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FOUR-, FIVE- AND SIX-COORDINATED COMPLEXES OF 3*d* METALS WITH SUBSTITUTED SALICYLALDIMINES

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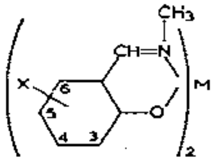
Complexes of first row transition metals with Schiff bases derived from salicylaldehyde, are particularly interesting for the following reasons: 1) a large variety of coordination geometries is found among them; 2) the complexes often exist in many crystalline modifications; 3) the stereochemistry of these complexes is often labile so that very often the molecular configurations in solution are different from those in the solid state and conformational equilibria between different forms take place.

COMPLEXES OF 3*d* METALS WITH *N*-METHYLSALICYLALDIMINE

It has been recently shown[1,2] that the lability of the geometry of many metal complexes with Schiff bases also occurs in the solid state, giving rise to cases of anomalous isomorphism. The effect has been named "structure mimicry".

This phenomenon has been particularly investigated in complexes of 3*d* metals from Mn^{II} to Zn^{II} with *N*-methylsalicylaldimines (Msal-Me)[1] having the general formula (I)

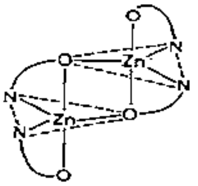


(I)

The complex Nisal-Me was the first example of "magnetically anomalous" nickel(II) complexes[3]. It exists in two planar diamagnetic forms, the α-form (orthorhombic)[4] and the β-form (monoclinic)[5]. Above 180 °C both forms transform to the γ-paramagnetic ($\mu_{eff} = 3.4$ *B.M.*) one[6]. This form is insoluble in all inert solvents. For this reason a polymeric structure involving the sharing of oxygen atoms by the nickel atoms, has been attributed to it[6].

The complex Cusal-Me exists in three crystalline modifications: α and γ, both orthorhombic, and β, which is monoclinic. The forms α and β are isomorphous with the corresponding forms of the nickel derivative[7]. In these complexes the copper has a planar coordination geometry[8].

The manganese(II) (orange in colour), cobalt(II) (green in colour) and zinc(II) complexes with *N*-methylsalicylaldimine, are mutually isomorphous[1]. They exist as dimers in the solid state. The metal atom which is hound to three oxygen and two nitrogen atoms, has a coordination number of five in a distorted trigonal bipyramidal environment[9]. (II)



(II)

The cobalt(II) and manganese(II) complexes have magnetic moments of 4.62 and 5.95 respectively and represent the first example of five-coordinated high-spin complexes of these metals whose structure has been established by X-ray analysis[1].

The three complexes of Mn, Co and Zn easily form solid solutions, as was anticipated. On the other hand interesting effects are observed when binary mixtures of nickel, copper and zinc complexes crystallize from chloroform solutions.

System Nisal-Me-Znsal-Me. Phase A

When the ratio by weight between the quantities of Nisal-Me and Znsal-Me is greater than 30:70 a gray-green precipitate of violet shade separates. It is a solid solution of the two compounds. The weight per cent of the Nisal-Me in these solids ranges between 50 and 80%. The nickel(II) has a magnetic moment of *ca.* 3.1 *B.M.* The X-ray powder diagram is identical with that of the γ-form of Nisal-Me. These solid solutions therefore have the same lattice and molecular structure as the γ-form of Nisal-Me. This is confirmed by their reflectance spectra taken from 600 to 20,000 cm^{-1}, (Fig. 1, curve A), which are essentially identical with the spectra of γ-Nisal-Me (Fig. 1, curve C).

It is evident that the presence of Znsal-Me forces the complex Nisal-Me to assume its γ-form structure even at room temperature. The guest complex Znsal-Me within the host lattice of the nickel(II) complex assumes the configuration of the γ-form of Nisal-Me. Thus the guest complex imitates the lattice and molecular structure of its host. This phenomenon was designated by the term "structure mimicry"[1].

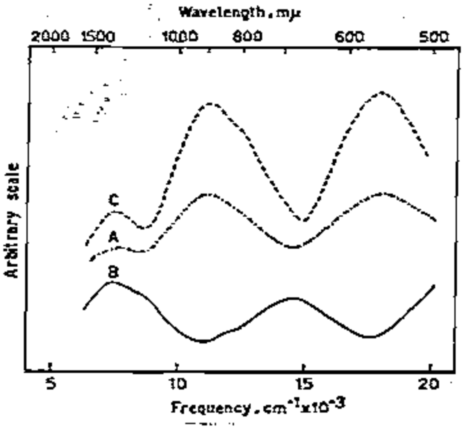


Fig. 1. Reflectance spectra of solid solutions Nisal-Me – Znsal-Me. A: Phase A, 50% Nisal-Me in Znsal-Me; B: phase B, 8% Nisal-Me in Znsal-Me; C: Polymeric γ form of Nisal-Me.

The system Nisal-Me-Znsal-Me. Phase B

When the weight ratio of Nisal-Me to Znsal-Me in chloroform is less than 30:70, triclinic yellow–green crystals are obtained[1]. The crystalline habit and the X-ray powder diagram are identical with those of Znsal-Me. Thus, these are solid solutions in which the molecule of Nisal-Me substitutes into the lattice of Znsal-Me, assuming the structure of the latter. Each nickel(II) atom, therefore, is five-coordinated in a trigonal bipyramid. This type of substitution takes place up to 10% *ca.* by weight. The nickel(II) in these solid solutions has a magnetic moment of 3.1–3.2 *B.M.* This represents the first known complex of high-spin five-coordinated nickel(II) complex with trigonal bipyramidal coordination geometry.

Reflectance spectra of these solid solutions of Nisal-Me in Znsal-Me show two bands with peaks to 7300 and 14,000 cm^{-1} and with shoulders at 9100 and 11,800 cm^{-1} (Fig. 1, curve B). This spectrum differs from those of other high-spin nickel(II) complexes with salicylaldimine having tetrahedral or octahedral structures[10], and may be considered as that of nickel(II) in a triplet state, pentacoordinated in the center of a distorted bipyramid.

Assuming an average crystal field of D_{3h} symmetry the band at 7300 cm^{-1} can be assigned to the $^3E'(F) \rightarrow {}^3E''(F)$ transition and the band at 14,500 cm^{-1} to unresolved transitions from the ground state $^3E'(F)$ to the states $^3A_1''(F)$, $^3A_2''(F)$ and $^3A_2'(F)$. The shoulder may be assigned to transitions to the singlet states $^1A_1'(D)$ and $^1E'(D)$ respectively[11].

The system Cusal-Me and Znsal-Me

By evaporating chloroform solutions containing Cusal-Me (olive-green in colour) and Znsal-Me salad-green crystals are obtained[1]. Their crystal habits and X-ray powder patterns are identical with those of pure Znsal-Me. Thus, the usually planar molecules of Cusal-Me also assume the stereochemistry of the host Znsal-Me in these solid solutions. The copper atoms therefore are situated in the center of a trigonal bipyramid. The copper compounds have the normal magnetic moment of one unpaired electron (μ_{eff} = *ca.* 2.0 *B.M.*)[1]. The reflectance spectrum of Cusal-Me in the host lattice shows a large band with a peak at 13,000 cm^{-1} and a shoulder at *ca.* 11,000 cm^{-1} (Fig. 2, curve A).

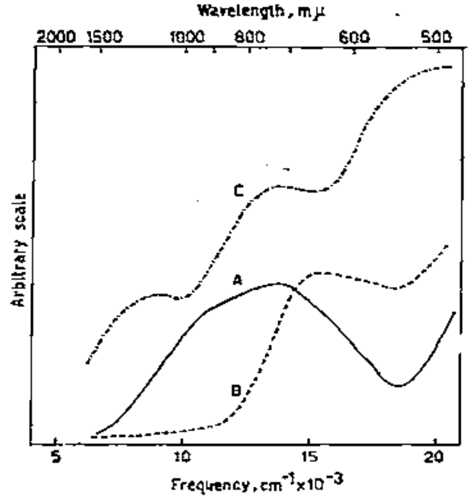


Fig. 2. Reflectance spectra of: A: solid solution of Cusal–Znsal-Me, 12% Cusal-Me; B: planar β form of Cusal-Me; C: tetrahedral bis(*N*-isopropylsalicylaldiminato)-Cu(II) [Reproduced, with permission, from ref. 1.]

This spectrum is similar in shape to those of other trigonal bipyramidal copper(II) complexes showing at least two transitions in the 10,000 cm^{-1} region. Diverse point-charge[12] and molecular orbital[13,14] treatments have been performed for the energy levels of copper(II) in a trigonal bipyramidal environment. According to a recent molecular orbital treatment[13] four transitions are expected in the 10,000 cm^{-1} region, *i.e.* those from the $5A_1'$ ground state to the $5E'$, $3A_2''$, $4E'$ and $3E'$ states. These transitions are probably included under the envelope of the broad band exhibited by the solid solutions of Cusal-Me in Znsal-Me.

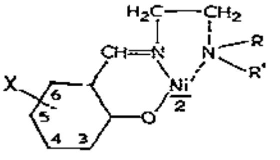
The occurrence of this "structure mimicry" in solid solutions of these complexes shows that their molecular structures are unstable and that the difference in energies between the different structures of each complex is very small. The influence of the host lattice suffices to induce the guest complex to change its own structure in favour of that of the host complex. The effect of the host lattice is comparable to that of the solvent in the case of many nickel(II) and copper(II) complexes with *N*-alkylsalicylaldimines dissolved in inert solvents. In these cases, as is well known, the nickel(II)[10,15] and copper(II)[16] complexes which are planar or tetrahedral in the solid state, in solution in "inert solvents" transform partially into mixtures of the two species.

Also the dimer complex Cosal-Me in solution undergoes a conformational equilibrium[1]. This complex, emerald-green in the solid state, gives rise to reddish-brown benzene solutions. The absorption spectra of these solutions show bands at 7800, 11,800 and 12,500 cm^{-1}, indicating the presence of tetrahedral forms in equilibrium with the dimeric species. An increase in temperature as well as in dilution results in the simultaneous increase in the proportion of the monomeric tetrahedral form.

METAL COMPLEXES OF SCHIFF BASES FORMED FROM SALICYLALDEHYDES AND N-SUBSTITUTED ETHYLENEDIAMINES

Nickel(II) complexes

The nickel(II) Schiff bases complexes of the general formula [Xsal en-N(R)R']$_2$Ni

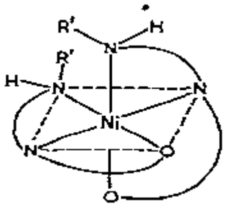


(III)

where R, R' = H, *n*-alkyl, aryl, benzyl; R = R' and NR_2 is $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N(CH_2)_4$ (pyrrolidino) and $-N(CH_2)_5$ (piperidino); X is H, 3-Cl, 5-Cl, 3-CH_3, 5-CH_3, 5-C_2H_5, 5-NO_2, 3,4-benzo, 5,6-benzo, exhibit a variety of structures. In fact the ligands can behave as bi- or tri-dentate depending on the nature of the X, R and R' substituents. Consequently planar, octahedral and high-spin five-coordinated complexes are formed. In solution, conformational equilibria between different forms very often take place.

Series 1. R = H; R' = n-alkyl, benzyl

Colour: mustard; $\mu_{eff} = 3.08\text{–}3.28$ *B.M.* Reflectance and absorption spectra (Fig. 3) $\nu_1 = 11{,}500\text{–}14{,}800\ cm^{-1}$, $\varepsilon_1 \simeq 35$; $\nu_2 = 17{,}900\text{–}18{,}300\ cm^{-1}$, $\varepsilon_2 \simeq 20$. Dipole moments: 8–10 *D*. Structure assigned to these complexes: *cis*-octahedral (IV)



(IV)

No adducts are formed in solutions of pyridine.

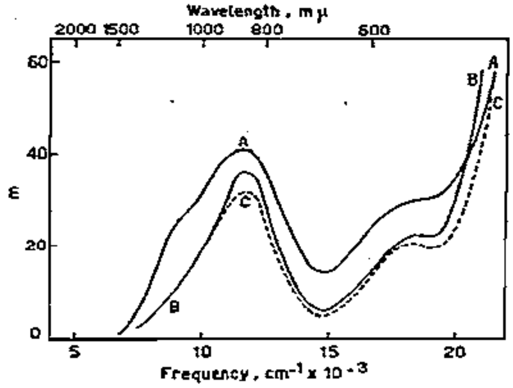
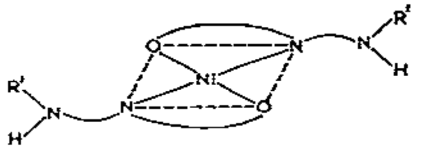


Fig. 3. Absorption and reflectance spectra of $[\text{H-sal en NHCH}_3]_2\text{Ni}$: A, reflectance spectrum; B, in chloroform; C, in pyridine.

Series 2. R = H, R′ = o-tolyl, α-naphthyl

These compounds are olive green in colour and diamagnetic. Their reflectance spectra are characteristic of square planar complexes with no appreciable absorption below 13,000 cm^{-1} and are similar to the spectra of compounds of series 4 (see below). Structure assigned: *trans*-planar (V).



(V)

The electron-attracting effect of the *N*-aryl group and the steric effects of this group hinder the *β*-nitrogen atom from coordinating and square-planar complexes are formed. In pyridine the compounds are transformed into octahedral adducts.

Series 3. R = H, R′ = phenyl, p-tolyl

X = H, 3-CH_3, 5-NO_2, 5,6-benzo. The solid compounds are green and diamagnetic. The reflectance spectra are characteristic of planar complexes.

If X = 3-Cl, 5-Cl or 3,4-benzo, the solids are green with μ_{eff} ranging from 2.83 to 3.20 *B.M.* The reflectance spectra indicate a distorted octahedral structure.

Thus, when the R′ aryl group is *para*-substituted the steric repulsion is less and the nitrogen atom can, in suitable circumstances, be bound to the nickel atom, giving an octahedral complex. The nature and position of the group X are here the determining circumstances inducing the stereochemistry of the complex, probably through an electronic effect.

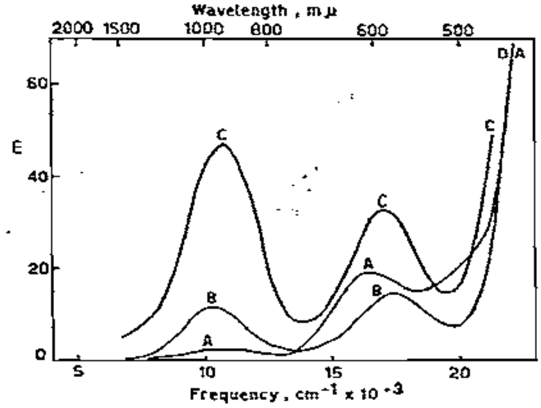


Fig. 4. Reflectance and absorption spectra of [H-sal en NHC$_6$H$_5$]$_2$Ni: A, reflectance spectrum; B, in pyridine; C, in chloroform.

The compounds of series 2 and 3 give two absorption bands in non-coordinating solvents at *ca.* 10,000 and 17,000 cm^{-1}. (Fig. 4). The ratio between the apparent maximum extinction coefficients of the two bands ($\varepsilon_1/\varepsilon_2$) is less than that observed in compounds of series 1, which are present one hundred per cent in the octahedral form. This indicates that an equilibrium of planar and octahedral forms does exist. Evidently, when the lattice forces are removed the nitrogen atoms are able to coordinate in some way to the nickel atom. From the value of $\varepsilon_1/\varepsilon_2$ some measure of the relative proportion of the two species in equilibrium, the planar and the octahedral, can be obtained. Only when R′ = *o*-tolyl and X = 5,6-benzo is the compound substantially planar in solution.

The percentage of the octahedral form in chloroform solution appears to vary according to the nature of the ring substituent X in the order: 5,6-benzo < <3,4-benzo < H < 3-Cl < 5-Cl (when R′ = *o*-tolyl: 3-Cl < 3,4-benzo). The square-planar configuration is thus most strongly induced by the 5,6-benzo substituent. We remember that the same holds true in equilibria between tetrahedral and square-planar forms of *N*-isopropylsalicylaldimino nickel(II) complexes[10,15].

For a given substituent X, on the other hand, the proportion of the octahedral forms increases as R′ is varied in the order *o*-tolyl < phenyl < *p*-tolyl. This suggests the existence of competition between steric hindrance due to the methyl substituent in the tolyl groups and its inductive effect which should make the tolyl-substituted nitrogen atoms stronger donors than the phenyl-substituted ones.

The magnetic moment of the 3,4-benzo[sal enN H(phenyl)]$_2$Ni complex dissolved in bibenzyl decreases on going from 80 to 170°. This indicates an endothermic rearrangement from the octahedral to the planar form.

Series 4. R = phenyl, R' = CH_3, phenyl

The compounds are olive-green and diamagnetic both as solids and in "inert" solvents. Reflectance and solution spectra are diagnostic of the square-planar structure. The dipole moments in benzene are about 1 *D* indicating a *trans*-planar configuration. In pyridine the compounds are transformed into octahedral adducts. Evidently the steric repulsion and the electron-withdrawing effect of the phenyl substituents do not permit these Schiff bases to act as tridentate ligands.

Serie 5. $-NR_2 = -N(CH_3)_2$; Series 6. $-NR_2 = -N(CH_2)_4$

The compounds are green or ochre in colour and paramagnetic. The reflectance spectra are very close to those of compounds of series 1. A distorted octahedral structure therefore must be assigned to these complexes.

Series 7. $-NR_2 = -N(C_2H_5)_2$

When X = H the complex is paramagnetic and octahedral on the basis of reflectance spectra data (Fig. 5, curve B). When X = 3-CH_3, 5-CH_3, 5-C_2H_5, 5-NO_2 and 5,6-benzo the complexes are planar diamagnetic (curve A).

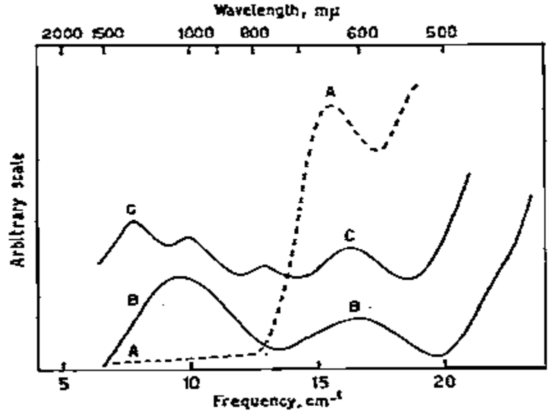
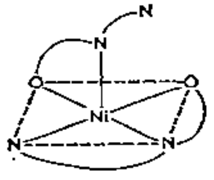


Fig. 5. Reflectance spectra of [X-sal enR(R')]$_2$Ni complexes: A, [3-CH_3-sal en$N(C_2H_5)_2$]$_2$Ni; B, [H-sal en$N(C_2H_5)_2$]$_2$Ni; C, [5-Cl-sal en$N(C_2H_5)_2$]$_2$Ni.

When X = 3-Cl, 5-Cl and 3,4-benzo the compounds are paramagnetic with μ_{eff} between 3.24 and 3.30 *B.M.* Their spectra show four bands at *ca.* 7700, 9800, 12,800 and 16,200 cm^{-1} (curve C).

A complete X-ray structure analysis on the 5-Cl derivative has shown that the nickel atom is five-coordinated[19]. One Schiff base ligand is tridentate, the other bidentate. The coordination polyhedron can be regarded as a distorted squarebased pyramid. A five-coordinate structure of this type must, therefore, be assigned to all three compounds of this group (VI).



(VI)

Series 8. $-NR_2 = -N(CH_2)_5$

All the compounds are green, diamagnetic and with the reflectance spectra characteristic of planar, probably *trans*-structure.

The crystals of series 5, 6, 7, 8, dissolved in benzene, *m*-xylene and chloroform have values of μ_{eff} ranging between 0 and 3.3 *B.M.* The spectra show the presence of the planar, octahedral and five-coordinated forms. The heights of the peaks at 16,200, 9500 and 7700 cm^{-1} give an indication of the relative amounts of the planar, octahedral and five-coordinated species respectively.

For the series 7 ($-NR_2 = -N(C_2H_5)_2$) the percentage of the planar diamagnetic species increases along the series of X substituents in the order 3,4-benzo $<$ 5-Cl $<$ H $\leqslant$ 5-$CH_3 \simeq$ 3-$CH_3 \simeq$ 5-$C_2H_5 <$ 5,6-benzo. The effect of the X substituent, therefore, is similar to its effect on the equilibrium between the planar and tetrahedral forms of the bis(*N-sec*-alkylsalicylaldimino)-nickel(II) complexes[10,15]. For all four series the percentage of planar form is maximum in benzene, the proportion of the five-coordinated form is greater in chloroform. In pyridine six-coordinated species are formed in all cases.

The percentage of the planar species for a given X substituent, increases according to the $-NR_2$ groups in the order: $-N(CH_3)_2 < -N(CH_2)_4 < -N(C_2H_5)_2 < -N(CH_2)_5$. Trials with Stuart models have shown that this is the order of increasing steric hindrance to coordination of the $-NR_2$ groups. On the other hand the donor power of the corresponding amines HNR_2 as measured in aprotic solvents towards the reference complex acceptor NiDBH decreases[20] in the order $HN(CH_3)_2 \simeq HN(CH_2)_4 > HN(CH_2)_5 > HN(C_2H_5)_2$. It is therefore clear that the bulkiness of the amino groups prevails on their donor power.

The effect of temperature on the equilibria can be studied in a solution of *m*-xylene or in the molten state by means of spectrophotometric and magnetic measurements. The paramagnetism decreases with rising temperature showing that the proportion of the planar species increases. The transformation to the planar form is therefore an endothermic process. We can assume that increasing thermal agitation will favour the rupture of bonds between the sterically hindered amino groups with the formation of the four-coordinated species. The solution equilibria can be represented by the following scheme:

octahedral
paramagnetic form
I $\Downarrow\!\Uparrow$ $\underset{}{\overset{\text{II}}{\rightleftharpoons}}$ planar diamagnetic form
five-coordinated
paramagnetic form

A complete survey of the structures of the nickel(II) complexes is given in Tables I and II.

TABLE I

STEREOCHEMISTRY OF THE [X-sal enN(R)R′]$_2$Ni COMPLEXES

R	H				phenyl
R′	*n*-alkyl, benzyl	*o*-substituted phenyl	phenyl or *p*-substituted phenyl		methyl
X	all substituents		3-Cl, 5-Cl, 3,4-benzo	H, 3-CH$_3$, 5-NO$_2$, 5,6-benzo	all substituents
stereochem. in the solid state	octahedral	*trans*-planar	octahedral	*trans*-planar	
in solution	octahedral	*trans*-planar	planar and octahedral forms in equilibrium		*trans*-planar
in pyridine	no adducts	octahedral adducts			

TABLE II

STEREOCHEMISTRY OF THE [X-sal enN(R)R′]$_2$Ni COMPLEXES

R	CH$_3$	CH$_2$–CH$_2$	CH$_2$–CH$_3$			CH$_2$–CH$_2$ CH$_2$
R′	CH$_3$	CH$_2$–CH$_2$	CH$_2$–CH$_3$			CH$_2$–CH$_2$
X	H, 3,4-benzo, 5,6-benzo	H, 5-CH$_3$, 5-Cl, 5,6-benzo	H	3-Cl, 5-CH$_3$, 3,4-benzo	3-CH$_3$, 5-CH$_3$, 5-C$_2$H$_5$, 5-NO$_2$, 5,6-benzo	all substituents
stereochem. in the solid state	octahedral			five-coordinated square-pyramidal	*trans*-planar	
in solution	octahedral, five-coordinated and planar forms in equilibrium					
in pyridine	octahedral adducts					

Cobalt(II) complexes[21]

The cobalt(II) complexes of the general formula [X-sal enN(R)R']$_2$Co are generally orange or red in colour. All the compounds are of high-spin type, the values of μ_{eff} ranging between 4.10 and 4.70 *B.M.*

Three main types of spectra are exhibited by these complexes (Fig. 6). The spectrum of the type A (Fig. 6) is diagnostic of a distorted octahedral structure, showing bands at 9300 and 11,500 cm^{-1} and a shoulder at 15,600 cm^{-1}. The first two bands correspond to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ in a cubic field which is split in fields of lower symmetry[22]. The complexes with this type of spectrum have high dipole moments (about 6.9 *D*). Therefore they must have a *cis*-octahedral structure of the type (VII):

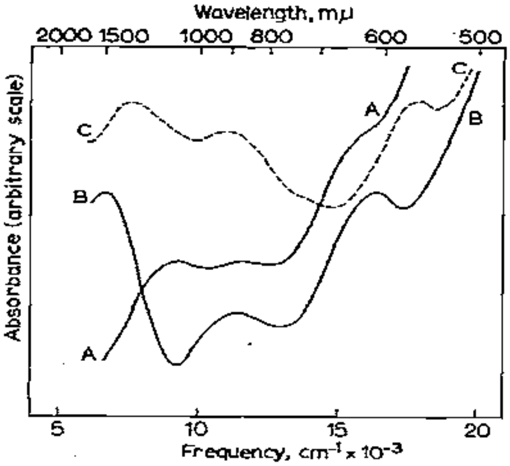
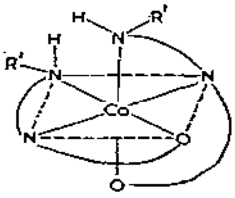


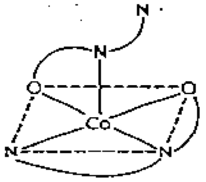
Fig. 6. Reflectance spectra of [X-sal enN(R)R']$_2$Co complexes: A, [H-sal enNHCH$_3$]$_2$Co; B, [H-sal enN(C$_6$H$_5$)$_2$]$_2$Co; C, [5-Cl-sal enN(C$_2$H$_5$)$_2$]$_2$Co.



(VII)

The spectrum of type B (Fig. 6) is characteristic of tetrahedral cobalt(II) complexes. This spectrum indeed shows three bands at *ca.* 7700, 11,200 and 18,000 cm^{-1} indicative of the tetrahedral configuration[23]. The dipole moments (about 3.5 *D*), of the complexes with this spectrum, are in accordance with a tetrahedral geometry.

The spectrum of type C (Fig. 6) has three bands at 6700, 11,400 and 16,800 cm^{-1}. This spectrum is exhibited among the others by the [5-Cl-sal en-$N(C_2H_5)_2]_2Co$ whose five-coordinated distorted square-pyramidal structure has been ascertained by X-ray analysis[19] (VIII).



(VIII)

In pyridine solution all the cobalt(II) complexes, with the exception of the *cis*-octahedral, have a spectrum with two bands at 10,000 cm^{-1} ($\varepsilon = 10$) and 17,000 cm^{-1} ($\varepsilon = 18$) characteristic of octahedral adducts with two molecules of pyridine[23].

TABLE III

STEREOCHEMISTRY OF THE [X-sal enN(R)R′]$_2$Co COMPLEXES

R	H	phenyl	H	CH_3
R′	*n*-alkyl	phenyl	*o*-tolyl, phenyl, *p*-tolyl	
X	H			
stereochem. in the solid state	octahedral	tetrahedral	unknown	
in solution	octahedral	mainly tetrehedral		
in pyridine	no adducts	octahedral adducts		

TABLE IV

STEREOCHEMISTRY OF THE [X-sal enN(R)R′]$_2$Co COMPLEXES

R	CH_2-CH_2		CH_2-CH_3	CH_2-CH_2 CH_2	
R′	CH_2-CH_2		CH_2-CH_3	CH_2-CH_2	
X	5-Cl	3-Cl	H, 3-Cl 5-Cl	3-CH_3, 5-CH_2, 3-Cl	H, 5-Cl
stereochem. in the solid state	octahedral	five-coordinated square pyramidal			octahedral
in solution	five-coordinated, octahedral and tetrahedral species in equilibrium				
in pyridine	octahedral adducts				

The factors which affect the structure of the cobalt(II) complexes are substantially the same as in the case of the analogous nickel(II) compounds. The geometry of the complexes is mainly ruled by the electronic effects and the steric requirements of the R and R′ groups. In most cases the same coordination number is reached with the two metals. For tetra-coordinated complexes, however, those of cobalt are tetrahedral while those of nickel are planar.

A complete survey of the cobalt(II) complexes and their structures is given in Tables III and IV.

REFERENCES

1 L. Sacconi, M. Ciampolini and G. P. Speroni, *J. Am. Chem. Soc.*, 87 (1965) 3102.
2 A. Chakravorty, *Inorg. Chem.*, 4 (1965) 127.
3 J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, 69 (1947) 1237.
4 J. Ferguson, *J. Chem. Phys.*, 34 (1961) 611.
5 E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, 63 (1959) 1908.
6 L. Sacconi, P. Paoletti and R. Cini, *J. Inorg. Nucl. Chem.*, 8 (1958) 492; *J. Am. Chem. Soc.*, 80 (1958) 3583; C. M. Harris, S. L. Lenzer and R. L. Martin, *Australian J. Chem.*, 11 (1958) 33.
7 J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, 4 (1962) 159.
8 B. Meuthen and M. von Stackelberg, *Z. Anorg. Allgem. Chem.*, 305 (1960) 279; E. C. Lingafelter, B. Morosin and G. L. Simmons, *Acta Cryst.*, 13 (1960) 1025.
9 P. L. Orioli, L. Sacconi and M. Di Vaira, *Chem. Comm. (London)*, 1 (1965) 103; *Inorg. Chem.*, in the press.
10 L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, (1962) 255; L. Sacconi, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, 85 (1963) 411.
11 M. Ciampolini, *Inorg. Chem.*, 5 (1966) 35.
12 P. Day, *Proc. Chem. Soc.*, (1964) 18; W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 3 (1964) 841.
13 W. E. Hatfield, H. D. Bedon and S. M. Horner, *Inorg. Chem.*, 4 (1965) 1181.
14 P. Day and C. K. Jørgensen, *J. Chem. Soc.*, (1964) 6226.
15 L. Sacconi, M. Ciampolini and N. Nardi, *J. Am. Chem. Soc.*, 86 (1964) 819; R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 2 (1963) 181.
16 L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, (1964) 276.
17 L. Sacconi, P. Nannelli and U. Campigli, *Inorg. Chem.*, 4 (1965) 818.
18 L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, *Inorg. Chem.*, 4 (1965) 943.
19 L. Sacconi, P. L. Orioli and M. Di Vaira, *J. Am. Chem. Soc.*, 87 (1965) 2059.
20 L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc.*, (1958) 848; L. Sacconi and G. Lombardo, *J. Am. Chem. Soc.*, 82 (1960) 6266.
21 L. Sacconi, M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 4 (1965) 1116.
22 C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, 9 (1955) 397.
23 L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, 84 (1962) 3246.