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Electronic and Esr Spectra of some Ternary Copper(II) Complexes Formed by Bidentate (O,N) Ligands

DOUGLAS X. WEST

Department of Chemistry, Illinois State University, Normal Ill. 61761, U.S.A.

and M. PALANIANDAVAR

Department of Inorganic Chemistry, Madurai Kamaraj University, Madurai 625 021, India

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Mixed ligand complexes of copper(II) involving two bidentate ligands have been increasingly studied [1–6]. Such complexes may be good models for protein bound metals since they contain donor groups such as phenolic and carboxylic oxygens as well as imino nitrogen donors [7]. One of us [8] has previously communicated the preparation and some of the physical properties of some of these complexes.

We report here the solid state electronic and esr spectra as well as the solution spectra recorded in chloroform of some mixed ligand $Cu(ON)_2$ complexes. The various ON donors employed in this study are 8-oxyquinoline (oxine), salicylimine (salimine), salicyloxime (oxime) and salicylphenylhydrazone (salphn). Of interest is the variation of the steric requirements of the ligands and, consequently, the distortion of the CuO_2N_2 chromophore from planar symmetry. Further, we are interested in making a judgement about the extent of interaction between adjacent Cu(II) ions in the solid state [9]. We have previously communicated our results on a similar series of CuO_4 [10] and CuO_3N [11] ternary complexes.

Experimental

The spectral measurements were carried out as described previously [10].

Results and Discussion

Both the solid state and solution electronic spectral data are included in Table I. The solid state and chloroform solution Esr data at room and liquid nitrogen temperatures are compiled in Tables II and III, respectively.

There appears to be little difference in the energy of the d–d maxima in comparing the chloroform spectra to the reflectance spectra of these substances. The resolution of the low-energy shoulder in some of the solution spectra is more than likely due to clarity of the spectra in this matrix rather than a change in nature of the Cu(II) complexes. Further, the similarity of d–d maxima would suggest that in the solid state these species can be treated as mononuclear Cu(II) chromophores. This lack of interaction is in contrast to the CuO_4 complexes [10], and is likely due to the stronger in-plane bonding provided by the

TABLE I. Solid State Reflectance and Chloroform Solution Electronic Bands (kK) for Some Mixed Ligand CuO_2N_2 Chromophores.

Compound	Color	Solid Reflectance	$CHCl_3$
Cu(oxine)(salimine)	yellow green	17.54	17.54, 15.82sh
Cu(oxine)(salphn)	beige	14.93	15.43, 14.51sh
Cu(oxine)(oxime)	yellow green	17.54, 14.93sh	17.86, 15.15sh
Cu(oxime)(salimine)	dull green	16.67	17.54, 15.67sh
Cu(oxime)(salphn)	beige	15.38	15.15

TABLE II. Powder Esr Spectra for Mixed Ligand CuO_2N_2 Chromophores.

Compound	Room Temp			77 K		
	$g_{\parallel}$	$g_{\perp}$	g_{av}	$g_{\parallel}$	$g_{\perp}$	g_{av}
Cu(oxine)(salimine)	2.156	2.060	2.092	2.167	2.059	2.095
Cu(oxine)(salphn)[a]	2.176	2.052	2.093	2.176	2.052	2.093
Cu(oxine)(oxime)	2.167	2.055	2.092	2.165	2.058	2.094
Cu(oxime)(salimine)	2.163	2.067	2.099	2.153	2.070	2.098
Cu(oxime)(salphn)	2.177	2.086 2.041	2.101	2.176	2.088 2.042	2.102

[a] Features also present which may be due to a dimeric species.

TABLE III. Solution ($CHCl_3$) Esr Parameters.

Compound	Room Temp.[a]		77 K[a]				
	g_0	A_0	$g_\parallel$	$g_\perp$	g_{av}	$A_\parallel$	$A_\perp$[b]
Cu(oxine)(salimine)	2.104	84	2.227	2.046	2.106	178	37
Cu(oxine)(salphn)	2.104	84	2.241	2.051	2.114	176	38
Cu(oxine)(oxime)	2.100	88	2.235	2.055	2.115	178	43
Cu(oxime)(salimine)	2.098	85	2.215	2.050	2.105	189	33
Cu(oxime)(salphn)[c]	2.096	89	2.223	2.051	2.108	182	43

[a] A-values expressed in gauss. [b] Calculated from $A_0(RT) = \frac{A_\parallel + 2A_\perp}{3}$. [c] In CH_3CN.

TABLE IV. Solution Spectra Assignments and Covalency Parameters for Some Ternary Copper(II) Complexes.

Compound	$g_\parallel$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$k_\parallel$	$g_\perp$	$^2B_{1g} \rightarrow {}^2E_g$	$k_\perp$
Cu(oxine)(salimine)	2.227	15.82	0.736	2.046	17.54	0.698
Cu(oxine)(salphn)	2.241	14.51	0.727	2.051	15.43	0.689
Cu(oxine)(oxime)	2.235	15.15	0.733	2.055	17.86	0.770
Cu(oxime)(salimine)	2.215	15.67	0.713	2.050	17.54	0.727
Cu(oxime)(salphn)	2.223	15.15	0.714	2.051	15.15	0.683

O_2N_2 donor atoms. The stronger ligand field is indicated by the higher energy of the d–d maxima which for these five solids average 16.41 kK, for the four CuO_3N solids, 14.99 kK [11] and for the seven CuO_4 solids, 13.10 kK [10]. The order of ligand field strength based on the data in Table I is oxine > salimine > oxime ≫ salphn. The difference between the first two is small and the order appeared to be reversed with the CuO_3N complexes [11].

Inspection of the Esr data in the solid state and in solutions also shows no major difference in the room temperature values of g (*i.e.*, g_{av} and g_0 in Tables II and III, respectively). This is consistent with the results of the electronic spectra discussed earlier. Also, there is no significant change in g's upon cooling the samples in either matrix.

There is little difference in the Esr spectra of the five samples except as noted below. The room temperature spectrum of solid Cu(oxine)(salphn) shows features which may be due to a dimeric species. Unfortunately, the signal is too weak to allow us to detect any spectral features at g *ca.* 4. The Cu(oxime)(salphn) solid yields a non-axial spectrum suggesting some rhombic distortion from square planar symmetry, probably due to the greater steric requirements of the salphn as well as oxime. We were required to go to a more polar solvent (*i.e.*, CH_3CN) in order to achieve the required Esr spectral intensity for this substance, but there is no significant g-value difference in solution except that the spectrum is axial. The more polar solvent could have been required because of some interaction between Cu(II) centers which could also contribute to the rhombic character of the solid spectrum.

The $A_\parallel$ values are well within the range suggested for CuO_2N_2 chromophores [12], but the $g_\parallel$ values are above or near the upper limit of 2.23. In Table IV we show the covalency parameters calculated [13] from the solution experiments. The values calculated are consistent with the ligands being primarily σ-bonded in that the values are near the 0.77 value considered for pure σ-bonding [13]. What π-bonding is present is likely to be 'out-of-plane' because $k_\parallel$ is generally greater than $k_\perp$.

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