

Electron Spin Resonance and Electronic Spectral Studies on Ligation of Dimeric Copper(II) Complex by Solvent Molecules

J. JEZIERSKA, B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, Wrocław University, Wrocław, Poland

and G. PETROVA

Department of Inorganic Chemistry, Leningrad University, U.S.S.R.

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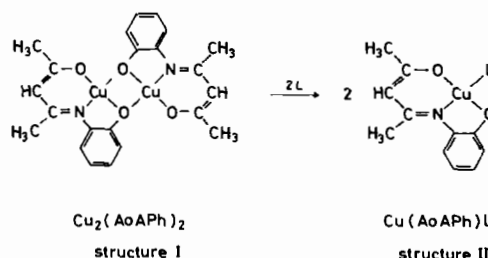
The problem of ligation by various organic solvents was investigated for $\text{Cu}_2(\text{AoAph})_2$, where AoAph represents tridentate Schiff base derived from acetylacetone and *o*-aminophenol. ESR and electronic spectra indicated the dissociation of $\text{Cu}_2(\text{AoAph})_2$ into two adduct complexes $\text{Cu}(\text{AoAph})\text{L}$ under the influence of the polar solvent ($\text{L} = \text{pyridine}$, piperidine, DMF, DMSO etc.). The Schiff base ^{14}N superhyperfine splitting was analysed in the ESR spectra. The adducts were isolated in crystalline form. Thermal analysis of these adducts showed the loss of the L ligand and formation of the dimeric complex in temperature range 330–390 K.

Introduction

The problem of the axial and basal ligation of monomeric Cu(II) complexes of bicoordinate ligands has been the subject of intense experimental conclusions but still very little satisfactory results associated with the dimeric Cu(II) molecules have been achieved.

Dimeric Cu(II) complex with tridentate Schiff base derived from acetylacetone and *o*-aminophenol, $\text{Cu}_2(\text{AoAph})_2$, exhibits in the solid state pairwise antiferromagnetic interactions and presents the ESR spectrum according to $S = 1$ and is characterized by following magnetic parameters: μ_{eff} (295 K) = 1.37 B.M., $J = -298 \text{ cm}^{-1}$, $D = 0.201 \text{ cm}^{-1}$, $E = 0.023 \text{ cm}^{-1}$ [1, 2]. These magnetic properties are indicative of the dimeric structure 'I' confirmed by the X-ray studies [3].

In the case of dimeric Cu(II) complex the problem of solvation should be more complicated than for monomeric Cu(II) complex. Binuclear structure predicts the possibility of dissociation of complex 'I' into two adducts 'II' under the influence of solvent 'L' and the following reaction takes place:



Only a few evidences of that type of dissociation were obtained on the basis of the magnetic and thermal analysis of pyridine adduct of type II [4] and from ESR studies of type I complexes in the solutions [5]. Similar type adducts were also examined for Ni(II) Schiff base complexes [6].

This work is devoted to investigation of the behaviour of $\text{Cu}_2(\text{AoAph})_2$ complex in various organic solvents of different polarity, coordination and hydrogen bonding ability. Furthermore, we report here the characterization studies on isolated crystalline adducts of type II with various L.

Experimental

$\text{Cu}_2(\text{AoAph})_2$ was prepared according to the general method described by Muto [4]. $\text{Cu}(\text{AoAph})$ (piperidine) and $\text{Cu}(\text{AoAph})$ (propylamine) adducts were isolated by dropwise addition of water to the saturated solution of $\text{Cu}_2(\text{AoAph})_2$ in piperidine or propylamine, until precipitation occurred. The resulted adducts were filtered off, washed and stored at a temperature below 285 K. $\text{Cu}(\text{AoAph})$ (DMSO), $\text{Cu}(\text{AoAph})$ (THF) and $\text{Cu}(\text{AoAph})$ (DMF) were prepared by the recrystallization of the dimeric complex from the boiling solutions of the appropriate solvent. The black crystals precipitated on cooling.

Electronic spectra were made on Cary 14 spectrometer (for the solutions) and on Beckman UV 5240

spectrometer (for the solids). IR spectra of the compounds were determined as Nujol or hexachlorobutadiene mulls as well as KBr pellets. Both Perkin Elmer 180 and Perkin Elmer 621 spectrometers were used to obtain the spectra in the range 100–4000 cm^{-1} . ESR measurements were made on JES-ME X-band spectrometer in the temperature range 120–295 K. Proton magnetometer, JES-SH frequencymeter and ESR standards were used. Magnetic susceptibilities were determined by the Gouy method. Thermal analysis data were obtained using MOM Budapest Derivatograph.

Results and Discussion

Electronic and ESR Spectra

The diffuse reflectance spectrum of $\text{Cu}_2(\text{AoAph})_2$ shows in the visible region one broad band at 16000 cm^{-1} , corresponding to the ligand field ('d-d') transitions (Fig. 1a). The band of the same energy exhibit the absorption spectra of toluene, benzene and CCl_4 solutions of the complex, suggesting the dimeric structure of the compound in these solutions; the more polar solvents give red shift of the band maximum (Fig. 1b).

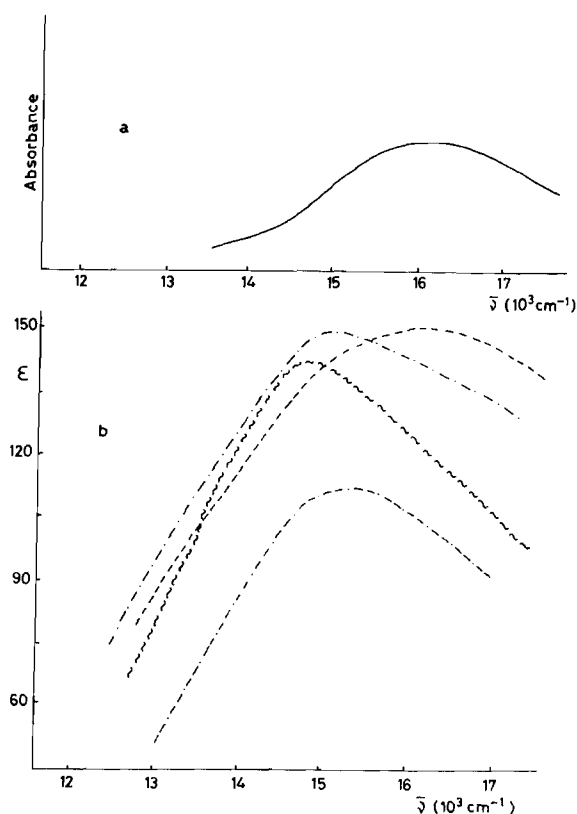


Fig. 1. Electronic spectra of $\text{Cu}_2(\text{AoAph})_2$ a) diffuse reflectance b) -----, in toluene; -.-.- in pyridine; ~~~~~ in DMSO; - - - - in n-propylamine.

The effect is much more pronounced for DMSO and pyridine solutions and could be due to the change of strength and symmetry of the ligand field associated with formation of monomeric adducts II. The tetrahedral distortion of the planar coordination around Cu(II) resulting from bulky effect of molecule L can be expected [7].

The UV spectra of the solutions consist of three intense bands at ca. 31000 cm^{-1} (σ -d ligand-metal charge transfer transition [8]), 26000 cm^{-1} and 37000 cm^{-1} (π - π^* transitions [8]). The energies corresponding to the latter two bands, collected in Table I, reveal the solvent dependence associated with interaction of the solvent molecule with the chelate ring of benzenoidal character. The relationship between the energies of d-d transitions for $\text{Cu}(\text{AoAph})\text{L}$ and dipole moments (μ), donor numbers (DN) and acceptor numbers (AN) of solvents L are illustrated in Fig. 2. The effects caused by donor-acceptor properties of solvents and their polar properties have the same trend and, generally, linear dependence. Figure 2 shows, however, that the comparatively high AN values observed for solvents forming hydrogen bond (e.g. alcohols) do not influence the energies of the d-d transitions of $\text{Cu}(\text{AoAph})\text{L}$ in alcohol solutions.

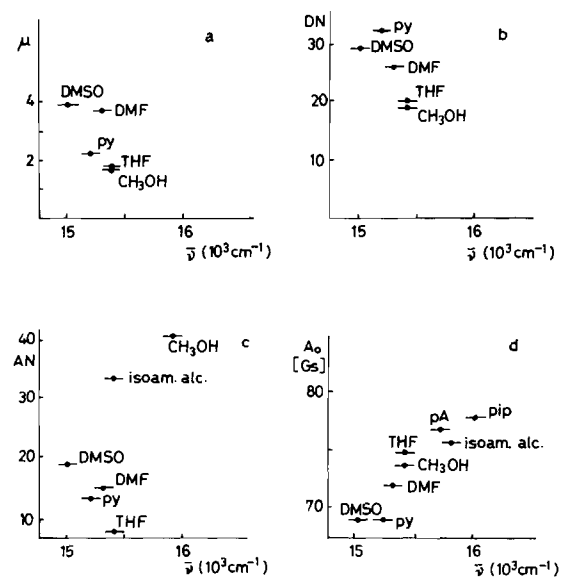


Fig. 2. Relationships between solvent parameters: μ = dipole moment, DN = Donor Number, AN = Acceptor Number [U. Mayer, *Coord. Chem. Rev.*, 21, 159 (1976)] (Figs. 2a, 2b, 2c, respectively); ESR isotropic hyperfine constant A_0 (Fig. 2d) and d-d transition energies for $\text{Cu}(\text{AoAph})\text{L}$.

ESR spectra are helpful for determination of structure of the complex molecules in solutions; the freshly prepared toluene, benzene and CCl_4 solutions of $\text{Cu}_2(\text{AoAph})_2$ do not have any ESR spectra because of the existence of the dimeric molecules in

TABLE I. Electronic Absorption Spectra Parameters for Solutions of $\text{Cu}_2(\text{AoAph})_2$ in Various Solvents.^a

Electronic transitions [10^3 cm^{-1}]	Solvent CCl_4	ben	tol	CHCl_3	pA	pip	THF	py	isoam alc	CH_3OH	DMF	DMSO
d-d ^b	16.0	16.0	16.0	16.3	15.7	16.0	15.4	15.2	15.8	15.4	15.3	15.0
$\pi-\pi^*$ ^c	27.3	27.2	27.2	26.6	25.9	25.9	27.2	26.1	26.7	26.8	26.3	26.0
$\sigma-d$ ^d	30.6	30.7	30.7	30.9	30.3	30.0	30.8	31.0	31.7	31.0	30.2	30.5
$\pi-\pi^*$ ^e	37.2	37.0	37.0	—	36.3	36.3	37.5	—	36.1	36.4	35.7	35.7

^a Abbreviations: ben = Benzene, tol = Toluene, pA = Propylamine, pip = Piperidine, THF = Tetrahydrofuran, py = Pyridine, isoam alc = isoAmyl alcohol, DMF = N,N-Dimethylformamide, DMSO = Dimethyl sulphoxide. ^b Extinction coefficients: 100–150. ^c Extinction coefficients: 11000–15000. ^d Extinction coefficients: 4000–8000. ^e Extinction coefficients: 10000–16000.

the solutions whereas the strong four-line ESR spectra characteristic for monomeric Cu(II) complexes are observed for solutions of $\text{Cu}_2(\text{AoAph})_2$ in polar solvents. Interaction of the unpaired electron with one ^{14}N nucleus of nitrogen coordinated to Cu(II) ion gives rise to superhyperfine structure readily observed for the fourth peak (high-field) of copper hyperfine lines. The superhyperfine structure characteristic for interaction with one ^{14}N nucleus exhibit the spectra of DMSO, DMF, THF, pyridine and piperidine solutions (Fig. 3a). Identity of the splittings for complexes in DMSO and nitrogen coordinating solvents suggests that the observable interaction occurs between the Schiff base nitrogen atom and the unpaired electron.

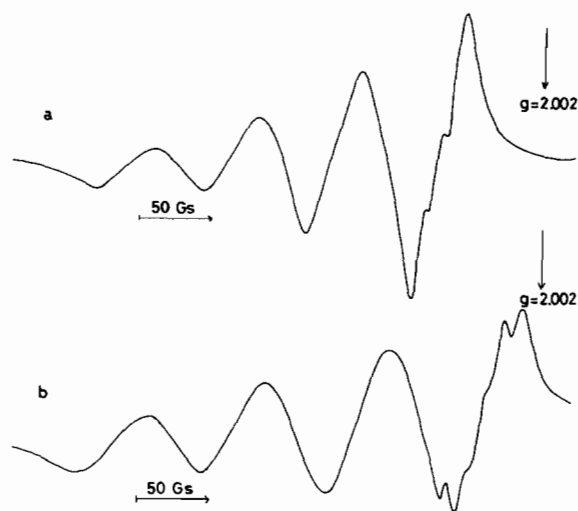


Fig. 3. ESR spectra at 295 K for $\text{Cu}_2(\text{AoAph})_2$ resolved a) in pyridine b) in THF with admixture of pyridine (Cu:py ratio = 1:1).

Addition of equimolar amount of pyridine (in relation to copper complex present in solution) both to the oxygen adduct solutions ($\text{Cu}(\text{AoAph})(\text{THF})$, $\text{Cu}(\text{AoAph})(\text{DMSO})$ etc.) and to solutions of dimeric molecules (in benzene, toluene) yields other type

nitrogen adducts. Analysis of ^{14}N superhyperfine splittings (Fig. 3b) shows that two equivalent nitrogen atoms are coordinated to Cu in the adduct molecule, moreover, the A_0 (Cu) parameter increases to 86 Gs. It may be concluded that structure of the adduct is nearly square planar [9]. ESR parameters for $\text{Cu}_2(\text{AoAph})_2$ resolved in various polar solvents are collected in Table II.

TABLE II. ESR Parameters for Solutions of $\text{Cu}(\text{AoAph})\text{L}$.^a

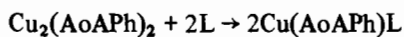
L	A_0 [Gs]	g_0	A_N [Gs]	$A_{ }$ [Gs]	$g_{ }$
piperidine	79	2.119	10.5	175	2.250
n-propylamine	78	2.117	—	174	2.250
isoamyl alcohol	77	2.110	12	182	2.234
THF	76	2.119	11	184	2.260
CH_3OH	74	2.120	—	181	2.241
DMF	73	2.112	12.5	172	2.254
DMSO	70	2.116	13	178	2.261
pyridine	70	2.116	12.5	176	2.241

^a A_0 and g_0 denote isotropic hyperfine constant and isotropic g parameter, respectively. They were calculated from liquid solution ESR spectra in second order of perturbation theory. The parallel components, $A_{||}$ i $g_{||}$, were determined from the anisotropic ESR spectra of frozen solutions.

It should be added that the remarkable linear relationship exists between the A_0 parameters observed for the first type of adducts and the energy of the d-d transitions in the range 15000–16000 cm^{-1} (Fig. 2d).

Investigations of Solid Adducts

The ESR and electronic spectra indicated that in presence of solvent L the reaction



is responsible for the dissociation of the dimeric molecule and the $\text{Cu}(\text{AoAph})\text{L}$ adducts are present in solution. However, since no solid adducts of type II

TABLE III. Analytical Data and Magnetic Moments for Cu(AoAph)L adducts.

Complex	Colour	Calcd. %			Found %			μ [B.M.]	T [K]
		C	H	N	C	H	N		
Cu ₂ (AoAph) ₂	green	52.00	4.39	5.54	52.20	4.35	5.52	1.30	298
Cu(AoAph)(py)	black	57.91	4.86	8.44	58.10	4.80	8.52	1.79	287
Cu(AoAph)(pip)	black	57.04	6.28	8.31	57.16	6.40	8.17	1.86	294
Cu(AoAph)(pA)	black	53.91	6.46	8.98	53.80	6.50	8.72	1.72 ^a	300
Cu(AoAph)(DMSO)	black	47.19	5.18	4.23	47.42	5.25	3.95	1.68 ^a	297

^aThe lowering of the magnetic moments is caused by some admixture of the dimeric compound formed as the result of decomposition of the adducts during preparation of the samples for the magnetic measurements.

other those with L = pyridine have been reported, we first attempted to prepare the complexes with L = piperidine, propylamine, DMSO, DMF, THF. The adducts were isolated from solutions as black crystalline solids. Their diffuse reflectance spectra showed only one band in visible region. Since the positions of the band are similar to those observed in absorption spectra of the corresponding solutions, it is the additional support of domination of monoadducts of type II in solutions. Magnetic moments of all solid adducts are consistent with paramagnetism of their monomeric structure (Table III). The monoadducts exhibit rather low thermal stability, especially the L = DMF and L = THF adducts decompose partially at room temperature; they are excluded from our discussion. For the remaining compounds the results of elementary analysis presented in Table III, confirmed the general molecular formula Cu(AoAph)L. The thermal analysis results (Fig. 4) indicate the stepwise decomposition of the adducts. The first step (α . 330–390 K), associated with the loss of molecule L, results in formation of the dimeric molecule Cu₂(AoAph)₂.

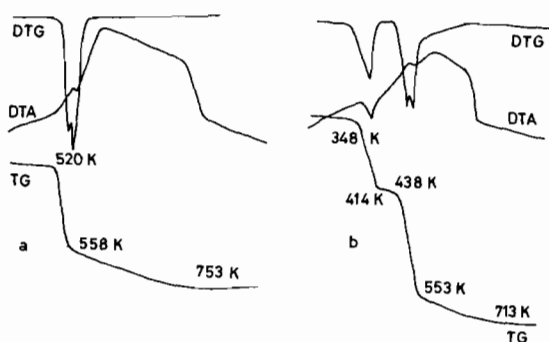


Fig. 4. Thermal analysis results of a) Cu₂(AoAph)₂ dimer b) Cu(AoAph)piperidine adduct.

The temperature range of this process (Table IV) and small *endo*-effect estimated on the basis of the plane under the DTA curve are quite markedly dependent on the molecule L. The *endo*-effect decreases in the order

TABLE IV. Thermal Decomposition Data for Cu(AoAph)L Adducts (first step).

Complex	Weight loss, %		Temperature range [K]
	Calcd.	Found	
Cu(AoAph)(py)	23.8	23.6	353–398
Cu(AoAph)(pip)	25.3	25.4	343–414
Cu(AoAph)(pA)	18.0	18.1	333–403
Cu(AoAph)(DMSO) ^a	23.6	19.0	303–403

^aPartially decomposed at room temperature.

Cu(AoAph)(piperidine) > Cu(AoAph)(pyridine) > Cu(AoAph)(propylamine) > Cu(AoAph)(DMSO), what suggest the decrease of Cu–L bond strength. Decomposition of the dimeric complex into CuO and Cu₂O at higher temperatures was confirmed by thermal analysis and X-ray analysis of the decomposition products.

The IR spectra of monoadducts revealed that the change of molecule L does not have a significant effect on vibrational frequencies of Schiff base ligand bonds. The apparent shifts accompanying the variation of L are observed in the region characteristic for the metal–ligand vibrations [10–12]. Vibrational frequencies of Cu–N_L and Cu–O_{chel} for the monoadducts are presented in Table V and Fig. 5. The decrease of Cu–N_L vibrational frequency in the order L = piperidine > L = propylamine > L = pyridine corresponds to the decrease of the basicity of the molecule L.

ESR spectra of the solid adducts resolved in polar solvents are identical with those obtained for solutions of Cu₂(AoAph)₂ in the same solvents which confirmed the dissociation of the dimer and presence of Cu(AoAph)L adducts in both solutions.

Acknowledgement

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TABLE V. Position of IR Bands Assigned to the Cu-N_L and Cu-O_{chel} Vibrational Frequencies.

Complex	$\nu_{\text{Cu-O}_{\text{chel}}}$ ^a [cm ⁻¹]	$\nu_{\text{Cu-N}_{\text{L}}}$ ^b [cm ⁻¹]	pK _b ^c
Cu(AoAph)(pip)	500	312	2.80
Cu(AoAph)(pA)	512	300	4.26
Cu(AoAph)(py)	515	285	8.77

^aO_{chel} represents oxygen atom of the chelate ring. ^bN_L represents nitrogen atom of the solvent molecule. ^cFor nitrogen base (L).

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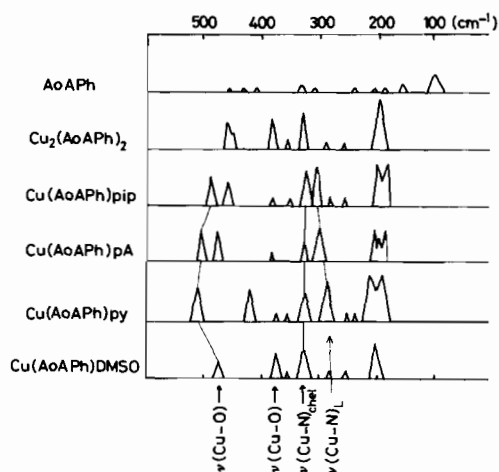


Fig. 5. IR spectra (500–100 cm⁻¹) of AoAph free ligand, Cu₂(AoAph)₂ dimer and Cu(AoAph)L adducts.

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