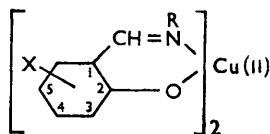


45. *Pseudo-tetrahedral Structure of Some α -Branched Copper(II) Chelates with Schiff Bases.*

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The complexes of copper(II) with *N*-isopropyl- and *N*-*s*-butyl-salicylideneamines are isomorphous with the analogous complexes of nickel(II), cobalt(II), and zinc(II), and thus pseudo-tetrahedral in structure, in contrast with the *N*-*n*-alkyl complexes which are planar. From their reflectance spectra, the configurations of three series of copper(II) complexes with substituted *N*-alkylsalicylideneamines have been assigned. The absorption spectra and the dielectric polarization data indicate that in solution in inert solvents the *t*-butyl compounds remain essentially tetrahedral and the *n*-alkyl essentially planar. The values for the *s*-alkyl complexes are intermediate.

UNTIL recently no tetrahedral chelate of nickel(II) or copper(II) had been unambiguously shown to exist.¹ Recently, however, tetrahedral co-ordination was first found to occur in the nickel(II) complexes of *N*-*s*-alkylsalicylideneamines² and then in the *N*-aryl-³ and the *N*-*n*-alkyl-salicylideneaminatonickel(II)⁴ complexes. In the course of these investigations it was found that the *N*-isopropyl complexes of cobalt(II), copper(II), and zinc(II) are isomorphous with that of nickel(II),⁵ which was found to have a distorted tetrahedral



(I)

co-ordination.⁶ Thus a pseudo-tetrahedral structure should also be attributed to the solid *N*-isopropyl copper(II) complex.⁵ In order to study the factors which influence the stereochemistry of the copper(II) chelates with Schiff bases and to obtain more information about this problem in general, some series of complexes of the type (I) were prepared, where R = *n*-propyl, isopropyl, *s*-butyl, or *t*-butyl, and X = 3- or 5-methyl-, 3- or 5-chloro, 5-nitro, and 3,4- or 5,6-benzo; spectrophotometric, magnetic, and electric dipole moment measurements were made on these compounds.

EXPERIMENTAL

Preparation of Copper and Cobalt Compounds.—A cold concentrated solution of the metal acetate (0.02 mole) in water was treated with the appropriate salicylaldehyde (0.04 mole) in ethanol (20 ml.). The resulting suspension was heated on a water-bath for 1 hr., cooled to room temperature, and filtered. The solid bis(salicylaldehydato)metal(II) was then refluxed in ethanol (20 ml.) with an excess of the appropriate amine (0.05 mole) until solution was complete. The crystals which separated on cooling were recrystallized from cyclohexane or from chloroform-ethanol.

Bis-(N-n-propylsalicylideneaminato)copper(II), m. p. 127—128°;⁷ *3-methyl derivative*, m. p. 139—140° (Found: Cu, 15.2; N, 6.8. C₂₂H₂₈CuN₂O₂ requires Cu, 15.3; N, 6.7%); *5-methyl derivative*, m. p. 152—153° (Found: Cu, 15.3; N, 6.9%); *3-chloro-derivative*, m. p. 152—153°

¹ Porai-Koshits, *Zhur. strukt. Khim.*, 1961, **2**, 218.

² Sacconi, Orioli, Paoletti, and Ciampolini, *Proc. Chem. Soc.*, 1962, 255; Sacconi, Paoletti, and Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 411.

³ Sacconi and Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 1750.

⁴ Sacconi, *J.*, 1963, 4608.

⁵ Sacconi and Orioli, *Ricerca sci. Rend.*, 1962, **32**, 645.

⁶ Fox, Lingafelter, Orioli, and Sacconi, *Nature*, 1963, **197**, 1104.

⁷ Sacconi, Ciampolini, Maggio, and Del Re, *J. Amer. Chem. Soc.*, 1960, **82**, 815; Sacconi, Ciampolini, Maggio, and Cavasino, *J. Inorg. Nuclear Chem.*, 1961, **19**, 73.

(Found: Cu, 13.8; N, 6.0. $C_{20}H_{22}Cl_2CuN_2O_2$ requires Cu, 13.9; N, 6.1%); 5-chloro-derivative, m. p. 168—169° (Found: Cu, 14.0; N, 6.2%); 5-nitro-derivative (Found: Cu, 13.2; N, 11.8. $C_{20}H_{22}CuN_4O_6$ requires Cu, 13.3; N, 11.7%); 3,4-benzo-derivative, m. p. 153—155° (Found: Cu, 13.0; N, 5.8. $C_{28}H_{28}CuN_2O_2$ requires Cu, 13.0; N, 5.7%); 5,6-benzo-derivative, m. p. 194—195° (Found: Cu, 12.9; N, 5.8%).

Bis-(*N*-isopropylsalicylideneaminato)copper(II), m. p. 143—144° (Found: Cu, 16.2; N, 7.4. $C_{20}H_{24}CuN_2O_2$ requires Cu, 16.4; N, 7.2%); 3-methyl derivative, m. p. 127—128° (Found: Cu, 15.5; N, 6.9%); 5-methyl derivative, m. p. 117—118° (Found: Cu, 15.2; N, 6.7%); 3-chloro-derivative, m. p. 126—127° (Found: Cu, 13.7; N, 6.1%); 5-chloro-derivative, m. p. 166—168° (Found: Cu, 13.9; N, 6.1%); 5-nitro-derivative (Found: Cu, 13.2; N, 11.8%); 3,4-benzo-derivative, m. p. 170—171° (Found: Cu, 13.0; N, 5.9%); 5,6-benzo-derivative, m. p. 198—200° (Found: Cu, 13.1; N, 5.7%).

Bis-(*N*-*s*-butylsalicylideneaminato)copper(II), m. p. 72—74° (Found: Cu, 15.2; N, 6.7. $C_{22}H_{28}CuN_2O_2$ requires Cu, 15.3; N, 6.7%).

Bis-(*N*-*t*-butylsalicylideneaminato)copper(II), m. p. 185—186° (Found: Cu, 15.1; N, 6.7%); 3-methyl derivative, m. p. 217—218° (Found: Cu, 14.4; N, 6.4. $C_{24}H_{32}CuN_2O_2$ requires Cu, 14.3; N, 6.3%); 5-methyl derivative, m. p. 210—211° (Found: Cu, 14.2; N, 6.3%); 3-chloro-derivative (Found: Cu, 12.9; N, 5.8. $C_{22}H_{26}Cl_2CuN_2O_2$ requires Cu, 13.1; N, 5.8%); 5-chloro-derivative, m. p. 205—206° (Found: Cu, 13.1; N, 5.6%); 5-nitro-derivative (Found: Cu, 12.7; N, 11.2. $C_{22}H_{26}CuN_4O_6$ requires Cu, 12.6; N, 11.1%); 3,4-benzo-derivative, m. p. 224—226° (Found: Cu, 12.2; N, 5.3. $C_{30}H_{32}CuN_2O_2$ requires Cu, 12.3; N, 5.4%); 5,6-benzo-derivative, m. p. 201—203° (Found: Cu, 12.2; N, 5.6%).

Bis-(*N*-isopropylsalicylideneaminato)cobalt(II); 3-chloro-derivative, m. p. 231—233° (Found: Co, 13.1; N, 6.2. $C_{20}H_{22}Cl_2CoN_2O_2$ requires Co, 13.0; N, 6.2%); 5-chloro-derivative, m. p. 185—186° (Found: Co, 12.9; N, 6.2%); 5,6-benzo-derivative (Found: Co, 12.1; N, 5.9. $C_{28}H_{28}CoN_2O_2$ requires Co, 12.2; N, 5.8%).

Bis-(*N*-*t*-butylsalicylideneaminato)cobalt(II); 3-chloro-derivative (Found: Co, 12.2; N, 5.8. $C_{22}H_{26}Cl_2CoN_2O_2$ requires Co, 12.4; N, 5.9%); 5-chloro-derivative, m. p. 252—254° (Found: Co, 12.4; N, 5.9%).

Measurements.—The absorption spectra were recorded with a Beckman DK 2 spectrophotometer fitted with 1-cm. silica cells. The reflectance spectra were measured by using the standard Beckman reflectance attachment and magnesium oxide as the reference. The methods for the measurements of the magnetic susceptibility and the dielectric polarization have been previously described.⁷

DISCUSSION

Stereochemistry of the Complexes in the Solid State.—A complete three-dimensional X-ray analysis of bis-(*N*-isopropylsalicylideneaminato)nickel(II) has shown that the metal atom has distorted tetrahedral co-ordination, with an angle of 81° between the two planes containing the salicylideneamine residues, and an N-Ni-O angle of 94° in the chelate rings.⁶ Furthermore, X-ray analysis on single crystals has demonstrated that this nickel(II) complex is isomorphous with the analogous ones of cobalt(II), zinc(II), and copper(II).⁵ The first three compounds are practically isometric whilst the lattice constants for the copper(II) compound are a little different from those of the other three complexes.* However, the differences are so small that a pseudo-tetrahedral structure can safely be assigned to the copper complex as well. The fact that the *N*-isopropylcopper(II) complex forms solid solutions with the pseudo-tetrahedral zinc(II) analogue but not with the palladium(II) analogue, which can be confidently considered to be planar, supports this conclusion. From similar considerations, a pseudo-tetrahedral structure can also be assigned to the *s*-butylsalicylideneaminatocopper(II) complex. To conclude, the *N*-propyl- and *N*-butyl-salicylideneaminato-complexes of copper(II)⁸ and nickel(II),^{3,8} in the solid state, have a planar

* The lattice constants found for the nickel(II) and copper(II) complexes are: space group *Pbca*, $Z = 8$; Ni, $a = 13.16$, $b = 19.64$, $c = 15.12$ Å, $D = 1.30$ g. cm.⁻³, $U = 488.49$ Å³; Cu, $a = 12.87$, $b = 20.68$, $c = 14.58$ Å, $D = 1.33$ g. cm.⁻³, $U = 485.09$ Å³.

⁸ Frasson, Panattoni, and Sacconi, *Ricerca sci. Rend.*, 1962, **32**, 649.

structure with n-alkyl groups, whilst the s-alkyl compounds have a pseudo-tetrahedral co-ordination probably imposed by forces of a steric nature.

To these two different types of co-ordination there correspond two different reflectance spectra in the region 5000—25,000 cm^{-1} . For example, the planar n-butyl complex has a single broad band at *ca.* 16,000 cm^{-1} , that, by analogy with the results obtained by Ferguson for the *N*-methyl complex,⁹ probably contains more than one transition under its envelope. A shoulder also appears at 22,000 cm^{-1} . On the other hand, the pseudo-tetrahedral *N*-isopropylsalicylideneaminatocopper(II) complex both as pure solid and in the solid solution with the analogous zinc(II) compound, has bands at 8500, 13,500, and 21,000 cm^{-1} . For a truly tetrahedral copper(II) complex, the crystal-field theory predicts only one transition, ${}^2T_2 \rightarrow {}^2E$.¹⁰ Nevertheless, Furlani and Morpurgo have shown that the flattening of the co-ordination tetrahedron results in the splitting of both the ground and the excited levels¹¹ so that four transitions are to be expected in the crystal-field region for a salicylideneaminatocopper(II) complex. Hence, both bands at 8500 and 13,500 cm^{-1} , on the basis of their frequencies and of their relatively low intensities (see below for the ϵ values), can be assigned to crystal-field transitions of the copper(II) ion. The other two bands expected may be located below 5000 cm^{-1} or may be hidden by the more intense bands at 20,000 cm^{-1} and beyond (see below) which can probably be attributed to charge-transfer or intra-ligand transition.

TABLE I.

Wave numbers (cm^{-1}) of the peaks in the reflectance spectra of X-substituted bis-(*N*-R-salicylideneaminatocopper(II) complexes.

R	X							
	X = H	3-Me	5-Me	3,4-Benzo	5,6-Benzo	3-Cl	5-Cl	5-NO ₂
Pr ^a	←		14,000—16,000		→			} Planar
Pr ^t					}			
Bu ^t ...	8700—10,000		12,800—13,800		19,200—20,800			} Pseudo-tetrahedral

From the preceding discussion it can be seen that the spectra of the salicylideneiminatocopper(II) complexes provide a means of distinguishing between a planar and a pseudo-tetrahedral structure. They have consequently been used to ascertain the configuration of several complexes with substituted *N*-alkylsalicylideneamines (Table I). All the planar compounds are olive green in colour, and the pseudo-tetrahedral compounds are maroon.

This assignment of structure is supported by the values of the magnetic susceptibility. In fact higher orbital contribution to the moment is expected for a tetrahedral arrangement of the ligands than for a planar one.¹² This prediction has been verified for the Cs_2CuCl_4 complex¹³ which has a slightly distorted tetrahedral structure.¹⁴ Table 2 shows that the salicylideneaminato complexes of copper(II), to which a pseudo-tetrahedral structure has been assigned on the basis of the spectral criterion, have magnetic moments (1.89—1.92 B.M. at room temperature) slightly but consistently higher than those of the planar compounds (1.83—1.86 B.M.).

Stereochemistry of the Complexes in Solution.—The absorption spectra in benzene show unambiguously that the pseudo-tetrahedral structure occurs even in solution in inert solvents. Independently of the nature of the substituent groups in the ring, the n-, iso-, and t-alkyl complexes exhibit three different types of spectrum. The spectrum of the

⁹ Ferguson, *J. Chem. Phys.*, 1961, **34**, 1612.

¹⁰ Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

¹¹ Furlani and Morpurgo, *Theor. Chim. Acta*, 1963, **1**, 102.

¹² Figgis, *Nature*, 1958, **182**, 1568; Griffith, *Trans. Faraday Soc.*, 1958, **54**, 1109.

¹³ Figgis and Harris, *J.*, 1959, 855.

¹⁴ Helmholz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

TABLE 2.

Magnetic data for X-substituted bis-(*N*-*R*-salicylideneaminato)copper(II) complexes.

X	R	$\chi_g \times 10^6$	$\chi_{Cu} \times 10^6$	Temp.	μ_{ef} (B.M.)	Stereochemistry ^a
H	Pr ⁿ ^b	3.18	1447	23°	1.86	Planar
	Pr ⁱ	3.30	1491	28	1.90	Pseudo-tetrahedral
	Bu ⁿ ^b	2.89	1439	23	1.85	Planar ^c
	Bu ^s	3.12	1532	21	1.91	Pseudo-tetrahedral
	Bu ^t	3.12	1533	21	1.91	"
3-Cl	Bu ^t	2.64	1548	22	1.92	"
5-Cl	Pr ⁱ	2.59	1428	21	1.84	Planar
	Bu ^t	2.62	1539	22	1.91	Pseudo-tetrahedral
3,4-Benzo	Bu ^t	2.22	1496	24	1.89	"

^a From reflectance spectra. ^b Data from ref. 7. ^c Ref. 8.

n-propyl complex has a shoulder at 17,000 cm.⁻¹ (ϵ 110) and bands at 27,300 (ϵ 11,500) and 32,600 (ϵ 10,500) cm.⁻¹. Thus, in the solutions, there is only evidence for planar forms. The *t*-butyl complex, on the other hand, has a spectrum with a shoulder at *ca.* 8500 cm.⁻¹ (ϵ 20) and bands at 13,400 (ϵ 260), 20,800 (ϵ 1500), 26,700 (ϵ 10,000), and 30,800 (ϵ 9000) cm.⁻¹. Therefore, in the solutions of the *t*-butyl copper(II) complexes there must be present the same tetrahedral forms which have already been shown to exist in the solid. The isopropyl complexes have spectra intermediate between those of the *n*-propyl and *t*-butyl derivatives.

Further information on the structure of these complexes has been furnished by measurements of the dielectric polarization in benzene solution (Table 3). That all the complexes of the three series have non-zero values of the orientation polarization, indicates the presence of asymmetric forms in the solutions. The polarity increases in the order *n*-propyl < isopropyl < *t*-butyl, indicating that the departure from the *trans*-planar

TABLE 3.

Polarizations and dipole moments for X-substituted bis-(*N*-*R*-salicylideneaminato)metal(II) complexes in benzene at 25°.

Copper(II) complexes						Cobalt(II) complexes						
X	R	∞P_2 (c.c.)	R_D (c.c.)	μ^P ^a (c.c.)	μ (D)	X	R	∞P_2 (c.c.)	R_D (c.c.)	μ^P ^a (c.c.)	μ (D)	
H	Pr ⁿ ^b	202	115	64	1.77	H	Pr ⁱ ^c	594	121	449	4.69	
	Pr ⁱ	290	115	152	2.72		Bu ^s ^c	595	130	439	4.63	
	Bu ⁿ ^b	220	124	71	1.86		Bu ^t ^c	679	130	523	5.05	
	Bu ^s	298	124	149	2.70		3-Cl	Pr ⁱ	1017	131	860	6.48
	Bu ^t	384	124	235	3.38			Bu ^t	1144	140	976	6.90
3-Cl	Pr ⁿ	260	125	110	2.32	5-Cl	Pr ⁱ	609	131	452	4.70	
	Pr ⁱ	365	125	215	3.24		Bu ^t	702	140	534	5.11	
	Bu ^t	529	134	368	4.24	5,6-Benzo	Pr ⁱ	513	155	327	4.00	
5-Cl	Pr ⁿ	238	125	88	2.07	^a Calc. by assuming $\mu^P = 1.20R_D$. ^b Data from ref. 7. ^c Data from ref. 2.						
	Pr ⁱ	336	125	186	3.01							
	Bu ^t	522	134	361	4.20							
5,6-Benzo	Pr ⁱ	264	149	85	2.04							

configuration increases with increasing bulkiness of the alkyl groups. These dielectric polarization data can be compared with those of the analogous cobalt(II) compounds which are pseudo-tetrahedral in structure even in solution.¹⁵

The values of the electric dipole moments of the *t*-butylsalicylideneaminatocopper(II) complexes are only 65–80% of those of the corresponding cobalt(II) complexes. These lower values may be ascribed either to a greater degree of flattening of the tetrahedral

¹⁵ Sacconi, Ciampolini, Maggio, and Cavasino, *Atti Accad. Sci., Lettere ed Arti Palermo*, 1960, **19**, 141 (*Chem. Abs.*, 1962, **56**, 6890); *J. Amer. Chem. Soc.*, 1962, **84**, 3246; Nishikowa, Yamada, and Tsuchida, *Z. Naturforsch.*, 1962, **17b**, 78.

structure of the copper(II) complexes or to the presence of a proportion of non-polar *trans*-planar forms. From a consideration of the steric requirements of the t-butyl group, the first hypothesis seems the more likely.

The values of the orientation polarization for the n-propyl copper(II) complexes are much lower than those of the t-butyl analogues. This fact, together with the lack of the characteristic transition of the pseudo-tetrahedral forms in the absorption spectra, can be explained as follows: (i) the departure from planarity is low (and not necessarily of the pseudo-tetrahedral type);⁷ (ii) the percentage of the pseudo-tetrahedral forms in equilibrium with the *trans*-planar form is very low.

Finally, the electric dipole moments as well as the absorption spectra of the isopropyl copper(II) complexes are intermediate between those of the n- and t-alkyl analogues. These data do not allow us to decide whether, in the solutions of the isopropyl complexes, there is a single species with a very flattened tetrahedral structure or whether there exists a conformational equilibrium with smaller percentage of the pseudo-tetrahedral forms than in the case of the t-butyl compounds.

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