed with the diffuse reflectance spectrum of the solid compound.

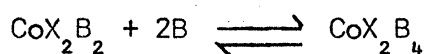
Thus it seems clear that dissociation in less polar solvents such as benzene, chloroform and even nitrobenzene does not result in serious disruption of these complexes. However in nitromethane their behaviour indicates considerable dissociation. Addition of free base to solutions in nitromethane results in extensive re-arrangement in the case of at least bromo and iodo complexes. The evidence used in support of only minor dissociation of the chloro complexes in mixtures of nitromethane with free base appears unconvincing.

The solution chemistry of only three compounds of a cobalt halide or pseudohalide with aromatic bases has been reported to date. Cotton and Holm⁽⁸⁶⁾ investigated visible absorption spectra and the solution magnetic moment of $\text{Co(NCS)}_2(p\text{-toluidine})_2$ in dimethylformamide. The solid-state magnetic moment was found to be 4.93 B.M. while that of the compound in solution was 4.88 B.M. However, the solution was in-

tensely blue, typical of tetrahedral cobalt(II) species, although 4.88 B.M. is indicative of octahedral cobalt(II). The solution had a spectrum with an intense band at 630 nm with a shoulder at 505 nm. This spectrum is not unlike that of compounds containing $\text{Co}(\text{NCS})_4^{2-}$ and the shoulder at 505 nm may be due to an octahedral cation formed as a result of the disproportionation reaction. Furthermore the magnetic moment of $\text{Co}(\text{NCS})_4^{2-}$ is approximately 4.5 B.M.⁽⁸³⁾ while that of octahedral cobalt(II) is likely to be 5.22 B.M. The root mean square of these is 4.88 B.M., the value of the moment of the Co(II) in the solution. In acetonitrile the blue solution has a band at 620 nm and a moment of 4.62 B.M., consistent with cobalt compounds with four nitrogen donors⁽⁸³⁾. The authors conclude that the compound is non-ionic in this solvent. It is of interest that they did not report conductance measurements in support of their conclusion.

Nyholm⁽⁸⁴⁾ investigated $\text{Co}(\text{NCS})_2\text{aniline}_2$ and found similar results for this compound as far as behaviour in solution was concerned. Ferguson⁽⁸⁵⁾ has examined the polarised reflectance and solution spectra of $\text{CoCl}_2(\text{p-toluidine})_2$.

The most interesting aspect of the solution chemistry of these complexes is the reaction below. By varying the nature of B and X a series of equilibrium constants may be obtained.



It may be seen that this reaction consists of the formation of compounds

of the type CoX_2B_4 from the bis (amine) cobalt(II) halide complex and two amine molecules. Thus, by measuring the value of the equilibrium constant for this reaction, a quantitative estimate of the tendency to form an octahedral complex starting from the tetrahedral complex may be gained. It must be remembered that the species are all solvated while undergoing this reaction. This aspect was considered by Nelson et al⁽⁷²⁾. By variation of the nature of the halide X or base B the effects of factors such as basicity, molecular size, polarisability may be determined. Nelson et al investigated complexes of pyridine, methyl pyridines, and xylidines with CoX_2 where X = Cl, Br, I, NCO, NCS and NCSe. Isolation of a solid complex in octahedral or tetrahedral form may be influenced by crystal packing factors and solubility. However an equilibrium constant gives vital information as to the tendency to increase co-ordination number in solution even though only one or even both of the species may be isolated as a solid.

5. Preferred Co-ordination Number and Stereochemistry

There have been several explanations proposed for the preferred stereochemistry of cobalt(II) halides with heterocyclic bases. However the only authors who have discussed the apparent preference of a few complexes of cobalt(II) halides with aromatic amines for the tetrahedral structure are Sharp et al⁽⁴¹⁾. The thiocyanate, chloride, bromide and iodide of cobalt(II) may all take on two and/or four heterocyclic base molecules dependent upon the substituent in the heterocyclic ring.

What factors decide the stereochemistry the cobalt will adopt in these complexes? Nyholm et al have considered the behaviour of some of the heterocyclic base complexes. These authors⁽⁸⁶⁾ conclude that with due regard to the importance of steric effects the co-ordination number of the cobalt(II) atom is most dependent on ligand polarisability. This is an extension of the Pauling Electroneutrality Principle and predicts that the metal ion takes up that number of ligands which will reduce its overall charge to nearly zero. Now the polarisability of halide ions increases with atomic number. Hence the iodide donates most charge to the cobalt and the co-ordination number of the iodo complexes is very frequently four. Bromide is less polarisable and may readily form four or six co-ordinate complexes. The complexes involving chloride ions may also take on either two or four molecules of base. This tendency of the cobalt to be either four or six co-ordinate must also be affected by polarisability or electron availability of the donor atoms of the base molecules. However examination of compounds formed by substituted pyridines has shown that the polarisability of the halogens is the most important factor.

Graddon et al^(28,29) have also extended this theory and used it to explain the behaviour of a series of heterocyclic base complexes. They consider that the main factor determining whether the cobalt co-ordinates two or four base molecules is the repulsion of electron pairs on donor atoms. It will be recalled that the Sidgwick-Powell theory of stereochemistry considers the relative strengths of repulsion of electron pairs to decrease as follows: non-bonding : non-bonding >

non-bonding : bonding > bonding : bonding. Thus each of the larger iodine atom's diffuse electron clouds in a compound such as $\text{CoI}_2\text{pyridine}_2$ experiences a larger repulsion from the other iodine atom's cloud and the pyridines' nitrogens than would the bromine atoms in $\text{CoBr}_2\text{pyridine}_2$. Similarly the chlorine atom under similar circumstances would experience a still lower repulsion. Evidence for this effect may be found in comparison of mean bond lengths in halide containing complexes of transition metals⁽²⁸⁾. The metal-halogen distance has been shown to increase with increasing atomic number of the halogen. This concept of repulsion of non-bonding pairs has also been used⁽²⁸⁾ to explain the positions of ligands in the Spectrochemical Series. Ligands with donor atoms having diffuse electron clouds containing four non-bonding pairs are those producing the lowest orbital separation energies. Thus donor atoms with diffuse electron clouds do not discriminate between the d_ϵ and d_γ orbitals as well as do donor atoms with concentrated clouds and their positions in the Spectrochemical Series reflect this fact. Accordingly the bulky iodide ion is the lowest of the halides in the Spectrochemical Series.

A further theory concerning the factors affecting stereochemistry of complexes of cobalt(II) halides with heterocyclic bases has been proposed by ^{KING}~~Nelson~~ et al⁽³²⁾. These workers have some evidence to support the theory that back π -bonding from the metal to the ligand controls the co-ordination number in these complexes. They have shown further how the tendency of tetrahedral complexes to bond two extra base molecules as measured by equilibrium constants may be interpreted using this

theory as part of their evidence.

It was found⁽⁷²⁾ that 4-alkyl pyridine complexes of CoX_2 where $\text{X} = \text{Cl}$, NCO and NCS showed a greater tendency to be six co-ordinate than the corresponding 3-alkylpyridines. This finding was explained as follows: Back co-ordination from the cobalt to pyridine antibonding π -orbitals would localise charge in the 2-, 4- and 6-positions of the ring, particularly. Alkyl substituents in the 3-position also localise charge at these positions, destabilising the system. However 4-alkyl substituents do not release as much charge at these positions and do not destabilise the system so much, permitting more back co-ordination and increasing the tendency towards six co-ordination. This theory was extended to halides and pseudohalides.

In some compounds simple steric effects may be responsible for limitation of the co-ordination number to four. This has been generally accepted and Underhill et al^(81,87) have shown how this effect applies to complexes of 2-substituted pyridines and quinoxalines with cobalt halides.

The extent to which basicity of heterocyclic bases affects the co-ordination number in the complexes has been the subject of some debate. ^{de O'CARVAL} ~~Nelson~~ et al⁽⁷²⁾ consider that this effect is a partial determinant in so far as π -acceptor capacity decreases with increasing basicity of the ligands they examined. However, as mentioned above, the position of the substituent in the pyridine ring affects co-ordination number in a manner that basicity considerations alone cannot

predict. Graddon, Heng and Watton⁽²⁹⁾ conclude that there is a small effect on co-ordination number due to basicity, with the weaker bases favouring six co-ordinate octahedral compounds. The small effect of basicity is explained in terms of the similar electron distribution about the donor atom in all of the bases studied. Billing and Underhill⁽⁸¹⁾ from a consideration of the π -acceptor properties of halogenopyridines have concluded that basicity of the base is a strong determinant of co-ordination number. Table 1 has been extracted from their paper and the results clearly show the strong correlation of basicity with co-ordination number and hence stereochemistry. In a further paper, ^{EILBECK ET AL} Underhill⁽⁸⁷⁾ have ~~has~~ used increasing basicity of the base to explain decreasing tendency to form octahedral complexes when the base goes from imidazole to 2-methylimidazole.

6. Comparison of Aromatic Amines with Heterocyclic Bases

From the foregoing it may be seen that while the chemistry of complexes of cobalt halides with heterocyclic bases has been extensively investigated, very little has been reported concerning complexes with aromatic amines. Aromatic amines differ from heterocyclic bases in several important respects. These are (a) basicity, (b) π -bonding capacity, (c) environment of the nitrogen donor atom, (d) significance of electronic effects of ring substituents on the nitrogen, (e) volatility and (f) ease of autoxidation. These characteristics will now be considered in more detail.

Stereochemistry of Some CoX_2B_2 Complexes					
B	= 4-Mepy	3-Mepy	Py	4-Clpy	3-Brpy
pKa	6.02	5.68	5.23	3.84	2.91
CoCl_2B_2	Tet	Tet	(Oct, (Tet*)	Oct	Oct
CoBr_2B_2	Tet	Tet	Tet	Oct	Oct
CoI_2B_2	Tet	Tet	Tet	Tet	Tet
Me = methyl, Oct = octahedral, Tet = tetrahedral, Py = pyridine, * unstable isomer.					

TABLE 1

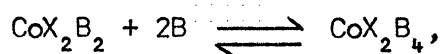
(a) *Basicity:*

The pKa values of several aromatic amines and heterocyclic bases are set out below in Table 2. It may be noted that aromatic amines are in many cases as much as 1 pKa unit less basic than the corresponding pyridine derivatives. Thus, at least as far as hydrogen ion is concerned as a Lewis acid, pyridines in many cases show a much greater tendency to donate an electron pair than do aromatic amines.

However, since pKa is not the sole determinant of stereochemistry of complexes with heterocyclic bases, no clear predictions may be made a priori concerning the behaviour of aromatic amines in related complexes.

(b) *π -Bonding Capacity:*

Examination of bonding of the ring to the nitrogen atom in aromatic amines reveals only a small conjugation with the aromatic nucleus. Conjugation would be expected to result in the molecules having π -acceptor capacity. Thus in the event of excess charge being transferred to the cobalt by the ligands, the aromatic amine cannot reduce this charge by acceptance of significant back co-ordination. Thus, in a borderline case between four co-ordination and six co-ordination as in the equilibrium,



pKa Values of Some Aromatic Amines and Heterocyclic Bases					
Aromatic Amines			Heterocyclic Bases		
Substituent	pKa	Ref.	Substituent	pKa	Ref.
(Para Position)			(Para Position)		
NH ₂	6.16	89			
OCH ₃ [*]	5.34	"			
CH ₃ [*]	5.10	"	CH ₃	6.03	29
NHCOCH ₃ [*]	4.57 ⁺	"			
H [*]	4.60	"	H	5.21	"
F [*]	4.60	"			
Cl [*]	3.98	"	Cl	3.83	"
Br [*]	3.86	"	Br	3.75	"
COCH ₃ [*]	2.19	"			
NO ₂ [*]	1.11	"			
(Ortho Position)					
OCH ₃ [*]	4.52	"			
CH ₃ [*]	4.45	"			
Cl	2.64	"			

⁺Value calculated using Hammett's constants⁽⁹³⁾.

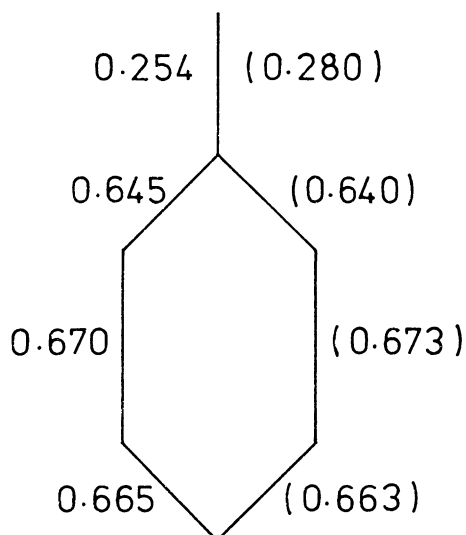
TABLE 2

a base which could not reduce this excess charge would be expected to favour the four co-ordinate structure. In the case of heterocyclic bases there is conjugation of the nitrogen into the aromatic ring with possibility of π -acceptor capacity. Hence in a borderline case of excess charge build up on the metal atom, a heterocyclic base in the equilibrium above would stabilise the six co-ordinate structure more than an aromatic amine, all other things being equal.

Figure 5a shows the bond orders of the bonds in the aniline molecule over and above the single bonds, whereas Figure 5b illustrates the electronic charge distribution calculated according to Huckel and to Pariser and Parr⁽⁸⁸⁾. The C-N bond has an order of approximately 0.254 above single bond indicating a small amount of double bond character. The electronic charge on the nitrogen indicates that in the delocalised bond there is a transfer of only about 0.07 of an electronic charge from the nitrogen into the ring. Thus the charge of the lone pair is 1.935 instead of 2.000.

The C-N bond length in p-iodoaniline has been found to be 1.40Å⁽⁹⁰⁾ compared with 1.47Å in aliphatic compounds such as trimethylamine or nitromethane⁽⁹¹⁾. The conjugated compound pyridine has a C-N bond length of 1.37Å⁽⁹¹⁾. Thus, while the C-N bond in aromatic amines is shorter than in aliphatic compounds, it is certainly not as short as in the fully conjugated system pyridine. Hence there is some conjugation with the aromatic π cloud but this is probably insufficient to justify any suggestion of π bonding back from the metal to the amine

(a)



(b)

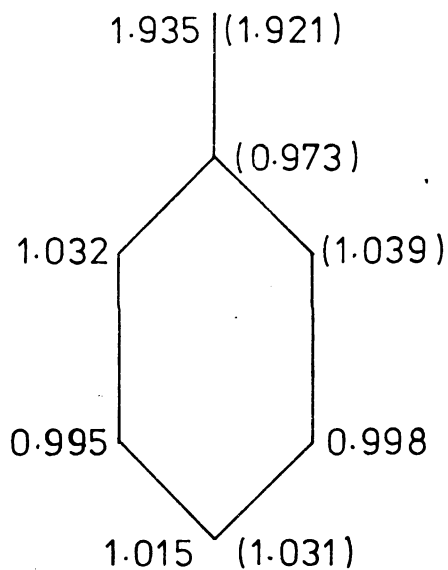


FIGURE 5.

(a) BOND ORDERS IN ANILINE.

(b) ELECTRONIC CHARGE DISTRIBUTION IN ANILINE.

Unbracketed values are obtained by the Method of Huckel and bracketed values are by that of Pariser and Parr.

in complexes of cobalt(II) with aromatic amines. The suggestion of back π bonding is controversial even in the case of pyridine complexes (28,81). Underhill et al⁽⁸¹⁾ and Stone⁽⁹²⁾ agree that the π bonding between the metal and aromatic amines should be small when the amino group separates the metal from the aromatic nucleus.

(c) Stereochemistry of the Nitrogen Atom:

Primary aromatic amines have two hydrogens bonded to the donor atom while pyridines have the donor as part of the aromatic ring. Differences in behaviour due to this difference in structure might be the result of steric hindrance. Any effect from this source would probably be much less than that already noted between 2-methylpyridine and 4-methylpyridine in complexes of the type considered here. However the extent of interaction with the two sets of d orbitals of the metal may be affected by the stereochemistry of the donor atom.

(d) Significance of Electronic Effects of Ring Substituents:

As with pKa variations caused by ring substituents, the mesomeric and inductive effects of substituents should affect the electronic environment of the heterocyclic nitrogen more than that of the aromatic amine nitrogen. The C-N bond in the latter class of base is effectively an insulation against the full force of such effects.

(e) *Volatility:*

Comparison of the boiling points of several representative pyridines and aromatic amines reveals that the latter are markedly less volatile (see Table 3). In fact, many aromatic amines are solid at room temperature. Accordingly, the effect of vaporisation of the base on complex stability should be less for aromatic amines.

J. de O. Cabral et al⁽⁷²⁾ have taken advantage of the volatility of heterocyclic bases to conduct investigations of stereochemical equilibria in the solid-state. Thermodynamic constants were determined for several bromo and iodo complexes which apparently undergo solvolysis in solution.

Boiling Points ⁽⁹⁴⁾ of Some Aromatic Amines and Heterocyclic Bases			
Compound	B.P. °C	Compound	B.P. °C
aniline	184	pyridine	115
p-toluidine	200	4-methylpyridine	144
p-chloroaniline	232	4-chloropyridine	147

TABLE 3

(f) *Ease of Autoxidation:*

One of the major reactivity differences between pyridine and aniline derivatives is their relative ease of autoxidation. Aromatic amines are far more readily autoxidised, particularly in the presence of transition metal ions. There has been a recent study reported in

which it was shown that electron releasing groups enhanced the rate of autoxidation of the amines⁽⁹⁵⁾. The stability of such complexes towards autoxidation remains to be investigated.

7. Scope of the Thesis

From the foregoing it is apparent that complexes of cobalt(II) halides with heterocyclic bases have been investigated extensively. The corresponding complexes with aromatic amines hitherto have been investigated much less completely by various independent workers.

This thesis embodies the results of an investigation aimed at assignment of the stereochemistry of complexes of aromatic amines with cobalt(II) halides and cobalt(II) thiocyanate. A series of compounds has been isolated using as ligands the amines asterisked in Table 2. These complexes have been characterised using information obtained from solid-state and solution studies. Physical measurements on solid complexes included magnetic moments and diffuse reflectance spectra. Infra-red spectra were also measured for the thiocyanate complexes. Absorption spectroscopy and electrical conductance measurements were used to elucidate the behaviour of complexes in solution. The equilibria $\text{CoBr}_2\text{B}_2 + 2\text{B} \rightleftharpoons \text{CoBr}_2\text{B}_4$, where B = aniline or p-toluidine, are discussed in detail.

RESULTS AND DISCUSSION

1. Stereochemistry of Complexes in the Solid-State

General

Compounds isolated during this study are classified below on the basis of the probable stereochemical environment of the cobalt atom. Stereochemical assignments are based on stiochiometry, magnetic moments, visible reflectance spectra (and colour), and in some instances IR spectra and thermogravimetric analysis. A list of the compounds isolated in a pure state is found in Table 4 which sets out their magnetic properties. The absence of a compound from this table does not mean necessarily that it is not formed. In many cases products isolated could not be obtained pure due to rapid oxidation of the amine or decomposition of the compound by some other mechanism.

The results of physical measurements on the compounds appear in Tables 5 to 10 (in which the amines are listed in order of decreasing basicity) while analytical results are set out in Table 18. The values of the absorption wavelength ($\lambda_{\frac{1}{2}}$) reported below are determined as the wavelength of the centre of the absorption envelope at half its height as shown in Figure 6. This value is used since these multicomponent bands are very poorly resolved. The relative intensities of the component bands may vary from one compound to another and so this

Magnetic Properties

Compound	Formula Weight	Temp. (°C)	$10^6 \chi_g$	$10^6 \chi_M$	$10^6 \chi'_M$	Magnetic Moment μ (B.M.)
$\text{Co(NCS)}_2\text{p-anis}_2$	421.4	18.0	25.80	10,872.6	11,082.8	5.09
$\text{Co(NCS)}_2\text{p-tol}_2$	389.4	19.0	26.71	10,400.9	10,601.9	5.00
$\text{Co(NCS)}_2\text{p-acetamidoan}_2$	475.5	26.5	21.55	10,247.0	10,478.2	5.03
$\text{Co(NCS)}_2\text{an}_2$	361.4	19.0	29.14	10,531.2	10,708.5	5.02
$\text{Co(NCS)}_2\text{p-flan}_2$	397.3	23.5	26.09	10,365.6	10,549.7	5.02
$\text{Co(NCS)}_2\text{p-clan}_2$	430.2	23.5	23.12	9,946.2	10,157.9	4.94
$\text{Co(NCS)}_2\text{p-bran}_2$	519.2	26.0	18.70	9,709.0	9,941.7	4.88
$\text{Co(NCS)}_2\text{p-acetamidoan}_2(\text{C}_2\text{H}_5\text{OH})_2$	567.6	17.0	17.41	9,881.9	10,181.5	4.87
$\text{CoCl}_2\text{p-anis}_2$	376.2	-	-	-	-	-
$\text{CoCl}_2\text{p-tol}_2$	344.2	17.0	24.89	8,567.1	8,755.2	4.52
CoCl_2an_2	316.1	23.0	26.78	8,465.2	8,629.6	4.54
$\text{CoCl}_2\text{p-flan}_2$	352.1	27.0	24.04	8,464.5	8,635.7	4.56
$\text{CoCl}_2\text{p-clan}_2$	385.0	18.0	22.55	8,681.8	8,815.8	4.61
$\text{CoCl}_2\text{p-bran}_2$	473.9	24.5	17.89	8,478.1	8,697.9	4.69
$\text{CoCl}_2\text{p-bran}_2(\text{H}_2\text{O})_2$	509.9	27.0	19.77	10,080.7	10,321.4	5.00

Cont....

TABLE 4

Magnetic Properties
(Cont.)

Compound	Formula Weight	Temp. (°C)	$10^6 \chi_g$	$10^6 \chi_M$	$10^6 \chi'_M$	Magnetic Moment μ (B.M.)
CoBr ₂ p-anis ₂	465.1	23.0	19.19	8,925.3	9,143.6	4.66
CoBr ₂ p-tol ₂	433.1	17.0	20.34	8,807.9	9,017.0	4.60
CoBr ₂ an ₂	405.0	22.0	21.01	8,509.5	8,694.9	4.55
CoBr ₂ p-flan ₂	441.0	27.0	18.86	8,317.3	8,509.5	4.52
CoBr ₂ p-clan ₂	473.9	19.0	17.98	8,519.9	8,739.7	4.54
CoBr ₂ p-bran ₂	562.8	17.0	15.42	8,678.4	8,919.2	4.57
CoBr ₂ p-acetamidoan ₂ (H ₂ O) ₃	573.2	23.0	18.81	10,781.9	11,060.7	5.14
CoI ₂ p-tol ₂	527.1	19.0	17.48	9,213.7	9,450.8	4.70
CoI ₂ an ₂	499.0	23.0	17.73	8,847.3	9,060.7	4.66
CoI ₂ p-bran ₂	656.8	19.0	13.98	9,182.1	9,450.9	4.70
Co(NCS) ₂ o-anis ₂	421.4	25.0	24.45	10,303.2	10,513.4	5.45

TABLE 4
(Cont.)

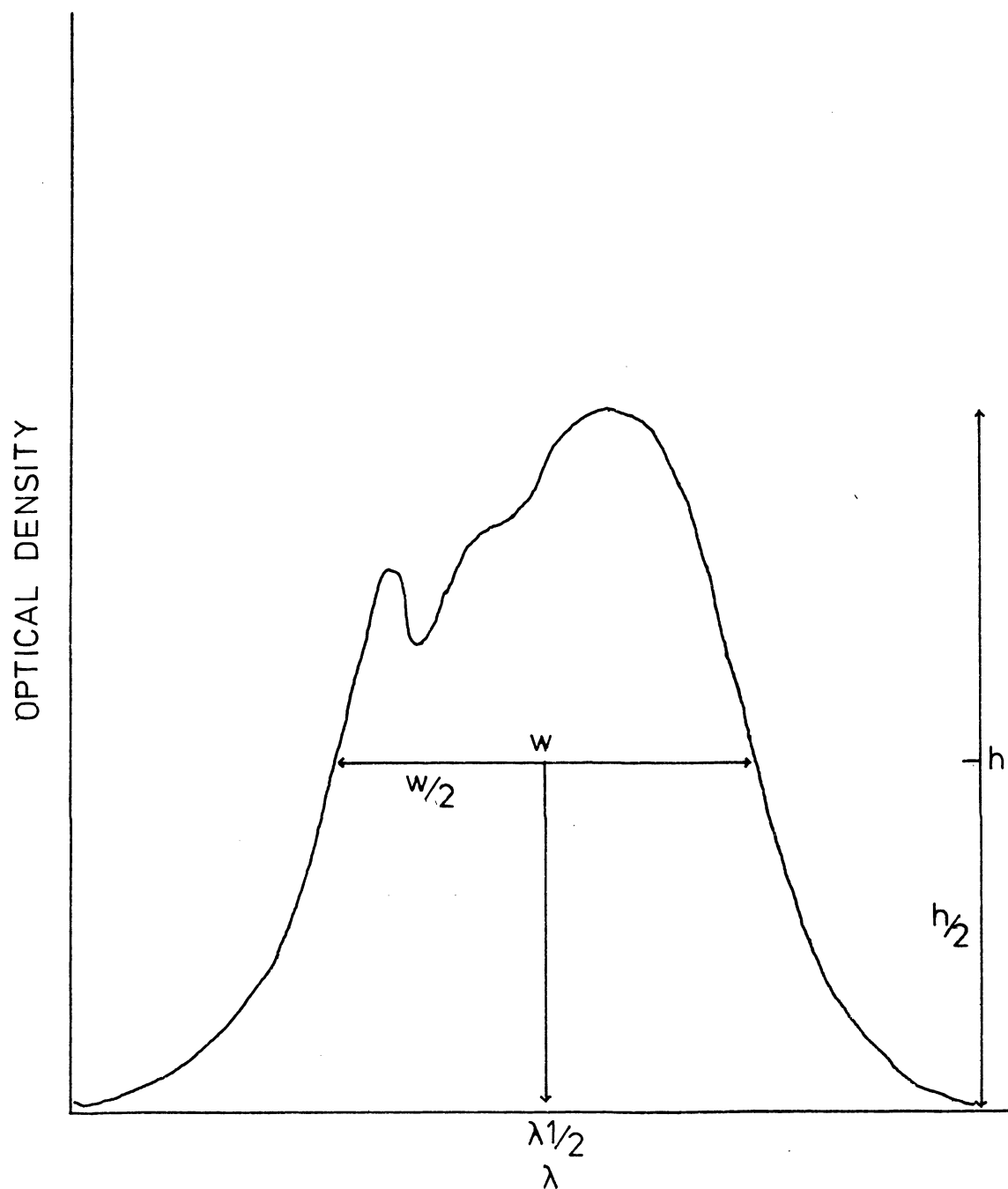


FIGURE 6.

DETERMINATION OF VALUE OF $\lambda_{1/2}$

average value provides a reasonable basis for studying the effects of ligand changes on ligand field strength⁽⁷⁵⁾. King, Koros and Nelson⁽⁹⁶⁾ have reported using the centre of gravity of the envelope for such comparisons while Beech and co-workers used a partial resolution followed by numerical averaging to give a basis for comparison^(19,23).

Tetrahedral Monomeric Compounds

Tables 5 to 7 below set out the colour, absorption wavelength in the visible region ($\lambda_{\frac{1}{2}}$) and room temperature magnetic moment (μ) of each of the compounds of the type CoX_2B_2 assigned tetrahedral stereochemistry about the metal atom. The last two columns indicate the preparative methods and whether the compounds were formed on decomposition of an adduct.

(a) Chloro Complexes:

Stable blue compounds were isolated with all ligands except p-acetamidoaniline, p-acetylaniline and p-nitroaniline. The first of these three amines formed either reddish-brown or impure blue products with cobalt chloride depending upon whether crystallisation was slow or fast respectively. The reddish-brown material turned blue to some extent over a period of time, even while a reflectance spectrum was being measured. The product formed using p-acetylaniline on the other hand was a clean pink when prepared but turned blue very slowly. In both of the above cases a mixture resulted and heating led to large

TABLE 5

CoCl₂B₂ - SOLID STATE PHYSICAL MEASUREMENTS

Substituent	Colour	$\lambda_{1/2}$ (nm)	μ (B.M.)	Preparative Method	Adduct
-OCH ₃	Blue	615	4.52	a	+
-CH ₃	Blue	630	4.52	a	-
-H	Blue	645	4.54	a	+
-F	Blue	610	4.56	a	+
-Cl	Blue	630	4.61	a	-
-Br	Blue	615	4.69	c	±

scale decomposition to a green material. The amine p-nitroaniline was the only one which failed to produce any compound whatsoever with cobalt chloride. Solvent evaporation led to isolation of discrete crystals of amine and metal halide.

Among the compounds isolated in a pure state, the position of the centre of the absorption band varied from 610 nm for $\text{CoCl}_2\text{p-fluoroaniline}_2$ to 645 nm for $\text{CoCl}_2\text{aniline}_2$. Such spectra are typical of those of tetrahedral cobalt compounds⁽⁹⁷⁾. Examination of Table 5 shows that the absorption wavelengths for other chloro complexes varied randomly between the above limits. A variation as large as 35 nm found above is indicative of a significant change in ligand field strength being equivalent to 2.57 kcal/mole. The spectra of the two compounds concerned are shown in Figure 7. While it is apparent that the peak due to $\text{CoCl}_2\text{aniline}_2$ is very slightly broader than the other, both peaks have the same general profile and are displaced with respect to one another. Cotton and Holm⁽⁴⁰⁾ have published spectra of the quinolinium salts of the form $\text{CoX}_4\text{quinolinium}_2$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}$. In their spectra the shifts of the absorption envelopes due to halide variation from Cl^- to Br^- were of the same magnitude as that found above caused by amine variation. With regard to the spectra of the other chloro complexes, it was found that while the positions of the envelopes were consistent with the $\lambda_{\frac{1}{2}}$ values in Table 5, the envelopes were not sufficiently well separated to suggest that the differences were not due to variations

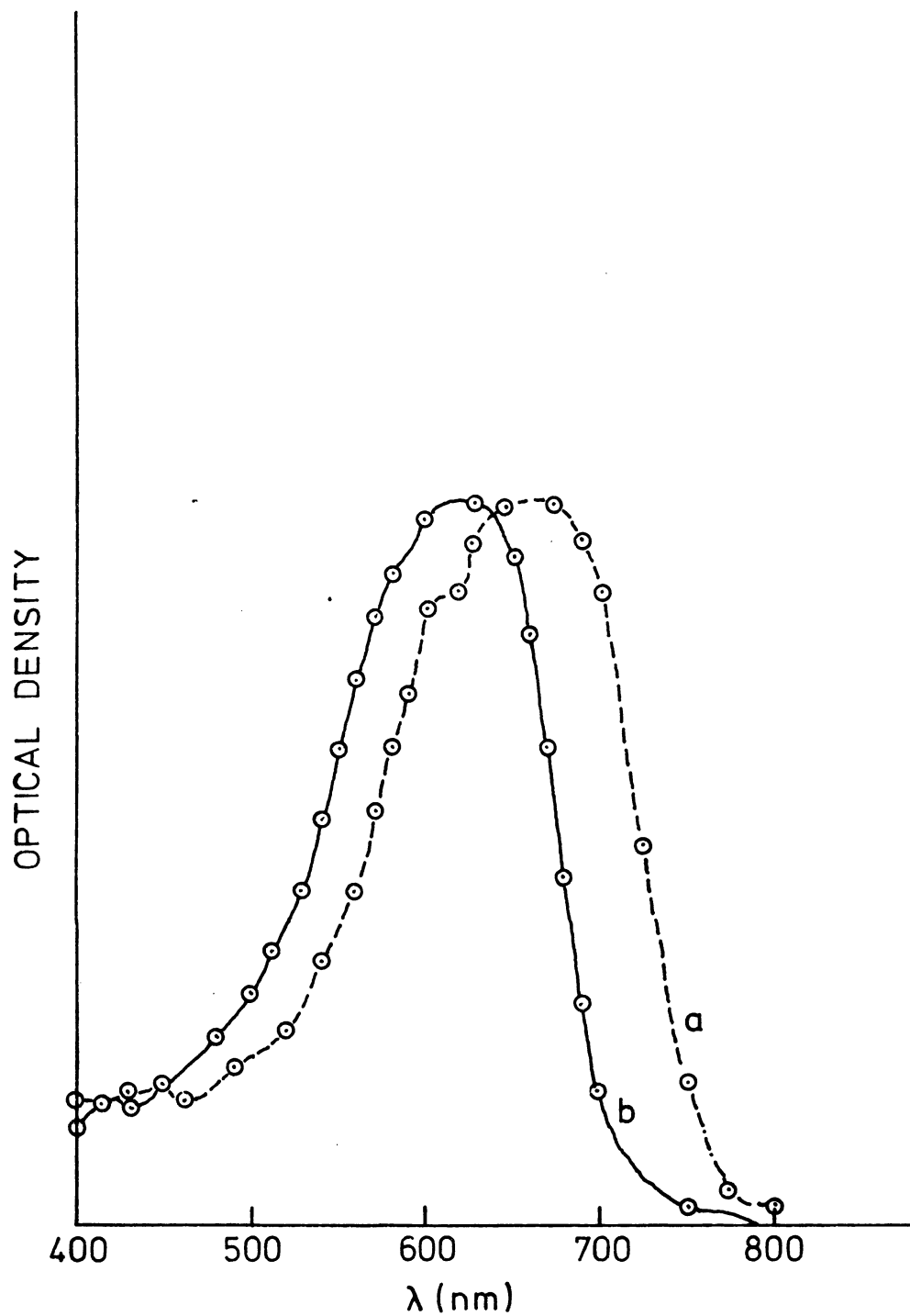


FIGURE 7.
DIFFUSE REFLECTANCE SPECTRA OF:
a,- $\text{CoCl}_2 \text{ ANILINE}_2$
b,- $\text{CoCl}_2 \text{ p-FLUOROANILINE}_2$

in the heights of their component peaks.

Sharp and his co-workers⁽⁴¹⁾ have reported the resolution of the peak for $\text{CoCl}_2\text{p-toluidine}_2$ into two components centred at 640 nm and 580 nm. These values are consistent with the weighted average value of 630 nm found during this investigation. Beech et al⁽¹⁹⁾ have examined the spectra in Nujol mulls of $\text{CoCl}_2\text{aniline}_2$ and $\text{CoCl}_2\text{p-chloroaniline}_2$ and found values of ν_3 which is the set of bands in question (originating from the transition from ${}^4\text{A}_2(\text{F})$ to ${}^4\text{T}_1(\text{P})$) by a resolution into two or three components followed by numerical averaging by the method of Wasson⁽⁹⁸⁾. They reported values for ν_3 of 612 nm and 614 nm for $\text{CoCl}_2\text{aniline}_2$ and $\text{CoCl}_2\text{p-chloroaniline}_2$ respectively. However it would appear that this does not allow for varying intensities of absorption of the individual components of the peak which is split by spin-orbit coupling. In a very recent note Beech et al⁽²³⁾ have determined ν_3 for $\text{CoCl}_2\text{p-fluoroaniline}_2$ to be 609 nm in excellent agreement with the present results.

The spectra, therefore, suggest that there is no significant effect of amine changes on the position of the absorption peak with the possible exception of aniline and p-fluoroaniline.

Examination of the magnetic moments in Table 5 reveals a small increase with decreasing basicity of the amine. The precision of magnetic moments determined by the Gouy method has been estimated to be ± 0.04 or 0.05 B.M. by Cotton⁽⁴⁰⁾ or ± 0.07 B.M. by Nelson⁽⁹⁹⁾. During this study Cotton's estimate has been found closer to reality. Thus

the moment of $\text{CoCl}_2\text{p-bromoaniline}_2$ must be considered significantly greater than the moments of the other chloro complexes.

Magnetic moments alone, therefore, suggest that the ligands in $\text{CoCl}_2\text{p-bromoaniline}_2$ exert a weaker ligand field than those in any other chloro complex except possibly $\text{CoCl}_2\text{p-chloroaniline}_2$. The difference, however, in view of the lack of corroborating evidence from the spectra cannot be claimed unequivocally to be due to ligand field differences. Rather, since the bromine atom is so large, crystal packing differences may arise leading to an anomalous magnetic moment. The effect of crystal packing factors on magnetic moments of a series of isoquinoline complexes with cobalt halides has been invoked by Nelson and co-workers⁽⁹⁹⁾. They found a lack of difference between the moments of complexes involving halides (and pseudohalides) from the iodide through to the selenocyanate. Their quinoline complexes in contrast had moments varying by up to 0.5 B.M. The effect of compression forces on tetrahalogeno ions of cobalt in crystals with various anions has been proposed by Cotton⁽¹⁰⁰⁾.

It is apparent, therefore, that amine basicity has no significant overall effect on ligand field strength in the chloro complexes. In isolated cases there is some evidence for variations in ligand field strength but such evidence is meagre and inconclusive.

(b) *Bromo Complexes:*

The ease of isolation of complexes of cobalt bromide was much the

same as it was with the chloride. Most of the compounds were prepared readily as pink ethanol adducts from ethanolic solution. This is considered to be the result of the higher solubility of bromo complexes. Ethanol adducts of chloro complexes were also isolated when crystallisation was slow. Most of these adducts decomposed completely to the blue tetrahedral compound on standing for a few days in a vacuum desiccator. Those which did not decompose thus turned blue on the surface on exposure to moist air, in some cases within seconds. Nyholm and co-workers found that moisture catalysed stereochemical change of $\text{CoCl}_2\text{pyridine}_2$ from the tetrahedral monomeric form to the octahedral polymer⁽³⁴⁾.

The ligands which failed to produce stable solid complexes with cobalt chloride also failed to produce stable bromo compounds. The compounds isolated pure are listed in Table 6. The colour of all the compounds of formula CoBr_2B_2 was blue and the absorption spectra showed bands centering between 620 nm and 630 nm. Magnetic moments varied from 4.52 B.M. to 4.66 B.M. All of these properties are typical of compounds with tetrahedrally co-ordinated cobalt(II)⁽¹⁰¹⁾. The variation in the wavelengths of the absorption spectra is not considered significant since all of the absorption envelopes were in essentially the same position. There is no significant trend in the values of the magnetic moments. The difference between those of $\text{CoBr}_2\text{p-anisidine}_2$ and $\text{CoBr}_2\text{p-fluoroaniline}_2$ is probably significant although only just so. Crystal packing requirements may account for this in view of the difference in the sizes of the substituents in the

TABLE 6

CoBr₂B₂ - SOLID STATE PHYSICAL MEASUREMENTS

Substituent	Colour	$\lambda_{1/2}$ (nm)	μ (B.M.)	Preparative Method	Adduct
-OCH ₃	Blue	630	4.66	a	-
-CH ₃	Blue	620	4.60	a	+
-H	Blue	620	4.55	a	+
-F	Blue	625	4.52	a	+
-Cl	Blue	630	4.54	b	-
-Br	Blue	625	4.57	a	-

benzene ring. It is apparent that there is no correlation of ligand field strength with basicity of the amine.

The spectra in Nujol mulls of $\text{CoBr}_2\text{aniline}_2$, $\text{CoBr}_2\text{p-chloroaniline}_2$ and $\text{CoBr}_2\text{p-fluoroaniline}_2$ have also been reported by Beech and co-workers^(19,23) and their average values for ν_3 were 631 nm, 627 nm and 625 nm respectively. The agreement with the present work as set out in Table 6 is excellent although it should be borne in mind that Beech's values are obtained by partial resolution followed by averaging as described previously. The magnetic moment of $\text{CoBr}_2\text{p-toluidine}_2$ has been reported by Cotton and Holm⁽⁶⁹⁾ to be 4.72 B.M., the same as that of their chloro compound. As with the chloro compound this value is higher than that found during the current investigation. Nyholm⁽¹⁰²⁾, however, studied the magnetic properties of $\text{CoCl}_2\text{aniline}_2$, $\text{CoBr}_2\text{aniline}_2$ and $\text{CoI}_2\text{aniline}_2$ and found values of 4.40 B.M., 4.46 B.M. and 4.61 B.M. respectively. Thus it appears that Cotton's estimates may be high, Nyholm's are low, and the current values lie in between.

(c) Iodo Compounds:

Only four of the amines gave blue products with cobalt iodide and the results of physical measurements are set out in Table 7. The amines p-acetylaniline and p-nitroaniline failed to give products while p-fluoroaniline and p-acetamidoaniline yielded pink compounds of other stoichiometry. Wavelengths of absorption of the compounds of

TABLE 7

CoI₂B₂ - SOLID STATE PHYSICAL MEASUREMENTS

Substituent	Colour	$\lambda_{1/2}$ (nm)	μ (B.M.)	Preparative Method	Adduct
-CH ₃	Blue-green	650	4.70	d	-
-H	Blue-green	650	4.66	d	-
-Cl	Blue-green	660*	-	d	-
-Br	Blue-green	655	4.70	d	-

* This compound could not be obtained pure by the methods used.

the type CoI_2B_2 were particularly constant at 650 nm to 655 nm, being quite independent of the basicity of the ligand. Magnetic moments were also equivalent within experimental error at 4.66 B.M. to 4.70 B.M. Both magnetic and spectroscopic properties are typical of tetrahedrally co-ordinated cobalt(II)⁽¹⁰¹⁾.

Beech⁽¹⁹⁾ found values for ν_3 for $\text{CoI}_2\text{aniline}_2$ and $\text{CoI}_2\text{p-chloroaniline}_2$ of 656 nm and 658 nm respectively. As with the bromo compounds these values are in agreement with those in Table 7.

The magnetic moments of $\text{CoI}_2\text{aniline}_2$ (Nyholm⁽¹⁰²⁾) and $\text{CoI}_2\text{p-toluidine}_2$ (Cotton⁽⁶⁹⁾) of 4.61 B.M. and 4.80 B.M. respectively bear the same relationship to the present results as was found with the bromo compounds.

The compounds were turquoise in the solid-state although they appeared brighter blue immediately after crystallisation, pointing to a small amount of oxidation of iodide to iodine. This decomposition was too minor to be detected in the microanalyses as shown by Table 18. None of these four blue compounds was formed by decomposition of ethanol adducts although all were prepared from ethanolic solution. The iodo compounds were particularly soluble in ethanol and crystallisation sometimes required several days.

Octahedral Polymers

The physical properties of compounds of the type CoX_2B_2 assigned

octahedral polymeric stereochemistry are set out in Table 8. The magnetic results are consistent with those of compounds of known octahedral stereochemistry⁽¹⁰³⁾ while the spectral wavelengths are similar to those of other postulated octahedral polymers. The compounds of this type were thiocyanates. All of the amines except p-acetylaniline and p-nitroaniline formed octahedral polymers. The amine p-acetylaniline gave a product with reflectance and IR spectra suggesting the presence of an impure octahedral polymer, while p-nitroaniline formed no compound.

The pure compounds were coloured shades of pink to mauve. Their absorption wavelengths varied from 550 nm to 585 nm with an average value of 560 nm. This value compares with an average of 549 nm found by other workers⁽²⁹⁾ for the related heterocyclic base complexes. This point will be discussed in more detail later. Magnetic moments varied from 4.88 B.M. to 5.09 B.M. (with an average value of 5.00 B.M.) decreasing with the basicity of the amine. The range of values of this property was 0.21 Bohr Magnetons which is greater than the ranges found for any of the other groups of halo complexes above. On the basis of the magnetic evidence it would appear that there is a significant difference between the ligand field strengths exerted by the most basic amines on the one hand and the least basic ones on the other. The correlation with spectral results is very low since the complex with p-anisidine is the only one with a very long absorption wavelength in agreement with its high magnetic moment. Further, this result suggests that reflectance spectroscopy is not sufficiently sensitive to

Co(NCS) ₂ B ₂ - Solid State Physical Measurements					
Substituent	Colour	$\lambda_{\frac{1}{2}}$ (nm)	μ (B.M.)	Preparative Method	ν_{NCS} (cm ⁻¹)
-OCH ₃	Buff	585	5.09	a	2110
-CH ₃	Pink	555	5.00	a	2110
-NHCOCH ₃	Buff	550	5.03	c	2115
-H	Pink	570	5.02	a	2110
-F	Mauve	555	5.02	a	2110
-Cl	Pink	560	4.94	a	2110
-Br	Pink	560	4.88	a	2100
-COCH ₃	Violet	-	-	a	2130

TABLE 8

permit detection of ligand field changes of the magnitude involved in the thiocyanato complexes.

The spectra of $\text{Co(NCS)}_2\text{p-acetamidoaniline}_2$ and its ethanol adduct are shown in Figure 8. The latter compound is assigned an octahedral monomeric configuration as will be explained later. The outstanding difference between the two spectra is in the region 400 nm - 450 nm. The compound $\text{Co(NCS)}_2\text{p-acetamidoaniline}_2$ exhibits particularly intense absorption in this region whereas the adduct does not. This absorption is the longer wavelength portion of a peak centering in the ultra-violet. The shifting of this peak towards the visible region in the case of octahedral polymeric thiocyanato complexes has been found to occur when the thiocyanate is "bridging" two cobalt atoms in octahedral polymers⁽⁵⁶⁾. The spectra in Figure 8 have another feature indicative of the octahedral polymeric nature of $\text{Co(NCS)}_2\text{p-acetamidoaniline}_2$. The peak for this compound is centered around 550 nm whereas that of the adduct is found at 505 nm. The adduct has as its donor atoms four nitrogens and two oxygens while an octahedral polymer would have four nitrogens and two sulphurs. From the positions of oxygen and sulphur donors in the Spectrochemical Series the polymer should absorb at a longer wavelength than the adduct. This is what is found in Figure 8.

Further evidence of the bidentate nature of the thiocyanate in the compounds in Table 8 may be found in the asymmetric stretch of the C-N band in the infra-red spectra shown in the last column of that table.

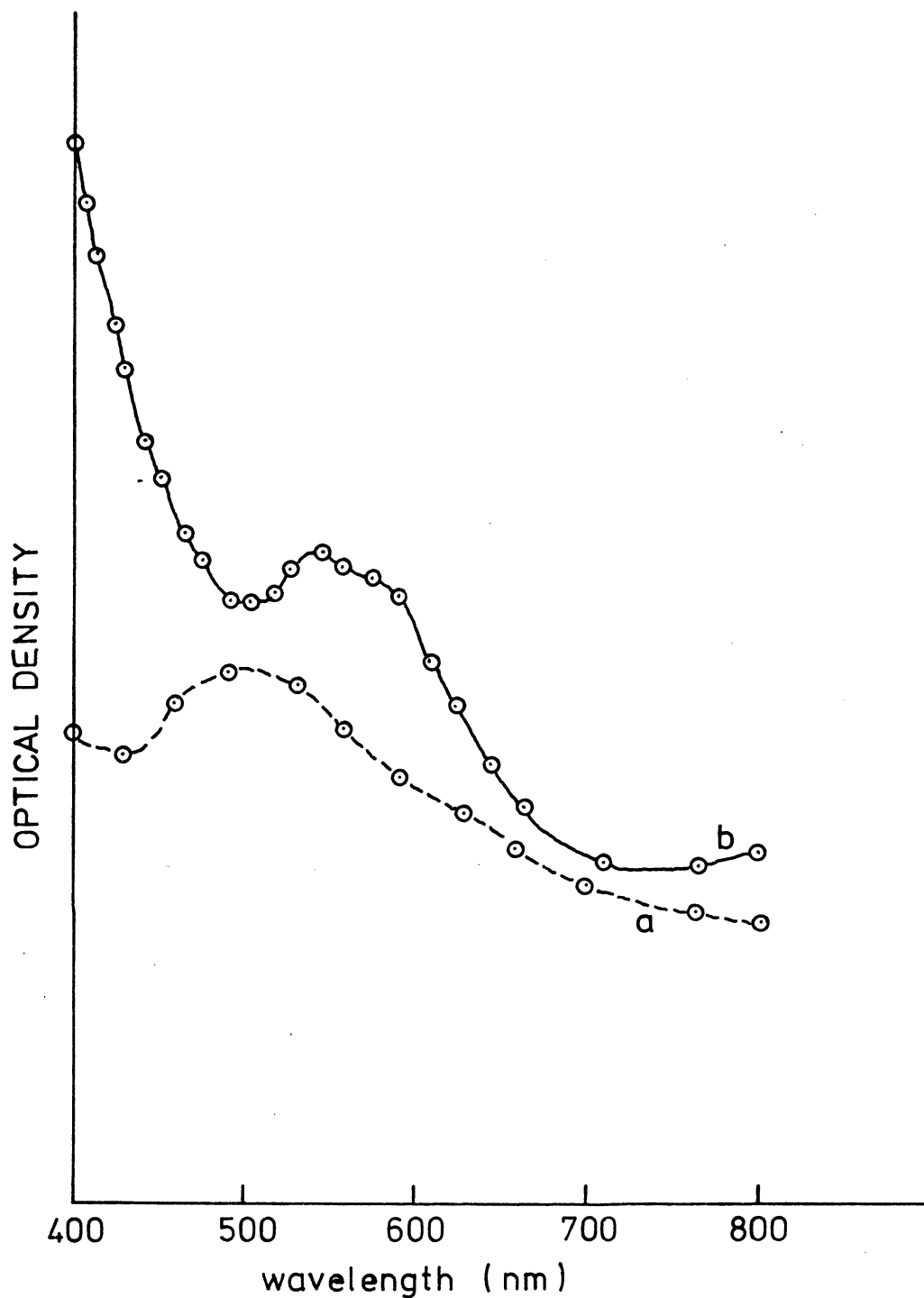


FIGURE 8.

DIFFUSE REFLECTANCE SPECTRA OF THIOCYANATE COMPLEXES:-

a,- $\text{Co}(\text{NCS})_2(\text{p-ACETAMIDOAN})_2(\text{C}_2\text{H}_5\text{OH})_2$

b,- $\text{Co}(\text{NCS})_2(\text{p-ACETAMIDOAN})_2$

In every case these compounds absorb at frequencies equal to or greater than 2100 cm^{-1} . The bridging thiocyanate absorbs at frequencies equal to or slightly greater than 2100 cm^{-1} while unidentate N-bonded thiocyanates absorb at slightly lower frequencies⁽⁷⁰⁾. Chatt and co-workers⁽⁷¹⁾ consider that a band at 2145 cm^{-1} is diagnostic of bridging thiocyanates. Larsson and Mieziš have discussed the assignment of the band around 2100 cm^{-1} to a C-N stretch influenced by metal-sulphur or metal-nitrogen bonding in a series of mixed palladium complexes⁽¹⁰⁴⁾.

It is concluded therefore that these complexes have a structure that is essentially the same as that of the violet form of $\text{CoCl}_2\text{pyridine}_2$ shown in Figure 2 on page 6. The difference is the replacement of "bridging" chlorides by "bridging" thiocyanates. There appears to be an effect of the substituent on ligand field strength in the case of the thiocyanates. This strength appears to increase with decreasing basicity of the amine, at least as far as the magnetic moments are concerned. This point will be discussed in more detail later.

Nyholm in an early paper⁽³³⁾ mentioned briefly that the complexes of cobalt thiocyanate with aniline and p-toluidine were probably octahedral polymers although no supporting evidence was given. However Cotton⁽¹⁰⁵⁾ has measured the magnetic moment of $\text{Co(NCS)}_2\text{p-toluidine}_2$ and found it to be 4.93 B.M. This value agrees with that in Table 8 within experimental error.

The theory proposed by Graddon and Watton provides an explanation

of the observed correlation of magnetic moment with basicity of the amine⁽²⁸⁾. This theory relies upon the fact that the position of ligands in the Spectrochemical Series describes their ability to discriminate between d_{ϵ} and d_{γ} orbitals on the metal. The ability of the donor atom to distinguish between d_{ϵ} and d_{γ} orbitals depends upon the number of electron pairs on the donor, particularly the non-bonding electrons. The more diffuse this electron cloud the less the ligand can discriminate between sets of orbitals on the metal. Accordingly, the more diffuse is the electron cloud, the weaker will be the ligand field. Hence increasing electronegativity of groups attached to the donor will result in electron withdrawal from the donor atom and a decrease in the size of its electron cloud. This results in less interaction with d_{ϵ} or d_{γ} orbitals and an increase in ligand field strength. This should result in lower magnetic moments. The magnetic moments of the thiocyanate polymers decrease with increasing electronegativity of the amine substituent. Thus this theory appears to provide an explanation for the observed magnetic moments.

Octahedral Monomeric Adducts

Stable six co-ordinate complexes were isolated by reaction of cobalt thiocyanate or cobalt bromide with p-acetamidoaniline in ethanol. The product of this reaction with cobalt iodide was pink but gave an unsatisfactory analysis. As mentioned in Section (a) no pure chloro complex could be isolated either. When the ligand and cobalt

iodide were reacted in isopropanol a reddish-brown product resulted and this material turned blue on the edges on standing. Heating resulted in decomposition. The physical properties of the stable adducts are shown in Table 9.

The thiocyanate complex had the empirical formula $\text{Co}(\text{NCS})_2\text{p-acetamidoaniline}_2\text{ethanol}_2$ and was pink and crystalline. The absorption wavelength was at 505 nm and the magnetic moment was 4.87 B.M. If the complex were an octahedral monomer, it would have an environment consisting of four nitrogen and two oxygen donor atoms. Graddon, Heng and Watton have summarised the absorption wavelengths of several octahedral complexes of the type $\text{Co}(\text{NCS})_2(\text{R-pyridine})_4$ (where R is a para-substituent) and found an average value of 499 nm⁽²⁹⁾. In view of the stronger ligand field of nitrogen donors above those of oxygen donors it would be expected that $\text{Co}(\text{NCS})_2\text{p-acetamidoaniline}_2\text{ethanol}_2$ would absorb at a slightly longer wavelength due to its two oxygen donors. Such an approach using the average value ligand field concept is justified in this case since the octahedral polymers described above have similar spectra to the corresponding substituted pyridine compounds. The magnetic moment of this compound is also within the range 4.6 B.M. - 5.3 B.M. expected of octahedral compounds. The compound is quite stable at temperatures up to 60°C and decomposes to a dull green material on heating above this.

The absorption spectrum shown in Figure 8 is typical in profile of an octahedral monomer as discussed in Section * above. Furthermore

Compounds of Other Stereochemistries Solid State Physical Measurements						
Substituent	Adduct	Colour	$\lambda_{\frac{1}{2}}$ (nm)	μ (B.M.)	Prep. Method	Halide
-NHCOCH ₃	2C ₂ H ₅ OH	Pink	505	4.87	a	NCS
-NHCOCH ₃	3H ₂ O	Pink	515	5.14	a	Br
-Br	2H ₂ O	Violet	565	5.00	a	Cl

TABLE 9

the C-N stretching frequency in the infra-red was found at 2080 cm^{-1} and this is characteristic⁽¹⁰⁶⁾ of the thiocyanate group which is bonded to the metal only through the nitrogen.

It is concluded, therefore, that this compound is an octahedral monomer and not a tetrahedral monomer or octahedral polymer containing occluded ethanol molecules.

The second compound in this category is $\text{CoBr}_2 \cdot \text{p-acetamidoaniline}_2 \cdot (\text{H}_2\text{O})_3$. Based on stoichiometry alone there are several feasible structures. These are a tetrahedral monomer with three lattice waters, an octahedral polymer with three lattice waters or an octahedral monomer with two co-ordinated waters and one lattice water. Seven co-ordinate cobalt(II) is rare and this and five co-ordinate cobalt seem to be ruled out by the physical measurements discussed below.

The reflectance spectrum of this compound is shown in Figure 9. The ligand field band is centred at 520 nm but is superimposed upon the tail of an intense band centring in the UV. This tail has a very shallow slope and disturbs the centre of the peak at 520 nm by 5 nm to 515 nm. Absorption in this region is characteristic of octahedral cobalt(II). Furthermore, the magnetic moment of 5.14 B.M. corroborates the spectral evidence. The question now arises as to whether the complex is a monomer or a polymer. A polymer would require the bromines to be "bridging" as is the case with chlorine in the stable violet form of $\text{CoCl}_2 \cdot \text{pyridine}_2$ ⁽³⁴⁾. The three molecules of water per cobalt atom may well be held by hydrogen bonding involving the amide groups. The infra-

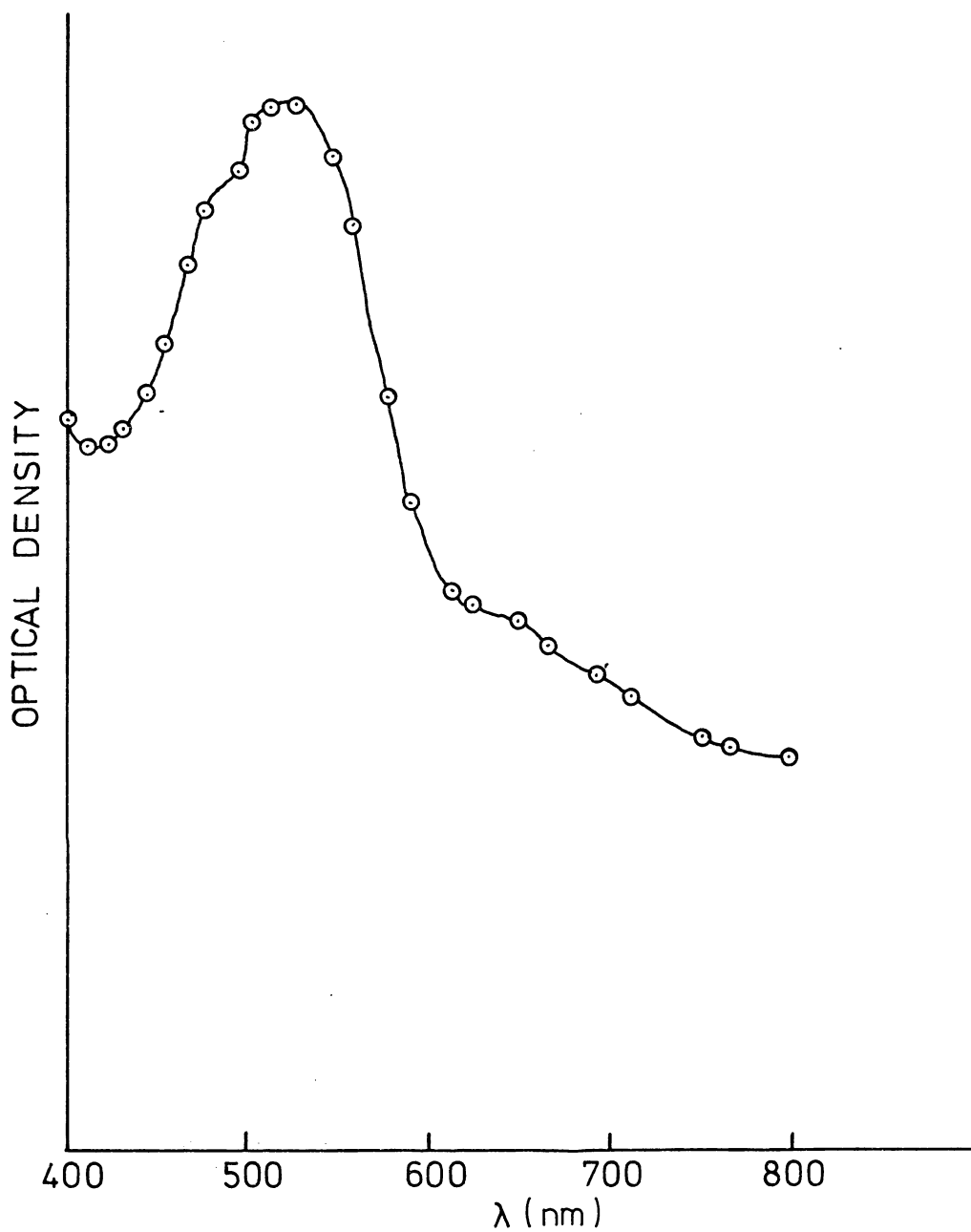


FIGURE 9.
DIFFUSE REFLECTANCE SPECTRUM OF
 $\text{CoBr}_2(\text{p-ACETAMIDOAN})_2(\text{H}_2\text{O})_3$

red spectrum is strongly suggestive of hydrogen bonding.

The thermogram of this compound is shown in Figure 10. The weight loss corresponded to 9.4% of the total weight. Loss of three water molecules per cobalt atom requires 9.4% weight loss. The weight loss occurred gradually between 65°C and 90°C, not sharply as expected when metal-oxygen bonds are broken. This low temperature of water release is suggestive of very weak bonding of the water. However covalent bonding of the water should not be ruled out in view of the instability of most of the ethanol adducts of the other complexes discussed earlier. The thermogravimetric decomposition of ethanol adducts of aniline complexes of cobalt halides has been reported by Sharp and co-workers who found that these decomposed over the range 60°C to 80°C⁽¹⁵⁾.

The spectral and magnetic properties of $\text{CoBr}_2\text{p-acetamidoaniline}_2(\text{H}_2\text{O})_3$ in Table 9 would also be consistent with this compound being an octahedral monomer. The values taken for these properties by the octahedral monomers and polymers of heterocyclic bases with cobalt bromide do not differ greatly⁽²⁹⁾. The monomers of the type $\text{CoBr}_2\text{B}_4^*$ have average magnetic moments and absorption wavelengths of 5.06 B.M. and 541 nm respectively. The polymers $\text{CoBr}_2\text{B}_2^*$ have values of 5.29 B.M. and 549 nm. In view of the shortage of measurements on other octahedral bromo complexes of cobalt with aromatic amines, the magnetic and spectral properties do not help much. The wide tail in the UV shown in Figure 9 is very much more significant than this tail in the

*B = heterocyclic base.

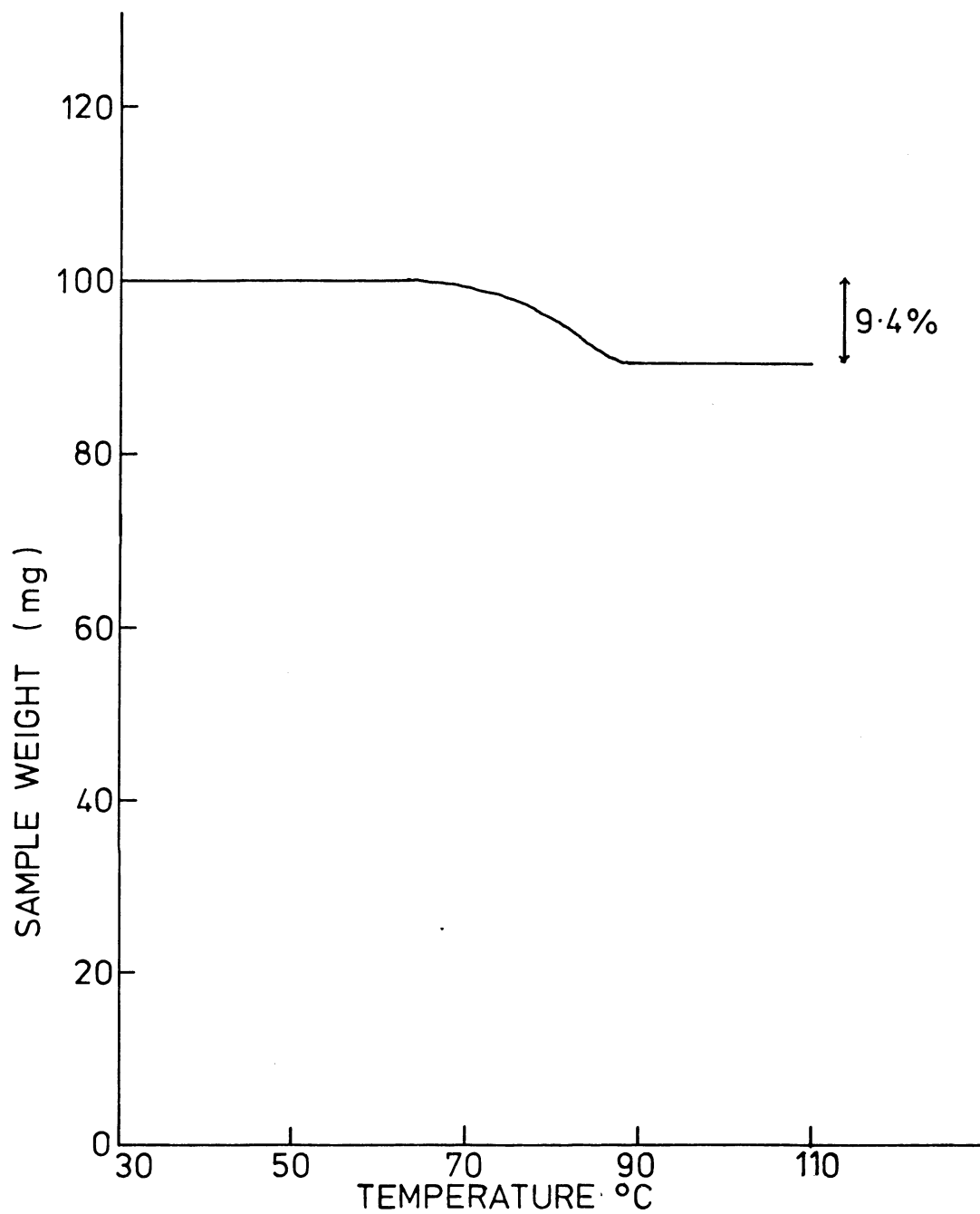


FIGURE 10.

THERMOGRAVIMETRIC CURVE FOR $\text{CoBr}_2 \cdot \text{P-ACETAMIDOAN}_2$
 $(\text{H}_2\text{O})_3$

spectra of $\text{CoBr}_2\text{p-chloropyridine}_2$ and $\text{CoBr}_2\text{p-cyanopyridine}_2$ (107). These compounds have been postulated to be octahedral polymers. Thus it would appear that the bromines may be "bridging" in $\text{CoBr}_2\text{p-acetamidoaniline}_2(\text{H}_2\text{O})_3$ also since the charge transfer would be shown at a shorter wavelength if the bromines were unidentate. This evidence however is insufficient for a stereochemical assignment. Contradicting evidence may be found in the values of absorption wavelength and magnetic moment. These values, 520 nm and 5.14 B.M., would be more likely to result from an environment of $2\text{Br} + 2\text{N} + 2\text{O}$ than from 4Br ("bridging") + 2N . This conclusion is based on the relative positions of the bromide ion and water in the Spectrochemical Series together with the published values for heterocyclic base polymers as mentioned above (29).

The thermogram is more difficult to interpret if the structure is considered monomeric. It would be necessary for the third molecule of water to be held with about the same strength as the covalently bound waters. Nevertheless this third water may account for the gradual loss of weight.

In conclusion, both of these structures are feasible, although the evidence appears to favour the polymer. This problem should be resolved by crystal structure analysis and a far IR spectrum showing the Co-Br stretch may indicate whether or not the bromines are bridging. Molecular weight determination would be suspect due to the possibility of dissociation of one or more water molecules.

This compound was not isolated as such from ethanolic solution.

The initially isolated compound was fawn in colour and solvent removal followed by drying in a vacuum desiccator resulted in a two colour product. A mixture of fawn and pink materials was formed. Brief exposure to the humid atmosphere resulted in the entire sample achieving the pink colour. Subsequent drying in the desiccator did not affect this compound. Apparently the initially isolated product was an ethanol adduct which was unstable in the presence of moisture. If such was the case, this may have been another case of Nyholm's stereochemical change catalysed by moisture. The reverse effect was noted during an earlier attempt at the preparation of the compound when a pink product was isolated and recrystallisation from ethanol yielded a fawn material with C, H and N analyses suggestive of stoichiometry $\text{CoBr}_2\text{p-acetamidoaniline}_2(\text{C}_2\text{H}_5\text{OH})_2$. Hence there is a possibility that the ethanol adduct may be isolated pure under suitable experimental conditions.

The third compound $\text{CoCl}_2\text{p-bromoaniline}_2(\text{H}_2\text{O})_2$ was less pure than the other two as may be observed from Table 18. As mentioned previously, reaction of cobalt chloride hexahydrate with p-bromoaniline in ethanol always resulted in a mixture of blue and pink crystals. Allowing this mixture to stand for a fortnight in a moist, dust-free atmosphere resulted in the formation of the hydrate. This was the only simple dihydrate obtained in such a pure state. From its physical measurements shown in Table 9 it is assigned octahedral stereochemistry.

Table 10 shows the C, H and N analytical results of the reactions

C, H and N Analyses of Products of Reactions of Cobalt Chloride and Cobalt Bromide with p-acetylaniline						
Found %			Calculated % for Possible Compound			
(1) Chloro Compounds:						
C	H	N	C	H	N	
43.5	4.7	4.8	44.1	5.1	6.4	$\text{CoCl}_2\text{p-acetylan}_2 \cdot 2\text{H}_2\text{O}$
44.6	5.2	5.2	43.5	5.6	6.4	$\text{CoCl}_2\text{p-acetylan}_2 \cdot \text{C}_2\text{H}_5\text{OH}$
45.5	5.5	6.5	49.0	6.1	5.7	$\text{CoCl}_2\text{p-acetylan}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$
(2) Bromo Compounds:						
C	H	N	C	H	N	
38.3	4.3	-	39.3	3.7	-	$\text{CoBr}_2\text{p-acetylan}_2$
37.2	4.3	-	40.6	4.5	-	$\text{CoBr}_2\text{p-acetylan}_2 \cdot \text{C}_2\text{H}_5\text{OH}$
51.5	5.5	-	50.7	4.8	7.4	$\text{CoBr}_2\text{p-acetylan}_4$
49.8	5.2	7.0				

TABLE 10

of cobalt chloride and cobalt bromide with p-acetylaniline in ethanol. In the case of the chloride, from which a pink product was isolated, analytical figures do not distinguish between a dihydrate, a mono-ethanolate or a diethanolate. Similarly, in the case of cobalt bromide the analyses suggest basically two compounds may be formed. One would be $\text{CoBr}_2\text{p-acetylaniline}_4$ whereas the other may be either $\text{CoBr}_2\text{p-acetylaniline}_2$ or $\text{CoBr}_2\text{p-acetylaniline}_2\text{C}_2\text{H}_5\text{OH}$. However no conclusions may be drawn as to exact stoichiometry from this information. What is important is that p-acetylaniline, weakly basic as it is, still reacts with the halides and the thiocyanate to form some type of reaction products in contrast with the inertness of the slightly less basic p-nitroaniline. The fact that no one compound was obtained pure may be due to the formation of more than one compound under the same conditions.

Several other cases of adduct formation could be cited but purities of products were so low as to render any conclusions suspect.

Effect of Halide on Ligand Field Strength

Table 11 below sets out the average values of $\lambda_{\frac{1}{2}}$ and μ for tetrahedral complexes of the three halides both with aromatic amines and heterocyclic bases. The latter results are taken from ref. (29). There is no significant difference between the average ligand field strength of chloro and bromo complexes with aromatic amines. This is

Average Values of $\lambda_{\frac{1}{2}}$ and μ in Solid Tetrahedral Complexes
(Bracketed Values are those for Heterocyclic Base Complexes⁽²⁹⁾)

Property	Halide Cl	Halide Br	Halide I
$\lambda_{\frac{1}{2}}$ (nm)	625 (611)	625 (626)	650 (659)
μ (B.M.)	4.56 (4.54)	4.57 (4.56)	4.69 (4.60)

TABLE 11

Octahedral Polymeric Complexes with o-substituted Amines

Complex	Colour	$\lambda_{\frac{1}{2}}$ (nm)	μ (B.M.)	Preparative Method
$\text{Co}(\text{NCS})_2\text{o-anis}_2$	Pink	555	5.45	a
$\text{Co}(\text{NCS})_2\text{o-tol}_2$	Pink	-	-	a

TABLE 12

shown both by magnetic and spectroscopic results. The iodo compounds however show weaker ligand fields.

The Spectrochemical Series predicts that the ligand field of the chloro complex should be stronger than that of the bromo complex. This was found to be the case with the heterocyclic base compounds although the difference between the average magnetic moments of the chloro and bromo complexes was very small indeed. Equivalent ligand fields apparently exist in the bromo compounds regardless of whether aromatic amines or heterocyclic bases are present. Heterocyclic bases result in a slightly stronger field in the case of chloro complexes. The position with the iodo complexes is not clear. What is important is that in the case of aromatic amine complexes the bromo and chloro compounds exhibit similar average ligand fields while iodo complexes exert weaker fields. Furthermore comparison of the physical properties of heterocyclic base and aromatic amine complexes reveals no consistent effect of replacing heterocyclic bases by aromatic amines.

The difference in strength of aromatic amine and heterocyclic base ligand fields (in conjunction with the appropriate halogen) may be explained in the following way. The pyridine molecule (and its p-substituted derivatives) are planar and the lone pair of electrons on the nitrogen and the two C-N bonds describe angles of 120° . The valency electrons of the nitrogen of primary amines are approximately tetrahedrally oriented⁽¹⁰⁸⁾, although the angle between the lone pair and the N-H bonds should be slightly less than tetrahedral.

When the amine is bonded to the cobalt atom this position would be expected to change slightly. However an interaction is to be expected between the d-electrons on the cobalt and the N-H bonding electrons of the amine. This interaction should be greater on geometrical grounds than the interaction between the cobalt d-electrons and those of the C-N bonds of heterocyclic bases. This effect would be more important in the aromatic amine complexes if the Co-N distances published for specific crystal structures were similar for other complexes. The Co-N distances in $\text{CoCl}_2\text{p-toluidine}_2$ and $\text{CoCl}_2\text{p-vinylpyridine}_2$ have been reported as $1.95\text{\AA}^{(20)}$ and $2.01\text{\AA}^{(27)}$ respectively. The ability of the bonding electrons (as distinct from non-bonding electrons) to discriminate between the d_ϵ and d_γ electrons on the cobalt should be less for aromatic amines than for heterocyclic bases. This is an extension of the theory of Graddon and Watton⁽²⁸⁾. Hence the degree of separation of d_ϵ and d_γ should be greater with heterocyclic bases than with aromatic amines. The foregoing would explain the results obtained in chloro complexes in which the other ligand, chlorine, is small and not very polarisable.

Now, going from the chloro complexes to the bromo complexes with heterocyclic bases, the larger, more polarisable bromine is able to discriminate less between d_γ and d_ϵ electrons and a weaker ligand field results. Furthermore bromine atoms exert more steric repulsion on each other than chlorines, resulting in longer cobalt-halogen distances and weaker ligand fields. In the case of aromatic amine com-

plexes the effect of the bulky bromines renders insignificant the effect of N-H bonding electrons on the cobalt d-electrons. This would be expected as a result of increased cobalt-nitrogen and cobalt-halogen distances found when chlorine is replaced by bromine. Thus there would be similar ligand fields expected for both heterocyclic base and aromatic amine complexes. This effect is magnified both with aromatic amine and heterocyclic base complexes when iodine is the other ligand. Mutual steric repulsions of iodines together with polarisability effects would lead to the observed weak ligand fields^(28,34).

Unfortunately no complete set of halo complexes of any one aromatic amine with cobalt(II) has been examined crystallographically. It is known^(20,21) that the Cobalt-Halogen distance goes from 2.26Å to 2.63Å for $\text{CoCl}_2\text{p-toluidine}_2$ and $\text{CoI}_2\text{p-toluidine}_2$ respectively. However the Cobalt-Nitrogen distance was not determined in the latter complex and that of $\text{CoBr}_2\text{p-toluidine}_2$ is also unknown. Supporting or contradicting evidence for the theory above will be found should such structures be determined completely.

The average magnetic moments and absorption wavelengths of the iodide complexes offer conflicting evidence as to the ligand field strength. It is not possible to state whether heterocyclic bases or aromatic amines exert significantly stronger ligand fields in iodo complexes.

The physical properties of the thiocyanate polymers bear much the same relationship to the stereochemically similar heterocyclic base

complexes as was observed for chloro complexes. In this case however the average magnetic moments are identical at 5.00 B.M. The average absorption wavelengths are 560 nm and 549 nm for the aromatic amine and heterocyclic base complexes respectively. In view of the similarity of the magnetic moments it seems probable that there is very little, if any, ligand field difference due to change in the type of base.

Effects of the Nature of the Halide or Pseudohalide on Co-ordination Number

The most significant effect noted was that observed in thiocyanate complexes. It was found that use of the methods described in this investigation would not yield tetrahedral thiocyanate compounds. In fact the only reported cases of tetrahedral thiocyanate complexes of cobalt(II) with heterocyclic bases are those formed with 2-methylpyridine, 3-methylpyridine, 3-ethylpyridine and 3,4-lutidine (28,72). The results in Table 12 suggest that the structure of $\text{Co}(\text{NCS})_2\text{o-anisidine}_2$ is an octahedral polymer as was shown to be the case with its para-substituted analogue.

Neither ortho- nor para-substituted amines yielded octahedral complexes of the type CoX_2B_4 with cobalt thiocyanate. This fact is significant in itself. It is clear that in the solid-state cobalt prefers octahedral stereochemistry in thiocyanate complexes with aromatic amines. This involves bonding of the metal to two of the

polarisable sulphurs of the thiocyanates. This is in preference to bonding with two extra nitrogens of amine molecules or two oxygens of ethanol molecules. Such a preference is in contrast with that of cobalt in the tetrahedral complexes of cobalt chloride. In these complexes chloride bridging is not used to form octahedral polymers such as is found in the violet form of $\text{CoCl}_2\text{pyridine}_2$.

Lewis⁽⁶³⁾ has placed SCN^- (S donor) next to Cl^- in the Spectrochemical Series and so their ligand fields should be similar. The thiocyanate and chloride complexes isolated during this study were all rather insoluble in ethanol, the reaction medium, although the chlorides were markedly more insoluble than the thiocyanates. Solubility, in the case of the thiocyanates, may explain why the tetrahedral monomer or octahedral monomer is not isolated. There is strong evidence from the blue colour that the tetrahedral monomer is present in solution when free base is not present. The solutions from which the thiocyanate complexes were isolated (which contained excess base) were pink or very pale blue, ~~and contained excess base~~. Thus some form of octahedral species was undoubtedly present under such circumstances.

To date, there have been only two reported cases of octahedral complexes of aromatic monoamines to be formed with cobalt halides. One is reported to be $\text{CoBr}_2\text{m-chloroaniline}_4$ ⁽¹⁹⁾. This compound precipitated fifteen hours after the tetrahedral monomer $\text{CoBr}_2\text{m-chloroaniline}_2$. The other is $\text{CoCl}_2\text{o-fluoroaniline}_2$ which has been assigned an octahedral polymeric stereochemistry⁽²³⁾. In the current

investigation second crops of tetrahedral monomers or octahedral polymers were frequently collected depending upon whether a halide or thiocyanate respectively was involved. In view of the failure to isolate complexes of the type $\text{Co}(\text{NCS})_2\text{B}_4$ and the resultant lack of their solubility data it may be concluded that solubility factors may account for the isolation of polymers.

However another possible explanation is a steric one. The thiocyanate ion is much less bulky than aromatic amine molecules. Hence by polymerisation the requirement of the cobalt for octahedral stereochemistry may be attained without the added steric strain of co-ordinating two extra amine molecules. Beech, Marr and Rockett⁽¹⁹⁾ examined molecular models of some tetrahedral aromatic amine complexes of the type CoX_2B_2 and concluded that steric strain would be small. However steric hindrance would be greater if two extra base molecules were co-ordinated. The co-ordination of the sulphur atoms in preference to the much more numerous ethanol (solvent) molecules cannot be explained using the theory of repulsion of non-bonding electron pairs on the donor atoms⁽²⁸⁾. The thiocyanate ion using sulphur as a donor has an average of $2\frac{1}{2}$ non-bonding electron pairs on the donor⁽²⁸⁾ while the ethanol has only 2 pairs. Furthermore the sulphur should be more polarisable than the oxygen. Hence either the cobalt requires the more polarisable sulphur to satisfy its electroneutrality requirements or the thiocyanate polymer possesses an over-riding freedom from inter-ligand repulsion and steric strain. This would be due to the small dimensions of the thiocyanate ion.

The finding that chloro, bromo and iodo complexes were mostly tetrahedral monomers may also be explained in a number of ways. Chloro compounds were generally first precipitated as the blue species within seconds of mixing the reactants. As a rule the reactant mass virtually solidified requiring dilution with ethanol to facilitate mixing. Ethanol adduct formation usually followed, if at all, in the solid compound which apparently recrystallised slowly in contact with the mother liquor. In view of the low solubility of the tetrahedral monomers, it is possible that octahedral monomer formation may have been prevented by removal of the cobalt(II) ion from solution as the tetrahedral monomer. The subsequent formation of pink ethanol adducts on standing suggests some tendency towards a preference for octahedral stereochemistry. Reaction in large excess of amine failed to produce solid tetrakisamine products and so the reaction with ethanol in the case of chloro complexes apparently indicates a preference for this over the aromatic amines. The ethanol adducts were unstable when isolated, particularly when exposed to the humid atmosphere. Such instability may be an effect of the higher vapour pressure of the ethanol. It is also possible that the stability of the tetrahedral monomers may be the result of limitation of coordination number due to repulsion of non-bonding electrons on the ligands. The size and shape of aromatic amines may be such that octahedral stereochemistry is just not feasible due to inter-ligand repulsions whereas the heterocyclic bases form compounds of both octahedral and tetrahedral stereochemistry.

The isolation of bromo complexes as unstable ethanol adducts is

probably explained using the same approach as was applied to chloro complexes above. Bromo compounds generally crystallised more slowly than their chloro counterparts and sometimes crystallised as ethanol adducts. The formation of octahedral six co-ordinate complexes with water indicates a preference for six co-ordination at least in the solid-state in some cases. This stability was found only in the case when water was the ligand. A stable pure ethanolate was obtained only with a thiocyanate. In every other case such compounds decomposed easily or were isolated impure.

No pure six co-ordinate complexes of cobalt iodide were isolated. The tetrahedral monomeric iodide complexes were found to be extremely soluble in ethanol. However in spite of this only the blue solids crystallised. This may probably be interpreted as a case of restriction of co-ordination number to four due to inter-ligand repulsions⁽²⁹⁾. The large diffuse electron clouds of the bonded iodines contain three non-bonding electron pairs. Repulsions of other non-bonding pairs on other donor atoms would prevent accommodation of more than four ligands about a cobalt atom. This failure of the iodide complexes to be isolated as octahedrally co-ordinated species has been found to be common when ligands were 2-methylimidazole⁽⁸⁷⁾, and some substituted pyridines⁽⁴³⁾.

It is concluded that the isolation of mainly tetrahedral monomeric halo complexes may be explained as due to solubility factors or by using the theory of repulsion of donor non-bonded electron pairs.

Isolation of thiocyanates as polymers is apparently due to insolubility of the polymer together with the preference of the cobalt for octahedral stereochemistry. Steric or other inter-ligand repulsion may be responsible for the failure of octahedral monomers to be isolated.

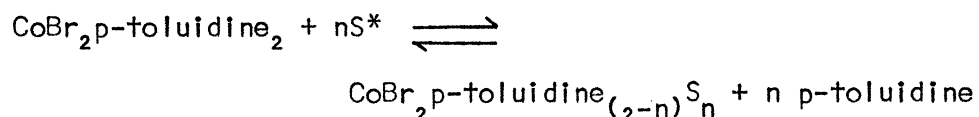
2. Behaviour of Complexes in Solution

Solubility in Solvents

The extent to which the complexes dissolved in any one solvent was found to increase on going from the chlorides and thiocyanates to the ioides. All complexes were quite insoluble in benzene and toluene, very slightly soluble (generally less than 10^{-3} M) in chloroform, 1,2-dichloroethane and nitrobenzene. However, in the more strongly dissociating and donor solvents the complexes were more soluble. Nitromethane dissolved all the compounds to as much as 10^{-4} M while tetrahydrofuran, ethanol, acetone and dimethylformamide were found to be much better solvents.

Spectral evidence suggested that in the better solvents species other than the complexes as found in the solid-state were present to a greater or lesser extent depending upon the nature of the solvent. For instance, the compound $\text{CoBr}_2\text{p-toluidine}_2$ 10^{-3} M in tetrahydro-

furan gave an absorption spectrum quite unlike its reflectance spectrum. These are shown in Figures 11 and 12. Also shown are spectra of solutions in which part of the tetrahydrofuran was replaced by p-toluidine. The spectrum of the compound in 100% tetrahydrofuran was a composite with a predominant band centring around 680 nm. When 5% p-toluidine was present the band at 680 nm was no longer present to any significant extent. Rather the band now centred around 630 nm as was the case with the reflectance spectrum. The band present in the spectrum of a solution containing 16% p-toluidine was similar in profile to the previous spectrum. However the maximum extinction coefficient at 650 nm was less, being 440 as against 505 when there was 5% p-toluidine in the solvent. This type of behaviour probably indicates solvolytic dissociation of the complex to form a tetrahedral complex with a weaker ligand field, resulting in absorption at 680 nm. The solvent must have replaced one or both of the amine molecules since the oxygen donor, tetrahydrofuran, would exert a weaker ligand field than the amine, but a stronger field than the bromide. Inclusion of free base (5%) in the solvent resulted in displacement of solvent molecules from the metal and reformation of $\text{CoBr}_2\text{p-toluidine}_2$ as expected from the following equation:



where $n = 1$ or 2 .

Further increase in the amount of free base in the solvent resulted

* tetrahydrofuran

FIGURE 11

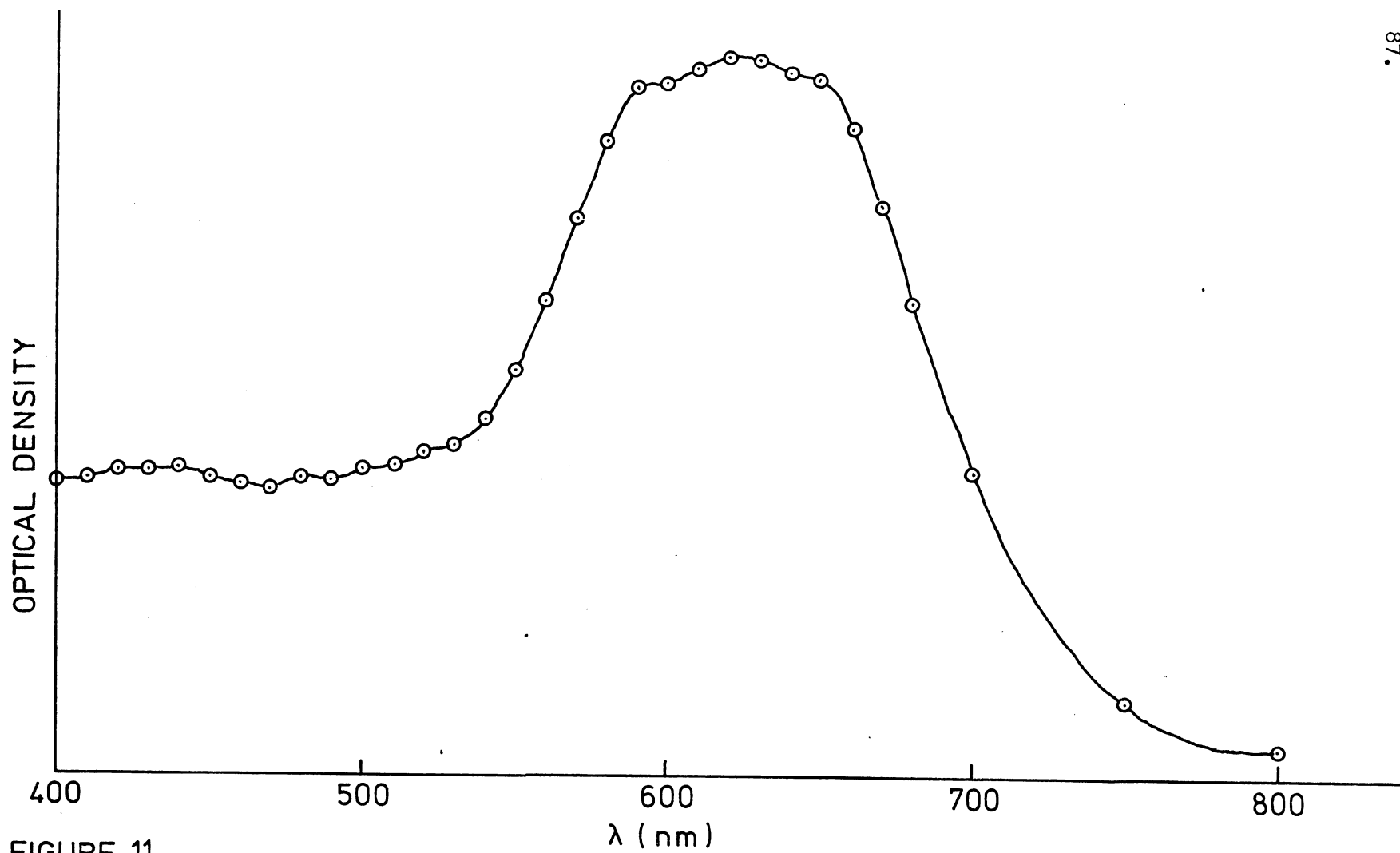


FIGURE 11.
DIFFUSE REFLECTANCE SPECTRUM OF $\text{CoBr}_2 \cdot \text{p-TOLUIDINE}_2$

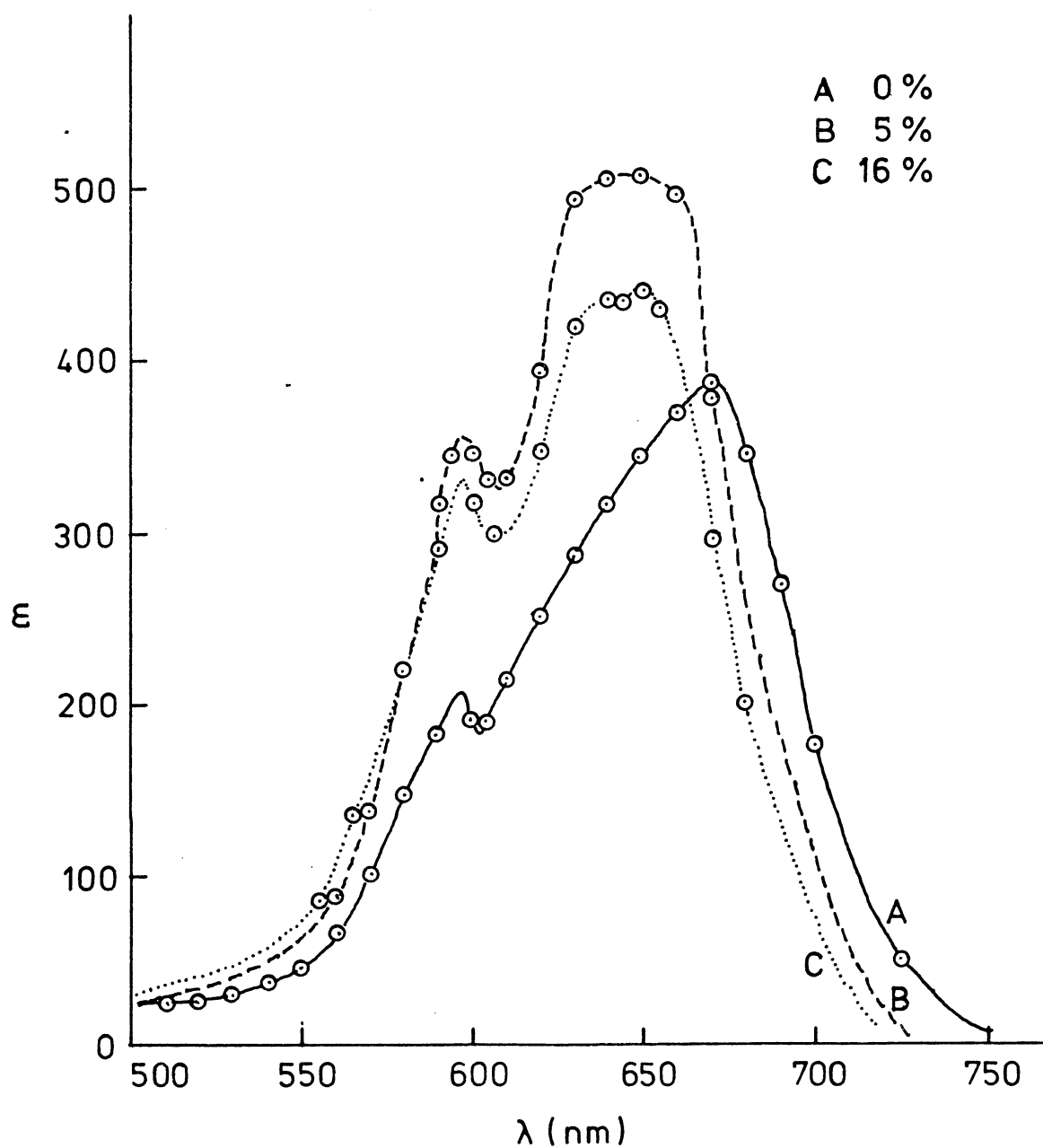
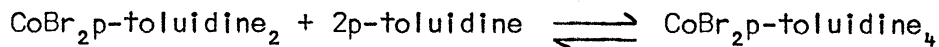
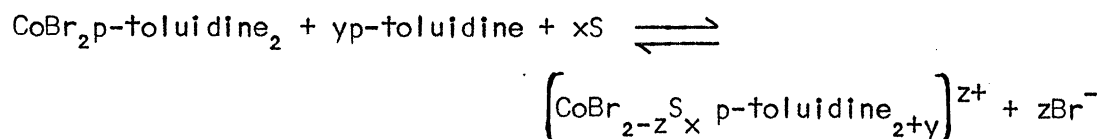


FIGURE 12. ABSORPTION SPECTRA OF CoBr_2 $p\text{-tol}_2$ 10^{-3}M IN TETRAHYDRO FURAN / p -TOLUIDINE MIXTURES. LEGEND SHOWS % $p\text{-tol}$ (W/V).

in a decrease in the amount of $\text{CoBr}_2\text{p-toluidine}_2$ in solution but without formation of another tetrahedral species. The reaction involved here was probably either of those shown below.



or



where $x + y - z = 2$; $0 \leq y \leq 4$; $0 \leq z \leq 2$; $x \leq 4$.

Behaviour in Nitrobenzene Solution

In order to facilitate comparison of the behaviour of aromatic amine and heterocyclic base complexes of cobalt halides in solution, nitrobenzene and nitromethane were used for more detailed studies. Nitrobenzene has been used by Graddon, Heng and Watton⁽²⁹⁾ while Nelson et al⁽⁷²⁾ studied heterocyclic base complexes in nitromethane. Table 13 shows the absorption wavelengths, $\lambda_{\frac{1}{2}}$, and maximum molar extinction coefficients, ϵ_{max} , of solutions of the complexes $0.5 \times 10^{-4}\text{M}$ in nitrobenzene. The last column sets out the molar conductance of those solutions in which the compound was fully dissolved. Extinction coefficients are not reported for those compounds which were partly insoluble. Chloro complexes were all rather insoluble in nitrobenzene and no satisfactory spectra could be obtained.

Physical Properties of Complexes $5 \times 10^{-4} \text{M}$ in Nitrobenzene					
Amine	Halide	ϵ_{max}	$\lambda_{\frac{1}{2}}$ (nm)	Molar Conduct. (mho)	Remarks
<u><i>p</i>-Substituent</u>					
$-\text{OCH}_3$	NCS	630	625	15.4	
$-\text{CH}_3$	"	620	625	17.4	
$-\text{H}$	"	430	625	10.1	
$-\text{F}$	"	-	627	-	Ptly. insol.
$-\text{NHCOCH}_3$	"	190	625	3.34	Ethanol adduct.
$-\text{Cl}$	"	-	624	-	Ptly. insol.
$-\text{Br}$	"	-	627	-	"
All amines	Cl	-	-	-	Insoluble.
$-\text{CH}_3$	Br	312	665	17.4	
$-\text{H}$	"	160	670	10.1	
$-\text{F}$	"	92	670	2.9	
$-\text{NHCOCH}_3$	"	-	660	-	Ptly. insol. Water Adduct
$-\text{Cl}$	"	80	670	3.1	
$-\text{Br}$	"	182	665	6.1	
$-\text{COCH}_3$	"	-	670	-	Impure.
$-\text{CH}_3$	I	686	707	-	
$-\text{H}$	I	590	704	15.6	
$-\text{Br}$	I	444	702	-	
<u><i>o</i>-Substituent</u>					
$-\text{OCH}_3$	NCS	420	625	10.1	

TABLE 13

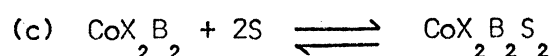
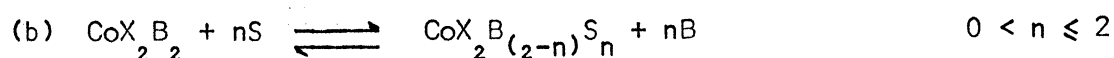
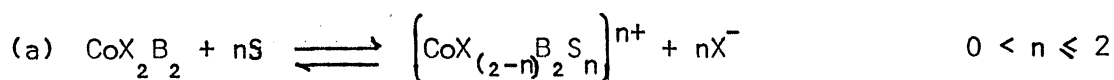
The values of $\lambda_{\frac{1}{2}}$ for the thiocyanates show remarkable constancy varying only from 624 nm to 627 nm. Three complexes were not completely dissolved. The extinction coefficients were found to be in the range⁽²⁹⁾ normally accepted for tetrahedrally co-ordinated cobalt (II). The exception was $\text{Co(NCS)}_2\text{p-acetamidoaniline}_2(\text{C}_2\text{H}_5\text{OH})_2$. Apparently this complex did not dissociate fully into tetrahedral species in solution.

None of the chloro complexes was soluble to any significant extent in nitrobenzene. However, most of the bromo compounds were soluble. Once again the range of absorption wavelengths was very small, varying only from 660 nm to 670 nm. The iodo complexes absorbed at 702 nm to 707 nm, again showing very little variation.

Nitrobenzene solutions of bromo and iodo complexes gave spectra which differ in two respects from the reflectance spectra of the corresponding solids. Firstly, the value of $\lambda_{\frac{1}{2}}$ in solution spectra was found to be at approximately 40 nm longer wavelength than in the reflectance spectra. Secondly the values of $\lambda_{\frac{1}{2}}$ in solution spectra show a remarkable constancy for all the complexes involving the same halide. This was found with thiocyanate compounds also. The fact that the absorption spectra were more highly resolved than the reflectance spectra may account for the constancy. An alternative explanation is that a species not present in the solid compounds predominates in the solutions of all of the complexes of a particular halide. This possibility will be discussed at greater length below.

There is a correlation in Table 13 of maximum extinction coefficient values with the molar conductances. Large extinction coefficients were found for solutions of complexes which showed high conductances and vice versa. Such behaviour was not found to be the case with solutions of heterocyclic base complexes 10^{-3}M in nitrobenzene⁽²⁹⁾. Furthermore the dissociation of compounds studied here appears to be much more extensive. The molar conductance of solutions of uni-univalent electrolytes $5 \times 10^{-4}\text{M}$ in nitrobenzene at 25°C was found to be approximately 30 mho⁽¹⁰⁹⁾. Thus the amount of ionic species present in these solutions varied between 10% and 60% of a uni-univalent electrolyte.

This behaviour may perhaps be explained using the following hypothesis. Octahedral polymeric complexes dissociated into tetrahedral monomeric units in solution. Tetrahedral monomeric species in solution can react with solvent molecules in a number of ways such as the following:



Equation (a) would result in ionisation and (compared with the reflectance spectrum) a wavelength shift to a slightly shorter value. This would be due to the stronger ligand field of the nitrobenzene over that of the chloride ion. Equation (b) would result in no ionisation

and the resultant species would have a slightly longer absorption wavelength than that in the reflectance spectrum. The nett result of (a) and (b) would be approximately the same spectrum as in the solid-state together with an electrically conducting solution. A high extinction coefficient would be the result of the presence of cobalt only in the form of tetrahedral species. Equation (c) would result in removal of tetrahedral species and would produce a non-conducting solution. Removal of the tetrahedral compound would decrease the extinction coefficient in the 600-700 nm region.

Thus complexes which undergo solvent replacement of large amounts of amine plus small amounts of halide would absorb at longer wavelengths than the original solid complex. Such solutions would have high extinction coefficients in the 600nm - 700 nm region and would be electrically conducting. A complex which increases its co-ordination number to six by adding two solvent molecules would give a solution absorbing around 500 nm and would be non-conducting. The gradation of properties in Tables 13 may be explained by the occurrence of these reactions to varying degrees. The constant value of the absorption wavelength for a particular halide would be explained by the influence of the solvated tetrahedral species on the spectrum. This solvated species would contain very little amine and would therefore be independent of the amine originally co-ordinated to the cobalt.

While this hypothesis is not unequivocally claimed to explain what actually occurred, such reactions are quite feasible. Further

possibilities would include undissociated polymers, failure of
 Co(NCS)_2 p-acetamidoaniline₂ $(\text{C}_2\text{H}_5\text{OH})_2$ to dissociate^{and}/the effect of
 traces of water in the solvent.

The above hypothesis does not explain why certain substituents in the aromatic amine result in particular behaviour. It does appear that the halide does not affect such behaviour although insolubility of chloro complexes does restrict generalisations. Electron releasing substituents correlate with high concentrations of tetrahedral monomers in more highly conducting solution. If the co-ordination of solvent to form octahedral adducts explains what actually happened with electron withdrawing substituents, then it appears that lower basicity favoured six co-ordination in this solvent. This would agree with the findings of Billing and Underhill⁽⁸¹⁾ who considered the stereochemistry in the solid-state of complexes of cobalt halides with several heterocyclic bases. These authors found that in the absence of significant π -bonding the tendency to form octahedral complexes decreased with increasing basicity. Other authors have reached similar conclusions⁽²⁹⁾.

Behaviour in Nitromethane Solution

The four p-chloroaniline compounds were selected for the initial study in nitromethane solution. Only the bromo and iodo compounds were soluble to the extent of $5 \times 10^{-4}\text{M}$. Accordingly the compounds were all dissolved in nitromethane solutions which were 0.5M with

respect to free p-chloroaniline. This excess base had the effect of increasing the solubility of the complexes. Solutions of the complexes in which the added base concentration was 1M were also studied in order to indicate the effect, if any, of base concentration on physical properties. The thiocyanate compound was insoluble at base concentrations less than 0.5M. However, the chloro and bromo compounds were soluble to 5×10^{-4} M in nitromethane 0.33M with respect to added base.

Table 14 shows the effect of added base concentration on absorption wavelength, maximum molar extinction coefficient and conductance. The change in base concentration had no effect on the absorption wavelength of any of the compounds. However the extinction coefficients were dependent upon base concentration. The thiocyanate compound showed an initial increase in extinction with increase in base concentration. The chloro compound showed an increase in extinction coefficient followed by a decrease as the base concentration was increased from 0.33M to 1M. The bromo complex showed only a decrease. These results would be explained by variable initial dissociation which was suppressed by addition of small amounts of base. Subsequent base addition removed some of the tetrahedral species by some other reaction.

The conductances did not vary much and showed no observable trend. Murray-Rust et al have reported the conductance of univalent electrolytes (tetraethylammonium salts) 5×10^{-4} M in nitromethane to be approximately 110 mho⁽¹¹⁰⁾. Hence the solutions of the

TABLE 14PHYSICAL PROPERTIES OF p-CHLOROANILINE COMPLEXES 5×10^{-4} M IN NITROMETHANE/p-CHLOROANILINE MIXTURES

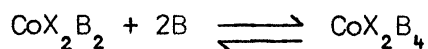
Halide	Base Concentration (M)	$\lambda_{1/2}$ (nm)	ϵ_{\max}	Molar Conductance (mho)
NCS	0.50	615	436	42.4
	1.00	615	476	48.0
Cl	0.33	635	292	34.2
	0.50	635	324	28.4
	1.00	635	210	32.0
Br	0.33	660	392	35.6
	0.50	660	388	39.2
	1.00	660	222	39.4

p-chloroaniline compounds have conductances which were between 25% and 45% of that of a uni-univalent electrolyte. Nelson and co-workers studied several heterocyclic base complexes 10^{-3} M in nitromethane plus free base. In the case of their thiocyanate and chloro complexes, conductances were similar to those reported above, varying little with base concentration up to 0.3M. Their bromo and iodo complexes, however, showed marked increases in conductance (to as much as 90 mho) as the base concentration was increased to 0.3M. As far as the p-chloroaniline complexes are concerned, it would appear that there is no significant difference between the ionisation behaviour of the bromo complexes on the one hand, the chloro and thiocyanate complexes on the other.

An idea of the effect of going from nitrobenzene to nitromethane as solvent may be obtained by comparing the physical properties of p-chloroaniline complexes in Tables 13 and 14. The thiocyanate complex absorbed at 625 nm in nitrobenzene and 615 nm in nitromethane. The bromo complex absorbed at 670 nm in the former and 660 nm in the latter solvent. This is not an uncommon effect of solvent variation. It appears that much the same behaviour is occurring in nitromethane and nitrobenzene solution.

Stereochemical Equilibria in Nitromethane Solution

In view of the fact that no tetrakisamine complexes were isolated by the methods used, it was decided to study the extent of the reaction



in solution. The solvent chosen was nitromethane. This solvent was used since it is the least polar solvent which dissolves the bromo complexes to a concentration greater than 10^{-3}M . Furthermore, nitromethane was used by Nelson and co-workers in their studies of the related complexes formed with heterocyclic bases⁽⁷²⁾. This would permit some comparison of results.

The experimental procedures and methods of calculation of equilibrium constants are set out under *Experimental*. Two tetrahedral monomeric compounds were chosen for study, $\text{CoBr}_2\text{p-toluidine}_2$ and $\text{CoBr}_2\text{aniline}_2$. Bromo compounds were chosen because they would be expected to be intermediate in tendency to increase co-ordination number between iodo complexes on one hand and chloro and thiocyanate complexes on the other.

Figure 15 shows some of the spectra of $\text{CoBr}_2\text{p-toluidine}_2$ $1.33 \times 10^{-3}\text{M}$ in nitromethane/p-toluidine solutions. In Figure 11 is shown the diffuse reflectance spectrum of the same compound with the ordinate plotted in arbitrary units. The absorption spectra shown in Figure 15 result from solutions containing the following percentages (w/v) of p-toluidine:

(a) 0%; (b) 16%; (c) 30%; (d) 64% (limit of solubility).

There is a definite change in character of these spectra as the concentration of p-toluidine is increased. Curve (a) has several

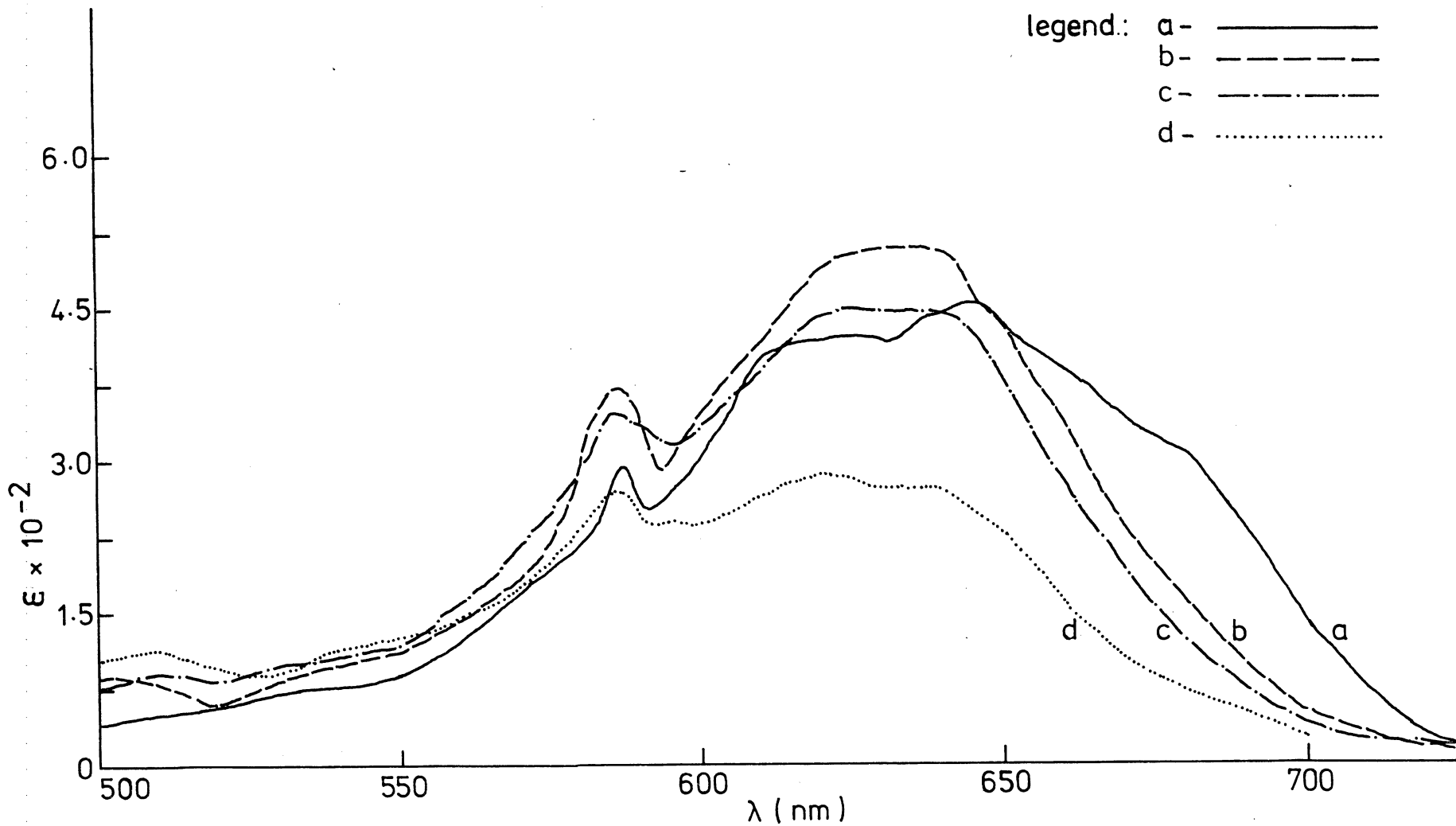


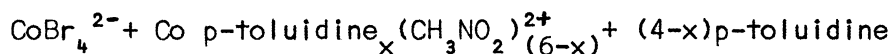
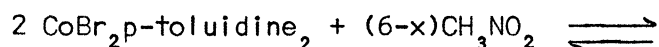
FIGURE 15.
ABSORPTION SPECTRA OF $\text{CoBr}_2 \cdot \text{p-TOLUIDINE}_2$ $1.33 \times 10^{-3} \text{ M}$ IN $\text{CH}_3\text{NO}_2 / \text{p-TOLUIDINE}$

features not found in the diffuse reflectance spectrum (Figure 11). In the region 660 nm - 690 nm there is a broad shoulder indicative of a species absorbing at a longer wavelength than does $\text{CoBr}_2\text{p-toluidine}_2$. Around 640 nm, 610 nm and 530 nm there are also signs of peaks inconsistent with curves (c) and (d) and the spectrum of the solid. In the spectrum of the solution containing 16% p-toluidine - curve (b) - the extinction of the main peak around 630 nm increases markedly. At the same time the significance of the peaks at 660 nm, 640 nm and 610 nm is very much less. The shoulder at 530 nm is now more significant. This latter fact may well be due to the increased height of the overlap from the main peak due to $\text{CoBr}_2\text{p-toluidine}_2$. This phenomenon is not unlike that found by King and co-workers⁽³²⁾. In spectra of solutions containing between 0 and 16% p-toluidine (not shown in Figure 15) the peak at 530 nm is more significant than in curve (b).

Curves (c) and (d) differ from curve (b) more due to height rather than from profile differences. The extra peaks attributable to other species in curves (a) and (b) are now missing. The peak due to $\text{CoBr}_2\text{p-toluidine}_2$ decreases in height as would be expected if $\text{CoBr}_2\text{p-toluidine}_4$ were being formed at the expense of $\text{CoBr}_2\text{p-toluidine}_2$. At 510 nm a low extinction peak is evident. It reaches maximum intensity when the peak due to $\text{CoBr}_2\text{p-toluidine}_2$ reaches a minimum.

This evidence leads to the following conclusions. When dissolved in pure nitromethane the compound $\text{CoBr}_2\text{p-toluidine}_2$ undergoes partial

disproportionation into species of tetrahedral and octahedral stereochemistries. The tetrahedral species so formed absorb most strongly around 660 nm - 690 nm, 650 nm and 630 nm. The octahedral species absorbs around 530 nm. Such a disproportionation reaction may well be:



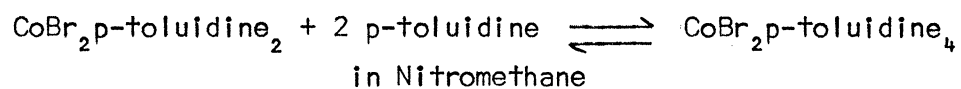
where $x = 0, 1, 2, 3$ or 4 .

Supporting evidence is to be found in the published spectral data for the tetrabromocobaltate ion⁽¹¹¹⁾. These authors resolved the spectrum of the tetrabromocobaltate ion in nitromethane into bands at 638 nm, 665 nm and 720 nm.

Increasing the amount of p-toluidine in solution to concentrations of around 15% results in reversing this reaction, increasing the concentration of $\text{CoBr}_2\text{p-toluidine}_2$ and reducing the concentration of the other species. Further additions of p-toluidine result in a decrease in concentration of $\text{CoBr}_2\text{p-toluidine}_2$ and the probable formation of $\text{CoBr}_2\text{p-toluidine}_4$. This latter type of reaction has been reported for many other related systems^(29,72). In order to test this hypothesis, equilibrium constants were calculated from spectra of solutions containing 15% or more p-toluidine. These values are set out in Table 16.

The value of the equilibrium constant varies depending upon the

Equilibrium Constants for the Reaction



% p-tol. by wt.	[p-tol.] (M)	ϵ at 625 nm	K moles ⁻² litres ²
16.1	1.5	499	0.150
21.4	2.0	461	0.140
32.1	3.0	446	0.074
42.8	4.0	375	0.093
53.5	5.0	315	0.130
58.9	5.5	289	0.169
$\epsilon_0 = 590$ $\epsilon_\infty = 230$			

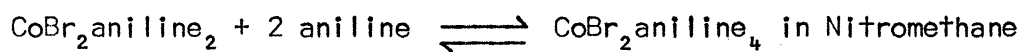
TABLE 16

concentration of p-toluidine. This variation is not random but consists of a decrease in the intermediate concentration range and an increase towards higher and lower concentrations. The mean value for the constant is 0.13 ± 0.05 . This variation indicates a small amount of side reaction occurring even in the presence of large amounts of p-toluidine.

Another type of side reaction which may occur in solutions containing very little added amine is that postulated by Dunn and Buffagni⁽⁸⁰⁾. In solutions of cobalt chloride and tetrachlorocobaltate ion in nitromethane it was shown that a series of equilibria could be set up involving the metal ion and the solvent. Such equilibria were proposed to involve species such as $\text{CoCl}_2(\text{CH}_3\text{NO}_2)_2$ and $(\text{CoCl}_3\text{CH}_3\text{NO}_2)^-$. The positions of the donors in the Spectrochemical Series suggest that the corresponding bromo species would have absorption spectra centering at wavelengths slightly longer than that of $\text{CoBr}_2\text{p-toluidine}_2$. It is in this region that the enhanced absorption is found in Figure 15 in the spectra of solutions containing least added amine. Driessen and Groeneveld have also investigated nitromethane as a ligand⁽¹¹²⁾.

In the case of $\text{CoBr}_2\text{aniline}_2$ a similar result is found. Table 17 shows the variation of the equilibrium constant with aniline concentration. In this case the mean value of the constant is 0.07 ± 0.03 . The equilibrium constants determined in this investigation are too small and variable to be compared with each other quantitatively.

Equilibrium Constants for the Reaction



% Aniline w/v	[Aniline] (Molarity)	ϵ at 635 nm	K $\text{moles}^{-2} \text{l}^2$	Ref. Code in Fig. 16
10	-	-		a
17	1.83	528	0.093	b
20	2.15	525	0.072	
25	2.69	513	0.065	
40	4.30	477	0.040	
50	5.38	454	0.036	
60	6.45	396	0.064	
70	7.53	378	0.068	c
80	8.60	360	0.083	
90	9.68	354	0.079	
100	10.75	349	0.078	d
$\epsilon_0 = 592$ $\epsilon_\infty = 270$				

TABLE 17

Spectra of solutions of $\text{Co}_2\text{Br}_2\text{aniline}_2$ $1.33 \times 10^{-3}\text{M}$ in nitromethane with varying concentrations of aniline show a similar trend to that found in the p-toluidine system. Figure 16 shows some of these spectra. The aniline concentrations corresponding to each of these spectra are shown in Table 17. Spectra a and b show the presence of species absorbing around 660 nm - 680 nm and 610 nm - 620 nm. Increasing the base concentration from 10% (curve a) to 17% (curve b) results in an increase in the extinction of the peak due to $\text{Co}_2\text{Br}_2\text{aniline}_2$. At the same time the significance of the absorptions at 660 nm - 680 nm and 610 nm - 620 nm becomes less. Subsequent aniline concentration increases from 40% upwards result in no significant profile changes. Most of these spectra are not shown in order to avoid complication of the figure. The only change is a decrease in extinction with increasing aniline concentration. Visible evidence as to the small tendency to form the octahedral complex is found in the very small change in peak height when the aniline concentration is increased from 70% (curve c) to 100% (curve d).

The behaviour of those solutions containing small quantities of aniline or p-toluidine is somewhat similar to that reported by King, Koros and Nelson⁽⁹⁹⁾ for solutions of $\text{CoCl}_2\text{quinoline}_2$ in nitromethane/quinoline solution. These authors successfully related the spectroscopic properties of such solutions to the solvolytic disproportionation reaction like that shown above, viz.

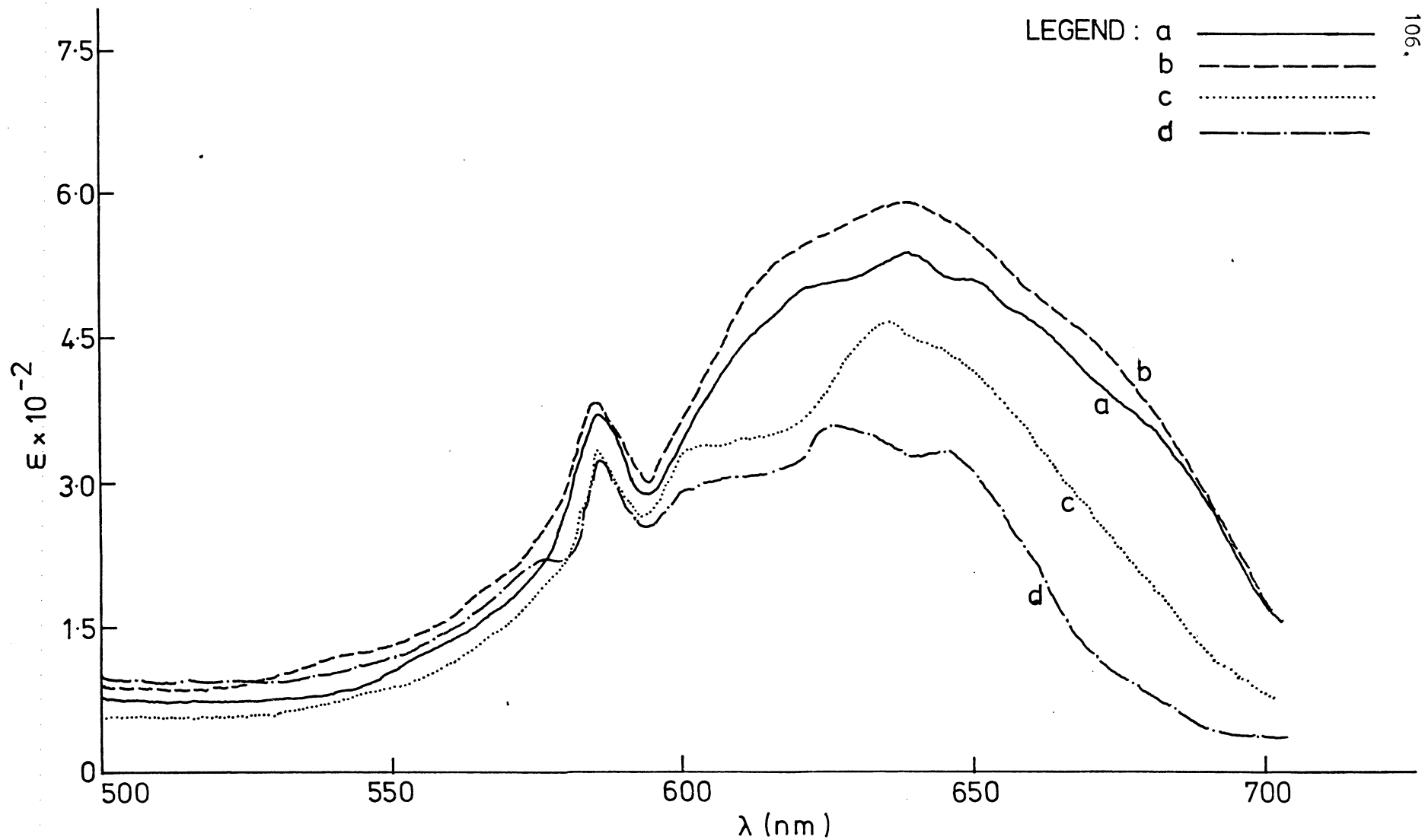
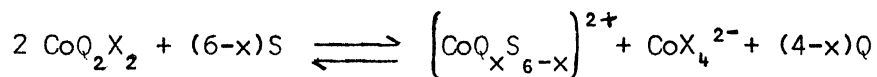


FIGURE 16.

ABSORPTION SPECTRA OF CoBr_2 ANILINE_2 $1.33 \times 10^{-3} \text{ M}$ IN $\text{CH}_3\text{NO}_2 / \text{ANILINE}$.



where Q = quinoline, s = solvent.

They did not, however, report examination of solutions of any quinoline complex containing any more than 10% base, considering that such systems would have very little or no tendency to form the tetrakisamine compounds. They reported a molar conductance of 28 mho at 20°C in 10^{-3}M solution in nitromethane of the chloro compound. Successive additions of quinoline resulted in a decrease in conductance to a steady value of 13.5 mho.

Conductance measurements carried out on the $\text{CoBr}_2\text{aniline}_2$ system as part of the current investigation were similar but more complete. They are set out below in Table 15.

Molar Conductance of Solutions of $\text{CoBr}_2\text{aniline}_2$ $1.33 \times 10^{-3}\text{M}$ in $\text{CH}_3\text{NO}_2/\text{aniline}$ at 25°C						
% aniline	0	7	10	50	70	100
Conductance (mho)	23.5	22	22	17.1	7.35	0

TABLE 15

The conductance of $\text{CoBr}_2\text{p-toluidine}_2$ $1.33 \times 10^{-3}\text{M}$ in nitromethane was 27 mho at 25°C.

Figure 17 is a plot of molar conductance vs aniline concentration

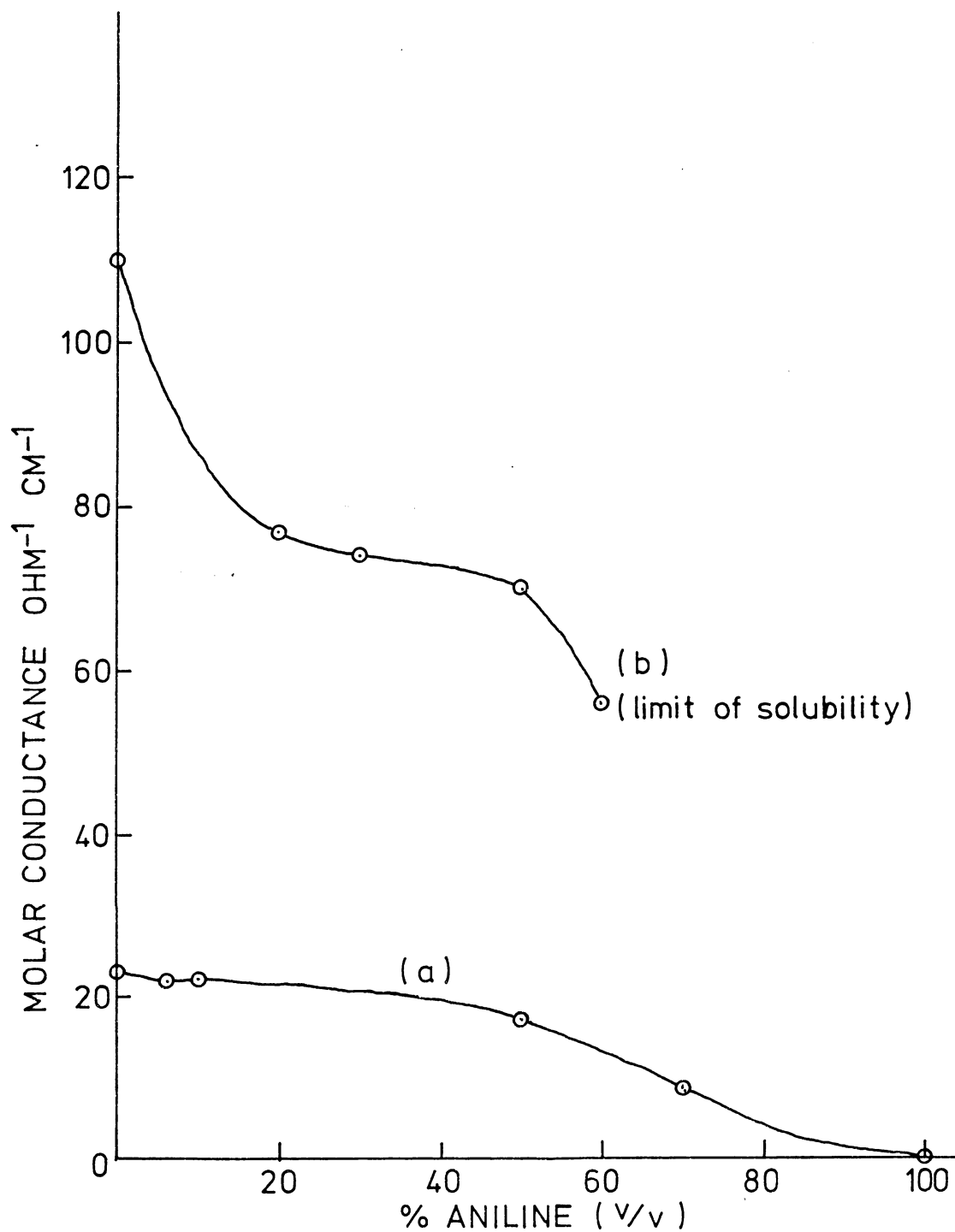
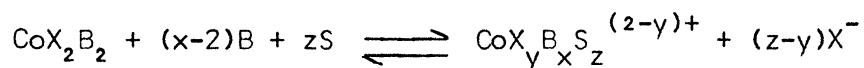


FIGURE 17.
 CONDUCTANCE OF SOLUTIONS OF (a) CoBr_2 ANILINE_2 ,
 AND (b) $(\text{CH}_3)_4\text{NBr}$, 1.33×10^{-3} M IN $\text{CH}_3\text{NO}_2/\text{ANILINE}$.

of solutions of $\text{CoBr}_2\text{aniline}_2$ and tetramethylammonium bromide, both $1.33 \times 10^{-3}\text{M}$ in nitromethane/aniline mixtures. Curve (b) is that of the quaternary ammonium salt while curve (a) is that of $\text{CoBr}_2\text{aniline}_2$. The latter compound is equivalent to 20% of a uni-univalent electrolyte, at least in solutions containing up to 60% aniline. While the trends shown by the two curves are not identical it appears that the decrease in conductance of $\text{CoBr}_2\text{aniline}_2$ may be explained by change in the dielectric properties of the solvent mixture.

The high conductance of the solutions in pure nitromethane may well be attributed to the solvolytic disproportionation reaction discussed above. However, the significant conductance of solutions containing up to 70% aniline is probably due largely to the lability of the halide ion formed by dissociation of $\text{CoBr}_2\text{aniline}_2$. This lability should become less as the ionising power of the solvent changes with increasing aniline concentration. Formation of $\text{CoBr}_2\text{aniline}_4$ may also reduce the halide ion lability. There is no evidence to suggest that the ligand exchange mechanism proposed by de O'Cabral and Nelson (72) for their class 2 complexes (bromo and iodo) of substituted pyridines is in action here. The ligand exchange reaction



where S = nitromethane and $x + y + z = 6$ requires increasing conductance (as much as 90 mho) with increasing base concentration. These latter authors also found very marked differences in spectral profile between solid-state and solution spectra. Such evidence is not

apparent in the present study in spectra of solutions containing large amounts of base.

From the above discussion it is apparent that, at least as far as the bromo complexes are concerned, the dissociation in nitromethane/amine solution is similar to that of quinoline complexes of all cobalt halides. The aromatic amine complexes, however, dissociate more significantly than de O'Cabral's class 1 complexes of cobalt thiocyanate and chloride with pyridines and to a lesser extent than his class 2 complexes. The variability in the values of the equilibrium constants suggests that side reactions may be occurring to a small extent. Furthermore, conductance measurements indicate that the character of the solvent system changes markedly over the range of amine concentrations studied.

CONCLUSION

The complexes of cobalt(III) halides with aromatic amines are all tetrahedral monomers in the solid-state. The thiocyanate complexes are octahedral polymers. Ethanol or water adducts may be isolated under suitable conditions. There is some evidence for small differences in ligand field strength depending upon amine basicity.

No tetrakisamine complexes were isolated. Equilibrium studies indicated that the tetrahedral-octahedral equilibrium exists in solutions containing free base but that equilibrium lies far on the tetrahedral side. Extensive dissociation occurs in relatively polar solvents such as nitromethane and nitrobenzene.

EXPERIMENTAL

Preparation of Complexes

Each of the complexes described in this thesis was prepared by one or more of the following methods. The codes (a), (b) and (c) refer to Tables 5-9, 12 under the heading, Preparative Method.

Cobalt(II) halides, A.R. grade were used as supplied. Amines were recrystallised if solids, or distilled if liquids at room temperature. The solvent for recrystallisation was ethanol/water in varying proportions. The exception was p-toluidine which was recrystallised from 40° - 60° petroleum ether.

Preparative Methods

(a) The cobalt halide 1 mol. was dissolved in a minimum volume of absolute ethanol on a steam bath. The amine 4 mol. was similarly dissolved and the metal halide solution added with stirring to the amine solution. The mixture was allowed to cool to room temperature. A precipitate formed immediately on mixing in the case of the chloro and thiocyanate complexes while bromo and iodo complexes required more time. The precipitate was collected on a sintered glass crucible and washed with cold absolute ethanol. When possible the complex was dried over calcium chloride and analysed without re-

crystallisation. When re-crystallisation was necessary it was carried out from absolute ethanol. However, in many cases heating the complex in solution resulted in formation of large amounts of black oxidised material, necessitating repeated preparation.

(b) This procedure was as for (a) above except that the amine was dissolved in toluene rather than in ethanol. This procedure was used when the complex was highly soluble in ethanol alone.

(c) Absolute isopropanol dried over anhydrous sodium sulphate was used in place of ethanol in method (a)

(d) Cobalt(II) iodide solution was prepared by heating solid sodium iodide and cobalt(II) sulphate with absolute ethanol. After concentration the sodium sulphate was removed by filtration and the ethanolic solution of cobalt(II) iodide used as such. This method leads to less free iodine formation than does use of cobalt(II) iodide as purchased. The complex was then prepared by adding excess amine in hot absolute ethanol to the hot cobalt(II) iodide solution. Invariably it was necessary to re-crystallise iodide complexes from ethanol to remove free iodine. The complex was dried as in method (a).

Physical Measurements - Solid State

Diffuse Reflectance Spectra:

Solid-state spectra were measured at ambient temperature on a Zeiss PMQ 11 or a Unicam SP500 spectrophotometer. Calibration was against magnesium oxide for the Zeiss instrument and against magnesium carbonate in the case of the Unicam instrument.

Magnetic Moments:

Room temperature magnetic moments were measured by the Gouy method with cobalt(II) mercury(II) tetrathiocyanate as calibrant. Diamagnetic corrections were made using tables of Pascals Constants.

Infrared Spectra:

A Perkin-Elmer 337 spectrometer was used for IR measurements. Halo carbon mulls between rock salt plates were used between 1500 and 4000cm^{-1} and Nujol mulls between potassium bromide plates were used from 400 to 1500cm^{-1} .

Physical Measurements - Solution

Absorption Spectra:

Visible region absorption spectra were measured principally on a Zeiss PMQ 11 spectrophotometer. Unless otherwise stated spectra

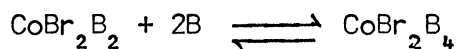
were measured at 25°C.

Electrical Conductance:

Electrical conductance measurements were made in a constant temperature bath using a Philipscope Model PR9500 manufactured by Philips Electrical Industries. The instrument was operated at 50 c/s and a Philips Model GM4221/01 immersion cell was used. The bath temperatures were at those specified $\pm 0.5^\circ\text{C}$.

Equilibrium Constant Determination

The equilibrium studied was the following:



where B = aniline or p-toluidine. The equilibrium constant K is defined as follows:

$$K = \frac{[\text{CoBr}_2\text{B}_4]}{[\text{CoBr}_2\text{B}_2][\text{B}]^2} \text{ in moles}^{-2} \text{ litres}^2.$$

The method of determination of equilibrium constants was that outlined by Watton⁽⁷⁵⁾. The method involved estimation of the relative concentrations of octahedral and tetrahedral species in solutions containing a constant amount of cobalt but increasing amounts of free base. This was achieved by dissolving a fixed weight of

tetrahedral complex in a solvent containing increasing concentrations of free base. The extinction coefficients of these solutions at the wavelength of maximum absorption of the tetrahedral complex were measured spectrophotometrically. Estimates were made of the extinction of the tetrahedral complex dissolved in pure nitromethane and in solution containing an infinite amount of base. These were termed ϵ_0 and ϵ_∞ respectively. If the extinction coefficient of any one solution was ϵ , then $\epsilon_0 - \epsilon$ was proportional to the amount of tetrahedral complex converted into octahedral species. The difference $\epsilon - \epsilon_\infty$ was proportional to the amount of tetrahedral complex remaining in that solution. Thus $\epsilon_0 - \epsilon / \epsilon - \epsilon_\infty$ was equal to the concentration ratio of octahedral complex to tetrahedral complex in that solution. From this and the concentration of free base in the solution the equilibrium constant was determined.

This procedure was carried out for as many as eleven solutions and as many values of the equilibrium constant were obtained. The process of estimating ϵ_0 and ϵ_∞ was repeated until the agreement of all estimates of the equilibrium constant was maximised. The final values of ϵ_0 and ϵ_∞ are shown in Tables 16 and 17 along with the pertinent concentration data.

In solutions containing less than about 15% free base there was evidence in the spectra of dissociation of the tetrahedral complexes. The free base suppressed this dissociation. The base concentrations in Tables 16 and 17 are not adjusted to allow for this base added to

suppress dissociation since such action was found to give worse agreement in the equilibrium constant values.

The range of percent conversion of tetrahedral species into octahedral species over which the equilibrium constant values apply can be estimated from the results in Tables 16 and 17. It is assumed that one hundred percent conversion would give an extinction coefficient at the wavelengths used of zero.

The data for the $\text{CoBr}_2\text{aniline}_2$ system are as follows:

$$\epsilon_{\infty} = 270$$

$$\epsilon_0 = 592$$

$$\begin{array}{l} \text{in 17\% aniline} \\ \epsilon = 528 \end{array}$$

$$\begin{array}{l} \text{in 100\% aniline} \\ \epsilon = 349 \end{array}$$

$$\epsilon_0 - \epsilon_{\infty} = 322.$$

$$\begin{aligned} \text{Hence in 17\% aniline solution \% conversion} &= \frac{592 - 528}{322} \times 100 \\ &= 20\% \end{aligned}$$

$$\begin{aligned} \text{In 100\% aniline solution \% conversion} &= \frac{592 - 349}{322} \times 100 \\ &= 75\%. \end{aligned}$$

The nitromethane ~~was~~ dried for five days over anhydrous magnesium carbonate prior to use. Distillation (even under reduced pressure) was found to decompose the solvent.

Cobalt Analyses

Analysis for cobalt was conducted by the pyridine/thiocyanate method as described by Vogel⁽¹¹³⁾ after destruction of organic matter.

C, H and N Analyses

Analyses for carbon, hydrogen and nitrogen were performed by Dr. E. Challen of the University of New South Wales.

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Analytical Results

Complex	Found %				Required %			
	C	H	N	Co	C	H	N	Co
$\text{Co(NCS)}_2\text{p-anis}_2$	46.0	4.3	13.0	14.0	45.6	4.3	13.3	14.0
$\text{Co(NCS)}_2\text{p-tol}_2$	49.3	4.8	14.4		49.4	4.7	14.3	
$\text{Co(NCS)}_2\text{p-acetamidooan}_2$	45.6	4.2	17.5	12.2	45.5	4.2	17.7	12.4
$\text{Co(NCS)}_2\text{an}_2$	46.6	4.0	15.4		46.5	3.9	15.5	
$\text{Co(NCS)}_2\text{p-flan}_2$	41.8	3.2	13.9	14.6	42.3	3.0	14.1	14.8
$\text{Co(NCS)}_2\text{p-clan}_2$	38.8	2.9	12.6	13.6	38.9	2.8	12.9	13.7
$\text{Co(NCS)}_2\text{p-bran}_2$	32.0	2.1	10.4	11.2	32.3	2.3	10.8	11.3
$\text{Co(NCS)}_2\text{p-acetamidooan}_2(\text{C}_2\text{H}_5\text{OH})_2$	46.6	5.7	14.5	10.2	46.6	5.7	14.8	10.9
$\text{CoCl}_2\text{p-anis}_2$	44.1	4.8	7.4		44.7	4.8	7.5	
$\text{CoCl}_2\text{p-tol}_2$	49.0	5.2	8.1		48.9	5.3	8.1	
CoCl_2an_2	44.9	4.6	8.9	18.8	45.6	4.5	8.9	18.6
$\text{CoCl}_2\text{p-flan}_2$	40.9	3.4	7.9	16.3	40.2	3.4	7.6	16.7
$\text{CoCl}_2\text{p-clan}_2$	37.1	3.4	7.1		37.4	3.1	7.3	
$\text{CoCl}_2\text{p-bran}_2$	30.3	2.9	5.7		30.5	2.6	5.9	
$\text{CoCl}_2\text{p-bran}_2(\text{H}_2\text{O})_2$	29.4	3.5	4.9		28.3	3.2	5.5	
							Cont...	

TABLE 18

Analytical Results
(Cont.)

Complex	Found %				Required %			
	C	H	N	Co	C	H	N	Co
CoBr ₂ p-anis ₂	35.3	4.1	5.9		36.1	3.9	6.0	
CoBr ₂ p-tol ₂	38.8	3.4	6.4		38.8	4.2	6.5	
CoBr ₂ an ₂	35.4	3.8	6.8		35.6	3.5	6.9	
CoBr ₂ p-flan ₂	32.7	2.9	6.5		32.7	2.8	6.4	
CoBr ₂ p-clan ₂	30.7	2.9	6.0		30.5	2.6	5.9	
CoBr ₂ p-bran ₂	25.5	2.1	5.2		25.6	2.2	5.0	
CoBr ₂ p-acetamidoan ₂ (H ₂ O) ₃	33.8	4.5	9.5		33.6	4.6	9.8	
CoI ₂ p-tol ₂	31.9	3.4	5.2		31.9	3.4	5.3	
CoI ₂ an ₂	29.0	2.7	5.6		28.9	2.8	5.6	
CoI ₂ p-clan ₂	27.2	2.3	-		25.4	2.1	-	
CoI ₂ p-bran ₂	21.7	1.9	4.2		21.9	1.8	4.3	
Co(NCS) ₂ o-anis ₂	45.7	4.3	13.0		45.6	4.3	13.3	
Co(NCS) ₂ o-tol ₂	49.6	-	14.2		49.4	4.7	14.4	

TABLE 18
(Cont.)

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