Electron Spin Resonance Studies on the Ligation of Dimeric and Tetrameric Copper(II) Complexes with Schiff Bases in Solution

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The interactions between polymeric copper(II) complexes of Schiff bases and the solvents of varying polar properties and coordination ability have been studied by the ESR method, both in liquid and frozen solutions. The depolymerization of the dimers and tetramers and adduct formation have been observed. On the basis of the ESR hyperfine structure parameters (Cu and N hyperfine tensors) the structure of the adducts has been proposed. The presence of two different types of the adducts with nitrogen coordinating solvents showing the symmetry of distorted tetrahedron or square pyramid respectively has been established. The dependence of the adduct formation on the structure of the copper polymers has been found.

Introduction

In continuation of our studies on ligation of polymeric Cu(II) complexes [1] we have investigated a number of dimeric and tetrameric complexes of Schiff bases.

In this paper we present the results obtained for the dimeric compounds of Schiff bases derived from:

i) benzoylhydrazine and various substituted salicylaldehydes or hydroxyacetophenone

ii) *o*-aminophenol and acetylacetone or benzoylacetone

iii) 3-amino-1-propanol and salicylaldehyde or acetylacetone

and tetrameric complexes of Schiff bases derived from acetylacetone and 1-amino-2-propanol or 2-amino-1-propanol.
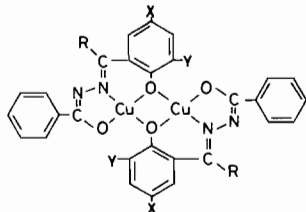
The problem of dissociation and ligation of the polymeric compounds in the polar and non-polar solvents has been studied mainly by the ESR method. The dependence of the adducts formation on the structure of the copper polymers and the properties of the solvents has been analysed.

Experimental

The complexes of (i)-type were prepared as previously described [2]; benzoylhydrazine and benzoylhydrazones were prepared as described in [3].

The complexes of (ii)-type were prepared according to the general method described by Muto [4]; the monomeric adducts of the Cu(TSB)L type, where TSB-tridentate Schiff base, L-monodentate ligand, were prepared by the method described in [1]. The complexes (iii) were described by Sinn [5] and Jeżowska-Trzebiatowska *et al.* [6]. The isomeric tetramers were prepared by the methods given in [7], [8] and [9].

The formulae of the four types of compounds are as follows:

Type	Formula	Substituents			No. of Compound
(i)		R=H	X=H	Y=H	(1)
		R=H	X=Br	Y=H	(2)
		R=H	X=NO$_2$	Y=H	(3)
		R=CH$_3$	X=H	Y=H	(4)
		R=H	X=H	Y=OCH$_3$	(5)

(continued overleaf)

Type	Formula	Substituents	No. of Compound
(ii)		R = CH₃ R = ⟨phenyl⟩	(6) (7)
(iii)			(8)
(iv)			(9)
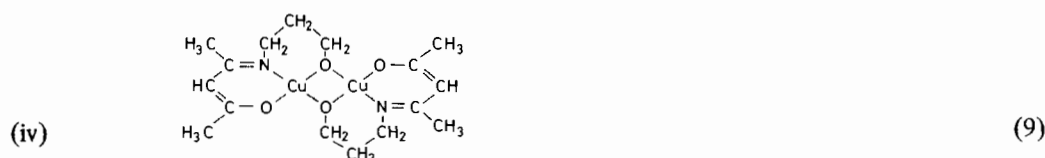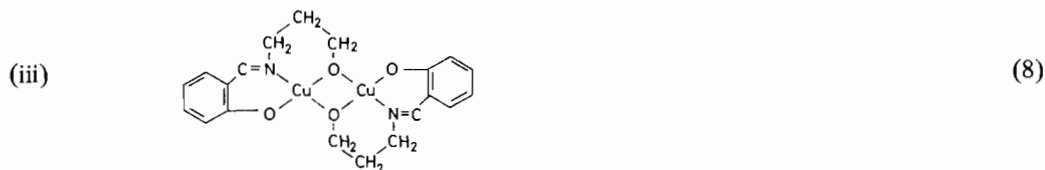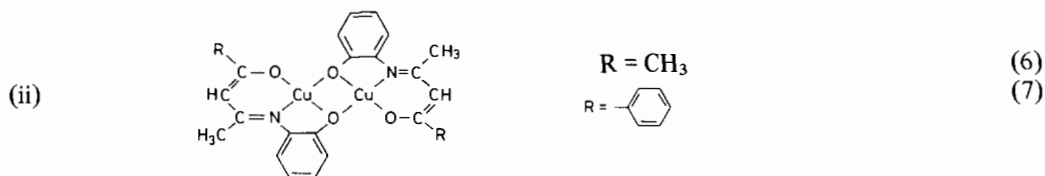
The schematic structure of the two isomeric tetramers and, in particular, the structure of the dimeric fragment of the tetramers is shown below:

	X=H Y=CH₃	(10)
	X=CH₃ Y=H	(11)
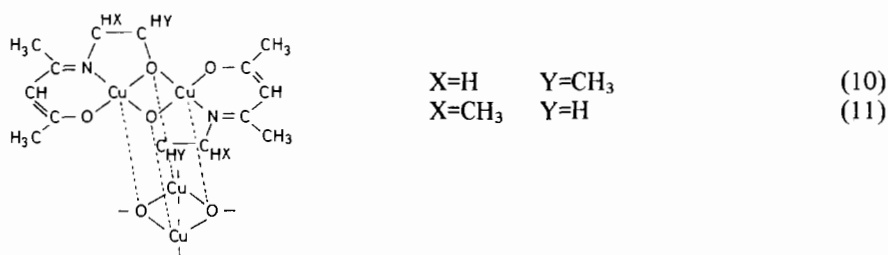
The ESR spectra were recorded on JEOL JES-ME X-band spectrometer using a nuclear magnetometer MJ 110R and microwave frequency meter JES-SH-30X.

Magnetic susceptibility measurements were made by the Gouy method over the temperature range 77–295 K and by the Faraday method over the range 4.2–300 K.

Exchange integrals were calculated using the programme described in [10].

Computer simulations of the ESR spectra with superhyperfine structure were made on a JEOL JEC-6 computer. For these calculations we prepared a special programme taking into account both the ^{63}Cu and ^{65}Cu isotopes present in natural Cu in a 69:31 ratio.

Electronic spectra were recorded on a Beckmann UV 5240 instrument.

Results and Discussion

Properties of the Polymeric Complexes in the Solid Phase

Dimeric Compounds

All the complexes exhibit the strong antiferromagnetic copper-copper interaction. The triplet-singlet separations calculated from the magnetic data are of the order of 400 cm⁻¹ (μ_{RT} = 1.2 BM) for (i) [11] and (ii) [6]; 800 cm⁻¹ (μ_{RT} = 0.4 BM) for (iii) [6].

Tetrameric Complexes

The compounds show both the weak antiferromagnetic and ferromagnetic interactions which result in the spin-quintet ground state (μ_{RT} = 2.0 BM,

TABLE I. ESR Parameters for the Dimeric and Tetrameric Complexes in Polar Solvents. Data for Cu(TSB)L Adducts.[a,b]

No. of Compound	Solvent	A_{iso} (Cu) [G]	g_{iso}	$A_{\parallel}$ (Cu) [G]	$g_{\parallel}$
(1)	THF	78	2.118	193	2.232
(1)	pyridine	72	2.120	178	2.230
(2)	THF	77	2.119	188	2.229
(2)	pyridine	70	2.118		
(3)	THF	76	2.122	181	2.249
(3)	pyridine	72	2.122		
(4)	THF	76	2.114	192	2.220
(4)	dioxane	77	2.117		
(4)	pyridine	74	2.118	184	2.230
(4)	n-propylamine	73	2.117		
(4)	piperidine	76	2.116		
(4)	aniline	83	2.102		
(4)	DMSO	71	2.118	181	2.244
(5)	THF	79	2.117		
(5)	pyridine	71	2.119		
(6)	THF	76	2.119	184	2.260
(6)	pyridine	70	2.116	176	2.241
(6)	DMF	73	2.112	172	2.254
(6)	DMSO	70	2.116	178	2.261
(7)	THF	74	2.116	180	2.259
(7)	pyridine	71	2.117	178	2.245
(10)	pyridine	78	2.108	178	2.236
(11)	pyridine	80	2.108	176	2.237
(11)	DMSO	79	2.109	175	2.240

[a]The A_{iso} and g_{iso} parameters were calculated at 295 K, the $A_{\parallel}$ and $g_{\parallel}$ at 150 K. [b]Simulated A_{iso} (^{14}N) parameter is 15 ± 1 G for all the complexes; anisotropic data for ^{14}N are discussed in the text.
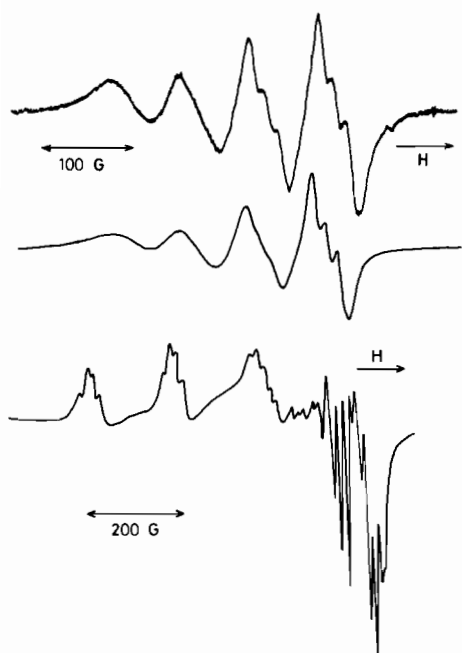

Fig. 1. ESR spectra of the compound (4) dissolved in THF (c = 0.44 mmol/l): a) at 295 K (top — experimental, bottom — simulated); b) at 130 K.

μ_{50K} = 2.4 BM). The exchange integrals for the tetramers are discussed in [9].

Properties of the Polymeric Complexes in Solution

In Non-Polar Solvents

In non-polar solvents (toluene, benzene, xylene, chloroform) the dimeric complexes of the type (ii) exist as dimers. The electronic spectra of the solutions are almost identical with the diffuse reflectance spectra of the solids. No ESR spectra for these solutions are observed. The remaining complexes [(i), (iii) and tetramers] are practically insoluble in non-polar solvents.

In Polar Solvents

The observed coordination effect is connected with dissociation of the polymers:
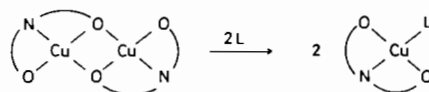
The monomeric adducts can be obtained as crystalline solids as described in [1]. The ESR results for liquid and frozen solutions of the compounds are shown in Table I.
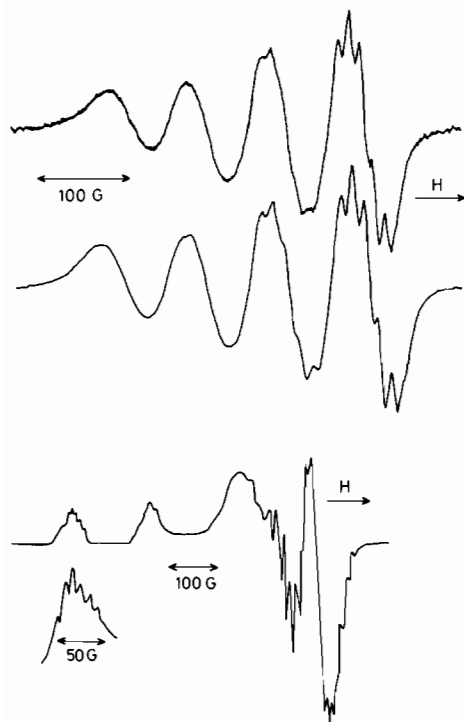
Fig. 2. ESR spectra of the compound (4) dissolved in THF with admixture of pyrazole (pyrazole: Cu molar ratio is 10:1): a) at 295 K (top — experimental, bottom — simulated); b) at 130 K.
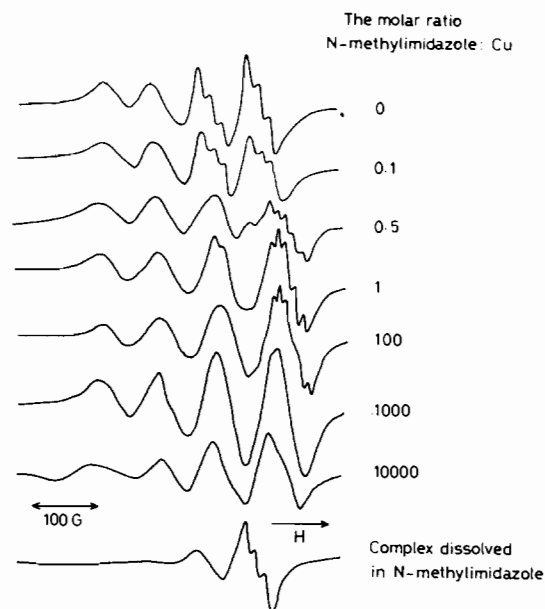

The molar ratio
N-methylimidazole : Cu

Fig. 3. The transition 'three-line' 'five-line' 'three-line' spectrum when N-methylimidazole is gradually added to the THF solution of compound (4). Temperature 295 K. Copper concentration c = 0.44 mmol/l.

All the complexes presented in Table I exhibit similar behaviour; in solution there exist the dissociation products Cu(TSB)L, where TSB = tridentate Schiff base ligand, L = monodentate ligand. The ESR spectra are also similar for the various complexes and exhibit typical superhyperfine splitting due to one ^{14}N atom bound to copper. This atom must be the Schiff base ligand nitrogen because the splitting is the same for the complexes dissolved in both nitrogen and oxygen coordinating solvents. The observed ESR parameters for the complexes are virtually independent of the nature of the solvent (Table I, Fig. 1).

From the frozen solution spectrum of compound (4) in the tetrahydrofuran (the best resolved spectrum, Fig. 1b) we have calculated the iso- and anisotropic parts of the superhyperfine tensor for ^{14}N of Schiff base ligand. If the z axis is perpendicular to the Schiff base plane, around $g_{\parallel}$ will be copper features $A_{\parallel}$ and $A_{\perp}$ for ^{14}N since the principal direction of the ^{14}N tensor is along the Cu—N bond. Hence, the ^{14}N hyperfine coupling on copper perpendicular features is $A_{\parallel}$ (^{14}N).

The parameters obtained on the basis of the analysis of the frozen solution spectrum are: (for ^{14}N nucleus) $A_{\perp}$ = 12.1 G, $A_{\parallel}$ = 15.2 G, A_{av} = 13.1 G.

The correction of the anisotropic part of the tensor, when the point dipole model is used, is A_d = 0.6 G [12]. Thus, the anisotropic part T_{zz} of the tensor is 1.5 G. From these data we can calculate the spin densities ρ on the nitrogen 2s and 2p orbitals; ρ_{2s} = 13.1/550 = 0.024 and ρ_{2p} = 1.5/34.1 = 0.044. The $\rho_{2p}:\rho_{2s}$ ratio is thus 1.85 and the hybridization may be regarded as sp^2.

The ESR spectra revealed that in the solutions of dimers (i), (ii) and the tetramers only the monomeric species of the type Cu(TSB)L are present. The formation of the adducts was confirmed by synthesis and analysis of these compounds (this paper and [1]).

Contrary to the dimers and tetramers described above, the complexes with a near planar copper environment (type (iii)) with a strong pairwise antiferromagnetic interaction, produce no monomers of this type. These complexes dissolve only in the strongly polar solvents (pyridine, n-propylamine) with decomposition accompanied by the rapid complete solvolysis, i.e. for the complexes (8) and (9) dissolved in n-propylamine we observe A_{iso}(Cu) = 61 G, g_{iso} = 2.09; the ESR parameters are identical with those for Cu(II) salts (e.g. CuCl$_2$) in n-propylamine. Obviously the effect of adduct formation must be connected with the symmetry of the polymers and with the nature of the chelate rings (see below).

Some information about the symmetry of the adducts could be obtained from the analysis of the superhyperfine splitting for nitrogen. The ESR

TABLE II. ESR Parameters for the 'five-line' Complexes.[a,b]

No. of Compound	Solvent L	Nitrogen Ligand L₁	A_{iso} (Cu) [G]	g_{iso}	$A_{\parallel}$ (Cu) [G]	$g_{\parallel}$
(1)	THF	pyrazole	87	2.107	196	2.213
(2)	THF	pyrazole	83	2.111	177	2.236
(3)	THF	pyrazole	81	2.112		
(4)	THF	pyridine	87	2.105	186	2.219
(4)	THF	piperidine	89	2.104	200	2.204
(4)	THF	n-propylamine	87	2.105		
(4)	THF	pyrazole	87	2.104	192	2.211
(4)	THF	imidazole	88	2.104		
(4)	THF	1H-indazole	89	2.107		
(5)	THF	pyrazole			183	2.236
(6)	DMSO	pyridine	82	2.114		
(6)	DMSO	piperidine	83	2.105		
(6)	isoamyl alcohol	imidazole	83	2.106	186	2.234
(6)	isoamyl alcohol	pyrazole	84	2.103	185	2.232
(6)	isoamyl alcohol	1H-indazole	84	2.107		
(6)	isoamyl alcohol	pyridine	88	2.107	178	2.242
(6)	isoamyl alcohol	piperidine	87	2.108	186	2.234
(7)	THF	pyridine	89	2.106	182	2.240
(7)	THF	imidazole	88	2.109	186	2.238
(10)	isoamyl alcohol	pyridine	88	2.105		
(11)	isoamyl alcohol	pyridine	89	2.103	186	2.225

[a]The A_{iso} and g_{iso} parameters were calculated at 295 K, the $A_{\parallel}$ and $g_{\parallel}$ at 150 K.   [b]Simulated A_{iso} parameters for ¹⁴N atoms are: 15.5 ± 1 G (for Schiff base nitrogen), 12.0 ± 1 G (for additional ligand L₁). Anisotropic data for ¹⁴N are discussed in the text.

spectra of the compounds (i), (ii) and of the tetramers dissolved in pyridine, N-methylimidazole, n-propylamine and other nitrogen coordinating solvents are identical with the spectra of these compounds in oxygen coordinating solvents; *i.e.* no splitting due to solvent nitrogen is observed (characteristic 'three-line' spectrum, see Fig. 1).

Therefore, the L ligand (solvent molecule) must lie far from the Cu-Schiff base plane and does not interact with the unpaired electron orbital. Hence, the superhyperfine splitting is concerned only with the Schiff base nitrogen.

Unusual Effect of 'Small Amount' of the Nitrogen Coordinating Ligand L

A very interesting feature appears on addition of a small amount of a ligand able to coordinate *via* nitrogen (pyridine, aliphatic amines, azoles *etc.*) to the solutions of the complexes in oxygen coordinating solvents. In this case we observe the superhyperfine structure composed from five lines due to two ¹⁴N nitrogen atoms (characteristic 'five-line' spectrum, see Fig. 2). This spectrum may be observed only under specific conditions — namely in the definite range of ligand L: complex ratio. In Figure 3 is shown the transition: 'three-line' complex → 'five-line' complex → 'three-line' complex at increase of

the L:Cu ratio. The ESR parameters for the 'five-line' complexes are given in Table II.

For the best resolved spectra the simulation of the isotropic superhypefine structure was made. The two coordinated nitrogen atoms were found to be not equivalent as far as superhyperfine structure is concerned. For the complex (4) in tetrahydrofuran when additional nitrogen ligand L₁ = pyrazole showing the best resolved ESR spectrum the parameters of the anisotropic superhyperfine nitrogen structure were calculated. However, only the average values (for the two nitrogen atoms) of the anisotropic part of superhyperfine coupling could be calculated. (Note: the isotropic constants for the two nitrogen atoms vary slightly, see Table II).

The parameters calculated from the frozen solution spectrum are: (for ¹⁴N nuclei) $A_{\perp} = 11.3$ G, $A_{\parallel} = 14.4$ G, $A_{av} = 12.3$ G, $T_{zz} = 1.5$ G (calculations under above-mentioned suppositions). Thus, the densities $\rho_{2s} = 0.022$ and $\rho_{2p} = 0.044$ and the $\rho_{2p}:\rho_{2s} = 2$. The same hybridization sp² must be assumed in this case.

On the basis of the ESR data for the liquid solutions (see Notes in Tables I and II) we have postulated that the splitting A_{iso} about 15 G is characteristic for the Schiff base nitrogen. Thus, the other splitting about 12 G observed for one of the nitrogen

TABLE III. Position of the d—d Transitions in Electronic Absorption Spectra of Some Complexes (in cm^{-1}).

No. of Compound	Solvent			
	pure THF	THF + pyridine (pyridine: Cu ratio 10:1)	THF + pyrazole (pyrazole: Cu ratio 10:1)	pure pyridine
(1)	16100	17500	17600	16000
(2)	16130	16950	17500	15750
(3)	15950	16750	17330	15700
(4)	16460	17400	17860	16200
(5)	15700	17100	17400	15870
(6)	15400	16200	16250	15200
(7)	14600	15100	15100	14500

atoms in a 'five-line' spectrum must be associated with an additional nitrogen ligand L_1. Contrary to the 'three-line' adducts, where only the Schiff base nitrogen gives the superhyperfine splitting, in case of the 'five-line' complexes the splitting due to two nitrogen atoms is observed and therefore the nitrogen coordinating ligand L must lie not far from the plane Cu-Schiff base chelate ring.

The characteristic differences between the 'three-line' and the 'five-line' complexes are observed both in the ESR (see Tables I and II) and electronic spectra (see Table III). The most essential changes when going from 'three-line' to 'five-line' complexes are: a decrease of g_{iso} (about 0.01), an increase of A_{iso}-(Cu) (about 10 G) and the blue shift in the electronic spectra (Table III).

On the basis of the results presented above we have postulated that the complexes giving the 'three-line' spectra are the more stable forms; they possess most probably a distorted tetrahedral structure in both oxygen and nitrogen coordinating solvents. Under the specific conditions described above an additional nitrogen ligand coordinates to the copper ion:
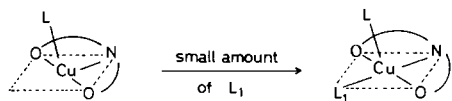
(L = oxygen coordinating ligand, L_1 = nitrogen coordinating ligand).

This additional nitrogen ligand L_1 coordinates in the chelate ring plane, approximately. In such a position the nitrogen atom of L_1 may interact with the unpaired copper electron and the characteristic 'five-line' spectrum appears.

In Figure 3 we start from a solution of compound (4) in the pure oxygen coordinating solvent

(tetrahydrofuran) and the concentration of the nitrogen coordinating ligand L_1 (N-methylimidazole) gradually increases. When the L_1:Cu ratio varies over the range 0.1 to 1 the mixture of 'three-line' and 'five-line' forms is observed as it was proved by simulation of the ESR spectra. When this ratio is within the limits 1 to 100 the pure 'five-line' form is observed. For higher values of the ratio a mixture of the both forms is also observed, and analysed on the basis of the changes of g_{iso} and A_{iso} (Cu) *versus* L_1 concentration. It is noteworthy that the ESR spectra observed at high L_1 concentration (L_1:Cu ratio higher than 100) are poorer resolved: the superhyperfine nitrogen structure was not observed. This phenomenon can be explained assuming a rapid exchange of the ligand L_1 [13]. If the ratio L_1:Cu exceeds 10000 the 'three-line' form appears again. The same forms exist in the pure nitrogen coordinating solvents (pyridine, N-methylimidazole, n-propylamine *etc.*)

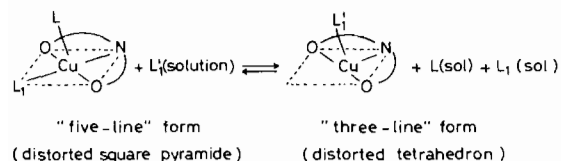The above facts led us to the following conclusions;

1. In pure solvents the most thermodynamically stable form is the tetracoordinate complex of distorted tetrahedral symmetry — Cu(TSB)L — the 'three-line' form.

2. When to the solution of Cu(TSB)L (L-oxygen coordinating ligand) in the solvent L a stoichiometric amount (*versus* Cu) of the nitrogen coordinating ligand L_1 is added, the pentacoordinate complex Cu(TSB)LL$_1$ exists, a 'five-line' form.

3. For lower and much higher concentrations than the stoichiometric one the equilibria between the five-coordinate and four-coordinate forms are observed. We have proposed two mechanisms of the ESR line broadening in the range of high L_1 concentrations:

a) nitrogen ligand L_1 in a planar position is rapidly exchanged Cu(TSB)LL$_1$ + L$_1'$(solution) $\rightleftarrows$ Cu(TSB)LL$_1'$ + L$_1$ (solution).

b) an equilibrium between the 'five-line' and 'three-line' forms exists with a rapid exchange of oxygen and nitrogen ligands in non-planar position

$$\text{O}\overset{\text{L}}{\underset{\text{L}_1}{\text{Cu}}}\text{N} + \text{L}_1'(\text{solution}) \rightleftharpoons \text{O}\overset{\text{L}_1'}{\underset{\text{O}}{\text{Cu}}}\text{N} + \text{L(sol)} + \text{L}_1\text{(sol)}$$

  " five - line " form   " three - line " form
(distorted square pyramide) (distorted tetrahedron)

The second mechanism also explains the existence of the 'three-line' form in the range of very high concentrations of nitrogen coordinating ligand L_1.

The lack of effect described above in the case of the (iii) complexes can be explained by the lowered stability of the six-membered chelate rings Cu-NCCCO without double bonds compared to the six-membered and five-membered rings of aromatic character in (i) and (ii) complexes. This explanation is confirmed by the fact that the complexes with shorter five-membered chelate rings without double bonds which should be more stable than the analogous six-membered rings — namely the described in this paper tetramers (10) and (11), all show the phenomena connected with the 'three-line' and 'five-line' complexes. The tetramers giving this effect are derivatives of α-aminoalcohols while the (iii) complexes, deriving from β-aminoalcohols, decompose in the polar solvents.

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