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

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One of us [1] has previously communicated the preparation and some of the physical properties of the mixed ligand complexes CuLL′. L is a bidentate ligand with two oxygen donor atoms and L′ is a bidentate ligand with an oxygen and a nitrogen donor atom. The various L's are trichloroacetate (TCA), acetylacetonate (ACAC) and salicylaldehyde (SAL) while the L's are 8-oxyquinoline (oxine) and salicylimine (salimine). Therefore, each of the complexes is a CuO_3N chromophore.

We report here the solid state electronic and ESR spectra as well as the solution spectra recorded in chloroform. Of interest is the variation of the steric requirements of the ligands and, consequently, the distortion of the CuO_3N chromophore from planar symmetry. Further, we are interested in establishing the extent of interaction between adjacent Cu(II) ions in the solid state [2]. We have already reported our results on a similar series of ternary CuO_4 complexes [3].

Experimental

The spectral measurements were carried out as described previously [3].

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 presented in Tables II and III, respectively.

Magnetic moment measurements suggest that these complexes are essentially monomeric [1]. Additionally, the infrared spectrum confirmed that TCA bonds to the Cu(II) center as a symmetrical bidentate ligand [3]. It is thought that the increased residual charge that TCA imparts to a Cu(II) ion compared to acetate ion [4] increases Cu–Cu repulsion and reduces the possibility of dimer formation by Cu(II) centers complexed by TCA.

However, a significant change in the d–d spectrum of a complex in solution from its solid state spectrum may be due to a loss of interaction between Cu(II) centers among a number of other factors. On this basis, only Cu(ACAC)(salimine) appears not to undergo a significant change in its solution spectrum. For the other three substances there is a blue shift in the d–d maxima in the $CHCl_3$ spectra. A shift in this direction, although attributable to a number of factors, is most likely due to a loss of axial bonding that is present in the solid state. The axial bonding must involve ligands from other Cu(II) centers and the change in the charge transfer bands is supportive of this suggestion. Bridging oxygen donors generally show an absorption band in the 23.0–26.0 kK region which is attributed to a charge transfer transition from the bridging oxygen to Cu(II) [5]. A shift to

TABLE I. Solid State Reflectance and Chloroform Solution Electronic Spectral Assignments (kK) for Some Mixed Ligand CuO_3N Chromophores.

Compound	Color	Solid State		$CHCl_3$	
		C.T.	d–d	C.T.	d–d
Cu(TCA)(oxine)	blue green	24.33	15.75sh, 13.61	24.15	14.22
Cu(ACAC)(oxine)	yellow green	24.69	14.97	24.75	16.31
Cu(SAL)(oxine)	mustard yellow	22.73	14.71	25.25	15.50
Cu(ACAC)(salimine)	dark olive green	24.27	16.67	27.10	16.53

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TABLE II. Powder ESR Spectra for Mixed Ligand CuO_3N Chromophores.

Compound	Room Temp.			77 K		
	$g_\parallel$	$g_\perp$	g_{av}	$g_\parallel$	$g_\perp$	g_{av}
Cu(TCA)(oxine)		$g_i = 2.106$			$g_i = 2.100$	
Cu(ACAC)(oxine)		$g_i = 2.112$			$g_i = 2.120$	
Cu(SAL)(oxine)	2.174	2.056	2.095	2.184	2.052	2.096
Cu(ACAC)(salimine)	2.158	2.069	2.099	2.164	2.067	2.099

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

Compound	Room Temp.[a]			77 K[a]			
	g_o	A_o	g	g	g_{av}	A	A^c
Cu(TCA)(oxine)	2.131	70	2.277	2.064	2.135	162	24
Cu(ACAC)(oxine)[b]	2.112	83	2.252	2.046	2.115	182	34
Cu(SAL)(oxine)[b]	2.110	78	2.250	2.050	2.117	176	29
Cu(ACAC)(salimine)[b]	2.102	81	2.227	2.050	2.109	188	28

[a] A values in gauss. [b] A(N) *ca.* 8G. [c] Calculated from $A_o(RT) = (A_\parallel + 2A_\perp)/3$.

higher energy occurs when the oxygen atom is non-bridging as can be seen in Table I.

If the solution spectra represent 4-coordinate Cu(II), then we see that ACAC > SAL > TCA and salimine > oxine in terms of Dq. The former trend is identical to our observation with the CuO_4 series [3]. We susggested that TCA promoted tetrahedral distortion and the energy of the d–d band of 14.22 kK is low compared to the other CuO_3N chromophores. The rigid ACAC ligand with its planar ring is among the strongest dioxygen donors known and its d–d bands reflect this.

Inspection of the ESR data in the solid state and in solution shows no significant difference in the room temperature values of g (*i.e.*, g_o and g_{av} in Tables II and III, respectively) for Cu(ACAC)(oxine) and Cu(ACAC)(salimine). Also, there is no significant change in g upon cooling the samples in either case. The broad isotropic lines in the powder spectra of the first two entries in Table II indicate that the samples are not sufficiently dilute magnetically.

Assuming that the $CHCl_3$ solution spectra represent 4-coordinate species, the ESR data agree with the electronic data. Values for g_o, A_o, $g_\parallel$ and $A_\parallel$ are in agreement with the ligand strength order of ACAC > SAL > TCA and salimine > oxine. Additionally, higher A-values, lower g-values and higher $\nu_{d\text{–}d}$ energies are found for these CuO_3N chromophores than the previously studied CuO_4 chromophores [3]. The greater ligand of salimine compared to oxine is probably due to its 6-membered chelate ring compared to oxine's 5-membered ring. While the latter generally has the entire ligand in the same plane [6], the former can bend much of the ligand out of the plane [7] and reduce steric interaction. Additionally, it has been postulated on ligand-field grounds that increased electron density on the chelate ring increases the tendency towards a tetrahedral configuration [8]. While spectral differences (*i.e.*, lower A-values and energies for $\nu_{d\text{–}d}$ as well as higher g-values) in the solid state are likely due to additional coordination sites being occupied, these same changes in the solutions of 4-coordinate complexes may be indicative of tetrahedral distortion.

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