Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

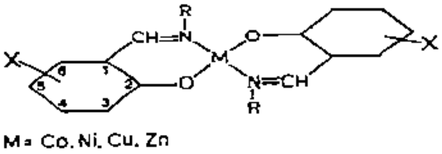
III. NATURE OF THE CHEMICAL BOND; STRUCTURAL PROPERTIES

TETRAHEDRAL COMPLEXES OF NICKEL(II) AND COPPER(II) WITH SCHIFF BASES

L. SACCONI

Istituto di Chimica Generale ed Inorganica dell'Universita, Florence (Italy)

Many tetrahedral complexes of nickel(II) and copper(II), with monodentate ligands, have been obtained, but only recently have internal complexes of these metals been prepared. Several metal chelate complexes with N-substituted salicylaldimines have been shown to have tetrahedral structures (I).



(I)

SALICYLALDIMINES COMPLEXES OF NICKEL(II)

The paramagnetism exhibited by certain diamagnetic nickel(II) complexes ($R = CH_3$, $X = H$) in inert solvents[1] was initially attributed to the presence, in solution, of tetrahedral species.

However this complex, and those of the homologous series ($R = n$-alkyl, $X = H$) do not have dipole moments[2] in benzene at room temperature, and thus the idea of a tetrahedral species in solution was abandoned. Moreover since these complexes become paramagnetic in the fused state, one could exclude the possibility that the solvent was solely responsible for the paramagnetism[3,4]. We have isolated a paramagnetic form of the complex bis(*N*-methylsalicylaldimino)nickel(II) whose exceptional insolubility implies an octahedral polymerised structure[5]. This discovery suggested that the paramagnetism of many nickel(II) complexes with salicylaldimines whether in solution or in the solid state, is due, at least in part, to molecular association. Holm[6] and Ferguson[8] have also found paramagnetic salicylaldimine complexes of nickel(II) which are paramagnetic in the solid state, and have shown from cryoscopic measurements in benzene, that nickel complexes of the type (I, R = *sec*-alkyl[6,7], methyl[8], aryl[9], X = H) are partially associated.

On the basis of these results, Holm drew the general conclusion that the paramagnetism of all such complexes of nickel(II) was due to association[6,9] excluding thereby the possibility of a conformational equilibrium between square and planar forms[10].

We found nevertheless that association phenomena could account only in part for the paramagnetism of *N-sec*-alkyl complexes in solution and this suggested that the problem should be studied further.

The two dimensional Patterson syntheses from X-ray studies of single crystals of the complexes (I, R = iso-propyl, X = H) with nickel(II), copper(II), cobalt(II) and zinc(II) have shown that all these complexes are isostructural[10]. Since the spectrum of the solid cobalt(II) complex, (I, R = iso-propyl, X = H) (from 5,000 to 20,000 cm^{-1}) is identical with the spectrum of the corresponding cobalt(II) complex (I, R = *n*-butyl, X = H) which has been shown, through an X-ray study[13], to have a tetrahedral structure, it is concluded that the nickel(II) complex (I, R = iso-propyl, X = H) also has a tetrahedral structure, albeit slightly distorted[11,14].

A complete X-ray analysis has confirmed this conclusion[15]. The reflectance spectrum of the nickel(II) complex (I, R = iso-propyl, X = H), which is similar to the spectrum of the tetrahalogenonickelates[16], is in good agreement with the energy level scheme proposed for tetrahedral complexes by Liehr and Ballhausen[17]. A band observed at *ca* 6700 cm^{-1} is attributed to the $\nu_2(^3T_1(F) \rightarrow {}^3A_2(F))$ transition whilst that at *ca* 10,900 cm^{-1} is probably a spin forbidden transition to an excited state derived from the ^1D term of the free ion. Three bands at *ca* 14,000, 16,900 and 19,600 cm^{-1} are assigned to the $\nu_3(^3T_1(F) \rightarrow {}^3T_1(P))$ transition.

Through studying the solutions of the nickel(II) complexes (I, R = *sec*-alkyl, X = H) we find:

a) that there is virtually no molecular association at the boiling point in benzene, as indicated by ebullioscopic measurements, whilst the paramagnetism in benzene, *m*-xylene and in dibenzyl, rises regularly with temperature from 20° to 200°;

b) that the absorption spectra of these complexes in inert solvents even at room temperature, are characteristic of tetrahedral stereochemistry, especially the band at *ca* 6700 cm^{-1} whose intensity rises with temperature;

c) that the *sec*-alkyl complexes possess a dipole moment in benzene, whilst the *n*-alkyl complexes are practically non-polar.

We concluded therefore that in non-coordinating solvents, the α-branched *n*-alkyl complexes of nickel(II) exist in a conformational equilibrium of the planar diamagnetic form and the pseudo-tetrahedral paramagnetic form. The equilibrium shifts towards the tetrahedral form with increasing temperature[11,14]. Holm using analogous techniques has corrected earlier statements and has reached similar conclusions[18]. Spectrophotometric measurements have also demonstrated that the paramagnetism of *n*-alkyl complexes of nickel(II) (I, R = alkyl, ethyl to *n*-decyl, X = H) whether in solution or in the fused state at 80°, is due to the presence of a tetrahedral form in equilibrium with a planar form; the concentration of the tetrahedral form increases with temperature[19]. This is in accord with earlier viscosity measurements which excluded the presence of association in the fused complexes[4].

The factors which favour the tetrahedral configuration have been studied in a series of complexes variously substituted in the benzene ring (I, R = *n*-propyl, *sec*-butyl, and *tert*-butyl; X = 3–CH_3, 5–CH_3, 3–Cl, 5–Cl, 3–Br, 3–NO_2, 5–NO_2, 3,4-benzo, 5,6-benzo). The structures of these complexes in the solid state were assigned on the basis of reflectance spectra and confirmed by magnetic measurements[20]. The results reported in Table I demonstrate that the structures of these complexes are influenced predominantly by steric effects. In the case of complexes with R = *n*-propyl the planar structure is the most stable. These complexes are olive green and diamagnetic. The larger size of the *tert*-butyl group on the other hand constrains complexes having this group to assume a tetrahedral configuration. These complexes are brown and paramagnetic. In the case of those complexes where R = iso-propyl and *sec*-butyl, the structure is strongly influenced by the electronic and geometric effect of the X substituent in the benzene ring. The way in which the molecule packs in the crystal lattice is also probably a factor influencing the structure.

TABLE I

THE STRUCTURES OF SOME BIS(R–*N*–SALICYLALDIMINO)NICKEL(II) COMPLEXES, SUBSTITUTED IN THE BENZENE RING, AS INDICATED BY THEIR REFLECTANCE SPECTRA*

R	H	3–CH_3	5–CH_3	3–Cl	5–Cl	3–Br	3–NO_2	5–NO_2	5,6–benzo	3,4–benzo
n-Propyl	P	P	P	P	P			P	P	P
Iso-propyl	T	P	P	P	P	P	P	P	P	T
tert-Butyl	T			T	T	T	T	T	T	T

* P = planar; T = tetrahedral; ν_{max} (planar form) *ca* 16,000 cm^{-1}; ν_{max} (tetrahedral form) *ca* 6700, 9500, 10,900, 14,000, 16,900, 19,600 cm^{-1}.

The values of the magnetic moments of the pseudo-tetrahedral complexes, 3.2–3.3 *B.M.*, are of the same order of magnitude as those found for distorted tetrahedral complexes of the type NiX_2L_2 (X = halogen)[21].

The equilibria between planar and tetrahedral forms has been studied spectrophotometrically in *m*-xylene and in dibenzyl. The percentage of tetrahedral form increases with increasing temperature except when R = *tert*-butyl when the reverse is found to hold.

The values of the enthalpy and entropy changes involved in the transformation of one form to the other were obtained from a graph of the logarithm of the equilibrium constant *versus* the absolute temperature (80–170°C) (Table II).

The free energy changes are rather small and depend mainly on steric effects. The heat of formation of the planar form of the *n*-propyl complexes is lower, by

TABLE II

THERMODYNAMIC FUNCTIONS FOR THE PLANAR–TETRAHEDRAL EQUILIBRIUM AT 120° IN DIBENZYL SOLUTION

R	*X*	*ΔF* *kcal/mol*	*ΔH* *kcal/mol*	*ΔS* *e.u.*
n-Propyl	H	2.9	4.6	4
	3–Cl	—	—	—
	5–CH_3	2.8	4.6	4
	5–Cl	2.7	5.2	6
Iso-propyl	H	0.52	3.2	10
	3–Cl	0.35	3.0	7
	5–CH_3	0.20	2.5	6
	5–Cl	0.16	2.0	4

some 4–5 kcal/mol, than that of the pseudo-tetrahedral form. This difference is sufficiently great that the percentage of tetrahedral form existing at room temperature may be neglected. In the case of the iso-propyl complexes, the corresponding difference in enthalpy is lower by 2–3 kcal/mol; this is probably due to repulsion between the iso-propyl group and the atoms of the chelate ring opposite.

As a consequence the percentage of the two forms in equilibrium are comparable at room temperature whilst at higher temperatures the tetrahedral form predominates. For the *tert*-butyl complexes the large repulsion makes the tetrahedral configuration the most stable even at very low temperatures. The free energy is also influenced by the position and nature of the ring (X) substituent. The planar form is favoured by benzo substitution in the 5,6 positions whilst the tetrahedral form is favoured by 3,4 substitution.

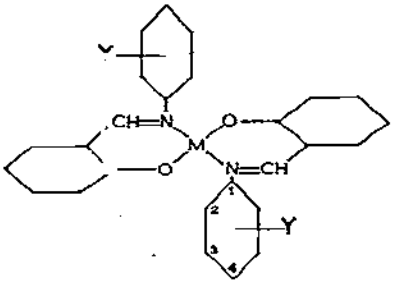
Nevertheless there are other factors present which act in this sense as indicated by the fact that the two complexes with R = iso-propyl and X = 3–Cl and 3–Br are both planar whilst one would have expected the reverse purely on the basis of steric considerations. The changes in entropy are all positive, from 4–10 e.u., thus favouring the formation of the tetrahedral stereochemistry. This is in part attributed to the influence of a statistical term derived from the different multiplicities of the fundamental electronic states, and in part to the greater facility with which the alkyl groups can rotate in a tetrahedral structure. Another entropy contribution is derived from the greater solvation of the planar form[22].

Some nickel(II) complexes with *N*-aryl-salicylaldimines (II, Y = 3–Cl, 4–Cl, 4–CH_3, 3,4–benzo) are paramagnetic and greatly associated in solution[6]. A preliminary study of the paramagnetism and of the spectra in solution up to 70° suggests the idea of an equilibrium between a planar diamagnetic form and a polymeric paramagnetic form. Holm has reaffirmed his conclusion that the relationship between paramagnetism and association is in fact general[9].

The magnetic and spectrophotometric measurements carried out by us between 80 and 200° have shown instead that there also exists a tetrahedral form of the complexes (II, Y = 3–Cl, 4–Cl, 4–CH_3, 3,4–benzo) and we have therefore concluded[23], that the following equilibrium is present.

Associated form ↔ planar form ↔ tetrahedral form

This equilibrium is displaced completely towards the right with increasing temperature (or increasing dilution).



(II)

SALICYLALDIMINE COMPLEXES OF COPPER(II)

The copper(II) complexes (I, R = *n*-alkyl, X = H) show a single crystal field band at *ca* 16,000 cm^{-1} which probably contains several transitions. There is also a shoulder[24,25] at 22,000 cm^{-1}. A planar structure has been established for the copper(II) complexes (I, R = methyl[26], *n*-butyl and *n*-amyl[27]) by means of X-ray studies. On the other hand the copper(II) complexes (R = iso-propyl and *sec*-butyl) in which the alkyl group is branched in the α position, are isomorphous with the corresponding complexes of nickel(II), cobalt(II) and zinc(II) and are therefore pseudo-tetrahedral[12]. This is confirmed by the fact that the reflectance spectra of a series of solid solutions of the copper complexes in the corresponding zinc salt, are practically identical[25]. The spectrum[28] of the iso-propyl complex shows three bands at *ca* 8900, 14,000 and 20,500 cm^{-1}. The crystal field theory predicts a single transition ($^2T_2 \rightarrow {}^2E$) for copper(II) complexes in a regular tetrahedral field. If the tetrahedron is distorted the ground or excited state may split giving rise to more than one band[29]. Three series of copper (II) complexes have been studied, namely (I, R = *n*-propyl, iso-propyl, and *tert*-butyl, X = 3-CH_3, 5-CH_3, 3-Br, 3-NO_2, 5-NO_2, 3,4-benzo, and 5,6-benzo)[25]. The results are reported in Table III.

The spectra of the olive green copper(II) complexes (R = *n*-propyl) are typical of a planar species. The *tert*-butyl complexes are a maroon colour, and their spectra are similar to the spectra of the tetrahedral iso-propyl derivatives; a pseudo-tetrahedral structure is attributed to these complexes. The iso-propyl complexes can either be green, with spectra typical of a planar species, or brown with spectra typical of a pseudo-tetrahedral species, according to the substituent X

TABLE III

THE STRUCTURES OF SOME BIS(R-*N*-SALICYLALDIMINO)COPPER(II) COMPLEXES SUBSTITUTED IN THE BENZENE RING, AS INDICATED BY THEIR REFLECTANCE SPECTRA*

R	*H*	3–CH_3	5–CH_3	3,4	5,6	3–Cl	5–Cl	3–Br	3–NO_2	5–NO_2
				benzo						
n-Propyl	P	P	P	P	P	P	P			P
Iso-propyl	T	T	T	T	P	P	P	P	P	P
tert-Butyl	T	T	T	T	T	T	T		T	T

* P = planar; T = tetrahedral. ν_{max} (planar form) 14,000–16,000 cm^{-1}; ν_{max} (tetrahedral form) 8700–10,000, 12,800–14,000, 19,200–20,800 cm^{-1}.

on the ring. A comparison of Table I with Table III shows that the copper(II) complexes have a greater tendency to assume a tetrahedral structure than the corresponding nickel(II) complexes. Thus the copper(II) complexes (I, R = isopropyl, X = 3-CH_3, and 5-CH_3) are tetrahedral whilst the corresponding nickel(II) complexes are square planar.

The magnetic moments of the planar complexes lie between 1.83 and 1.86 *B.M.*, and of the tetrahedral complexes between 1.89 and 1.92 *B.M.* Ligand field theory in fact predicts[30] a larger magnetic moment for tetrahedral copper(II) complexes.

The absorption spectra of the *n*-propyl and *tert*-butyl complexes in benzene solution are very similar to the corresponding reflectance spectra of the solids. The absorption spectra of the iso-propyl complexes are intermediate between those of the *n*-propyl and *tert*-butyl complexes. The dipole moments of the three series of complexes imply that there is a certain symmetry in the molecular structure. They increase in the order *n*-propyl < iso-propyl < *tert*-butyl corresponding with the increasing steric hindrance of the alkyl group. The dipole moments of the copper(II) complexes (I, R = *tert*-butyl) are definitely lower than those of the corresponding complexes of cobalt(II) and zinc(II), suggesting a probable flattening of the coordination tetrahedron. The low values in the case of the *n*-propyl and iso-propyl complexes show either they have a more flattened configuration or that there is a small percentage of a pseudo-tetrahedral form existing in conformational equilibrium.

REFERENCES

1 J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, 69 (1947) 1237.
H. C. Clark and A. L. Odell, *J. Chem. Soc.*, (1955) 3431; (1956) 520.
2 L. Sacconi, P. Paoletti and G. Del Re, *J. Am. Chem. Soc.*, 79 (1957) 4062.
3 L. Sacconi, R. Cini and F. Maggio, *J. Am. Chem. Soc.*, 79 (1957) 3933.
4 L. Sacconi, R. Cini, M. Ciampolini and F. Maggio, *J. Am. Chem. Soc.*, 82 (1960) 3487.
5 L. Sacconi, P. Paoletti and R. Cini, *4th Intern. Conf. Co-ord. Chem.*, Rome, September, 1957, in *J. Inorg. Nucl. Chem.*, 8 (1958) 492; *J. Am. Chem. Soc.*, 80 (1958) 3583.

6 R. H. Holm, in *Proceedings Sixth International Conference on Co-ordination Chemistry*, S. Kirschner (Editor), The Macmillan Company, New York 1961, p. 341.

7 R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, 82 (1960) 5506.

8 J. Ferguson, *Spectrochim. Acta*, 17 (1961) 316.

9 R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1 (1962) 599.

10 R. H. Holm, *J. Am. Chem. Soc.*, 83 (1961) 4683.

11 L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, (1962) 255.

12 L. Sacconi and P. L. Orioli, *Ric. Sci.*, (II-A) 32 (1962) 645.

13 L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *Atti Accad. Sci., Lettere Arti Palermo*, 19 (1960) 141; *Chem. Abstr.*, 56 (1962) 6890; *J. Am. Chem. Soc.*, 84 (1962) 3246; E. Frasson and C. Panattoni, *Z. Krist.*, 116 (1961) 154; H. Nishikowa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, (B) 17 (1962) 78; B. O. West, *J. Chem. Soc.*, (1962) 1374.

14 L. Sacconi, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, 85 (1963) 411.

15 M. R. Fox, E. C. Lingafelter, P. L. Orioli and L. Sacconi, *Nature*, 197 (1963) 1104.

16 C. Furlani and G. Morpurgo, *Z. Physik. Chem.*, 28 (1961) 93; D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 83 (1961) 4161.

17 A. D. Liehr and C. J. Ballhausen, *Ann. Physik*, 6 (1959) 1341.

18 R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 2 (1963) 181.

19 L. Sacconi, *J. Chem. Soc.*, (1963) 4608.

20 L. Sacconi, M. Ciampolini and N. Nardi, *J. Am. Chem. Soc.*, 86 (1964) 819.

21 J. R. Miller, *Adv. Inorg. Chem. Radiochem.*, 4 (1962) 133.

22 D. R. Eaton, W. D. Phillips and D. J. Caldwell, *J. Am. Chem. Soc.*, 85 (1963) 397.

23 L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, 85 (1963) 1750.

24 J. Ferguson, *J. Chem. Phys.*, 34 (1961) 1612.

25 L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, (1964) 276.

26 M. von Stackelberg, *Z. Anorg. Chem.*, 253 (1947) 136; E. C. Lingafelter, G. L. Simmons and B. Morosin, *Acta Cryst.*, (1961) 1222.

27 E. Frasson, C. Panattoni and L. Sacconi, *Ric. Sci.*, (II-A) 32 (1962) 649.

28 L. E. Orgel, *J. Chem. Phys.*, 34 (1961) 1612.

29 C. Furlani and G. Morpurgo, *Theoret. Chim. Acta*, 1 (1963) 102.

30 B. N. Figgis, *Nature*, 182 (1958) 1568; J. H. Griffiths, *Trans. Faraday Soc.*, 54 (1958) 1109.