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Electronic and ESR Spectra of Some Copper(II) Complexes Formed by Two Different Bidentate Dioxygen Donors

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*The solid state and solution ($CHCl_3$) electronic and electron spin resonance spectra of seven mixed ligand copper(II) compounds have been measured. Five of the compounds contain a trichloroacetato (TCA) ligand bound in a bidentate manner with the two other copper(II) sites being occupied by another O_2 donor (*e.g.*, acac). The two remaining Cu(II) compounds are combinations of the latter ligands. The results show that TCA seems to promote a tetrahedral distortion (*i.e.*, D_{2d}), particularly with ligands of some steric bulk. The high electron density in the chelate ring is cited as the principal reason for this distortion.*

Introduction

One of us [1] has previously communicated the preparation of the mixed ligand complexes CuLL′ where both L and L′ are potential bidentate ligands having two oxygen donor atoms. The principle ligand of interest was trichloroacetate ion (TCA) and the other ligands employed were acetylacetonate (acac), ethylacetoacetate (EAA), salicylaldehyde (SAL), *o*-hydroxyacetophenone (OHAP) and *o*-hydroxycrotonophenone (CROT). Magnetic measurements suggested that all but one of the complexes were essentially monomeric [1]. Additionally, the infrared spectra confirmed that TCA bonds to the Cu(II) center in these complexes as a symmetrical, bidentate chelating agent [2].

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 Cu(II) centers. Further, we are interested in establishing the extent of bridging ligand character in these complexes as has been reported for Cu(TCA)(SAL) [3].

Experimental

The solution electronic spectra were recorded on a Beckman Acta VI Spectrophotometer while reflectance measurements were made of the solids with a Perkin-Elmer 330 Spectrophotometer equipped with an integrating sphere. The ESR spectra were recorded on a Varian E104 Spectrometer. All spectra were calibrated with DPPH (g = 2.0036).

Results and Discussion

In Table I the details of the electronic spectra of the solids are presented. The powder ESR spectral parameters recorded at both room and liquid nitrogen temperature are tabulated in Table II. The solution ($CHCl_3$) electronic and ESR spectral data are reported in Tables III and IV, respectively.

TABLE I. Solid State Reflectance Bands (kK) for Mixed Ligand Copper(II) Complexes.

Compound	Color	C.T. Bands	d–d Bands
Cu(TCA)(acac)	aqua	24.04sh	15.63sh, 13.32
Cu(TCA)(EAA)	pale green	22.03sh	13.55sh, 10.81
Cu(TCA)(SAL)	gold	22.17sh	11.16
Cu(TCA)(OHAP)	gold	26.81sh, 21.14sh	13.18, 11.29sh
Cu(TCA)(CROT)	green	25.32sh, 20.92sh	11.47, 10.00sh
Cu(acac)(SAL)	olive green	27.03sh, 23.26sh	17.27, 14.62sh
Cu(OHAP)(SAL)	olive green	25.64sh, 23.81sh	17.00sh, 14.43

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Table II. Powder ESR spectra for Mixed Ligand Copper(II) Complexes.

	Room temp.			77 K		
Compound	$g_{\parallel}$	$g_{\perp}$	g_{ave}	$g_{\parallel}$	$g_{\perp}$	g_{ave}
Cu(TCA)(acac)		g_{iso} =	2.105		g_{iso} =	2.103
Cu(TCA)(EAA)		g_{iso} =	2.157		g_{iso} =	2.162
Cu(TCA)(SAL)	2.270	2.083	2.145	2.264	2.069	2.134
Cu(TCA)(OHAP)		g_{iso} =	2.155	2.264	2.074	2.137
Cu(TCA)(CROT)	g_3 = 2.391 g_1 = 2.059	g_2 = 2.107	2.186	g_3 = 2.367 g_1 = 2.057	g_2= 2.110	2.178
Cu(acac)(SAL)		g_{iso} =	2.096		g_{iso} =	2.101
Cu(OHAP)(SAL)		g_{iso} =	2.109		g_{iso} =	2.121

TABLE III. Solution ($CHCl_3$) d–d Band Assignments (kK).

Compound	d–d Bands
Cu(TCA)(acac)	14.29, 13.30sh
Cu(TCA)(EAA)	13.61, 12.99sh
Cu(TCA)(SAL)[a]	13.11
Cu(TCA)(OHAP)	13.28, 12.64sh
Cu(TCA)(CROT)	12.50sh, 11.49
Cu(acac)(SAL)	17.86sh, 1506
Cu(OHAP)(SAL)	16.56sh, 14.93

[a] Color change on dissolution (*i.e.*, gold → green).

As opposed to the dimeric copper(II) acetate, $Cu(TCA)_2$ is considered to be monomeric [4]. It is thought that the increased residual charge that is left on the Cu(II) ion in $Cu(TCA)_2$ causes the copper(II) acetate structure to be destabilized through Cu-Cu repulsion [4]. Therefore, among the mixed complexes involving TCA, the most likely species to be dimeric should be the complexes with the poorer donating ligands, providing steric factors preventing the dimer formation are not present. Of the complexes being considered here Cu(TCA)(SAL) has been suggested to have a polymeric structure based on a sub-normal magnetic moment [3].

Inspection of the reflectance data in Table I shows all compounds have a band in the 20–25 kK region of their spectra which would be expected to give the compounds a yellowish tinge. However, in some cases the position of the d–d band(s) diminishes the importance of yellow in the apparent color (*e.g.*, Cu(TCA)(acac)). From the energies shown in Table I it would appear that the lowest energy $O(\pi) \rightarrow Cu(II)$ band is due to the TCA ligand when we have been able to observe two bands. One basis for this suggestion is that neither of the latter two compounds in Table I have a band at as low an energy as the complexes involving TCA. Also, our earlier statements regarding the lack of a dimeric structure for $Cu(TCA)_2$ might suggest a relatively low energy CT band involving TCA. In the case of the solids having a single band, we expect that this is a combination of at least two bands and the band originating with the TCA ligand would comprise the lower energy portion of the composite band.

In the solid state these compounds generally show at least one shoulder on the d–d envelope and examples with the shoulder at both higher and lower energies with respect to the main band have been found. Of significance is that these compounds may have varying amounts of axial coordination from ligands on other Cu(II) centers as suggested for Cu(TCA)(SAL) [1, 3]. That is, some or all of these complexes could be tetragonal involving four strong bonds and two weaker bonds from ligands attached to adjacent Cu(II) ions. A steric effect, in addition to affecting the extent of axial coordination, also can cause a distortion toward tetrahedral of essentially 4-coordinate complexes. Shifts to longer wavelength of the d–d band maxima are therefore expected with both increased axial coordination and tetrahedral distortion.

The energy of the d–d bands for the first five entries in Table I decreases with increasing steric requirements of the ligand suggesting tetrahedral distortion to be of greater importance. For example, acac would be expected to supply the least steric hindrance of the five ligands while most certainly CROT would be expected to provide the most. This is even more evident in Table III where the bands are more representative of a 4-coordinate complex since any bridging from ligands on other Cu(II) centers would be minimized. The decreases in the energy of the chloroform solution bands in comparison with the solid state bands are probably a measure of tetrahedral distortion while increases might be a measure of axial coordination. The color change of Cu(TCA)(acac) with the corresponding large change in the d–d maxima suggest that axial coordination is greatest with this solid.

The higher energy for the d–d maxima of the two complexes not involving TCA would seem to suggest

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

	Room temp.[a]				77 K[a]			
Compound	g_o	A_o	$g_\parallel$	$g_\perp$	g_{ave}	$A_\parallel$	$A_\perp$	A_{ave}
Cu(TCA)(acac)	2.121	72	2.277	2.066	2.136	170	30	77
Cu(TCA)(EAA)	2.146	66	2.402	2.069	2.180	114	42[b]	
Cu(TCA)(SAL)	2.169	43	2.390	2.071	2.177	123	3[b]	
Cu(TCA)(OHAP)	2.174	43	2.397	2.071	2.179	113	8[b]	
Cu(TCA)(CROT)	2.172	44	2.393	2.074	2.180	120	6[b]	
Cu(acac)(SAL)	2.121	74	2.281	2.037	2.118	158	31	73
Cu(OHAP)(SAL)	2.127	57	2.289	2.063	2.138	143	27	66

[a] Hyperfine coupling constants (A) in gauss. [b] Calculated from $A_o(RT) = (A_\parallel + 2A_\perp)/3$.

TABLE V. 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(TCA)(acac)	2.277	13.30	0.746	2.066	14.29	0.755
Cu(TCA)(EAA)	2.402	12.99	0.888	2.069	13.61	0.753
Cu(TCA)(SAL)	2.390	13.11	0.879	2.071	13.11	0.750
Cu(TCA)(OHAP)	2.397	12.64	0.870	2.071	13.28	0.755
Cu(TCA)(CROT)	2.393	11.49	0.826	2.074	12.50	0.747
Cu(acac)(SAL)	2.281	15.06	0.799	2.037	17.86	0.632
Cu(OHAP)(SAL)	2.289	14.93	0.807	2.063	16.56	0.794

that TCA promotes tetrahedral distortion. The energies for the main bands of these two compounds are in good agreement with those reported previously [5] for these two substances but no high energy shoulders were reported in earlier work.

Inspection of the ESR parameters in Table II which were obtained with powdered samples shows that many have an isotropic line indicating that the samples are not sufficiently dilute magnetically. Only with the larger ligands whose steric requirements are sufficient to magnetically dilute the samples are we able to resolve the spectra. In the case of Cu(TCA)(SAL) additional spectral features which may be due to dimeric Cu(II)–Cu(II) interactions are observed at g *ca.* 2.17, but the signal is of insufficient strength to study in the $\Delta M = 2$ region of the spectrum.

The existence of an orthorhombic spectrum for Cu(TCA)(CROT) is probably an indication of a significant tetrahedral distortion. Some flattening occurs at lower temperature with the decrease in the magnitude of g_3 and therefore g_{av}. The change in temperature has a similar affect on the other two similar compounds (*i.e.*, Cu(TCA)(SAL) and Cu(TCA)(OHAP)). With the two latter entries in Table II the change in g_{iso} is in the opposite direction suggesting greater axial bonding in these tetragonal complexes. Again we see circumstantial evidence that TCA seems to promote a tetrahedral distortion in mixed ligand 4-coordinate copper(II) complexes.

In $CHCl_3$ solution there is great variation in the room temperature spectra, and, in particular, the values of A_o. Again the three SAL-like ligands have values indicating D_{2d} symmetry rather than D_{4h}. The high values of A_o (low values for g_o) for the two acac complexes suggest strong in-plane bonding which appears to be independent of the other ligand. Upon cooling the samples, the values of the parameters are what one would expect with the exception of Cu(TCA)(EAA). Note that there is nothing unusual about the parameters at either temperature for Cu(TCA)(SAL) suggesting that the color change upon dissolution is due to the loss of axial bonding in the solid.

It should be noted that $CHCl_3$ frozen solution values of $g_\parallel = 2.261$ and $A_\parallel = 181$ G have been reported [6] for $Cu(acac)_2$. Note that the analogous parameters for Cu(TCA)(acac) and Cu(acac)(SAL) suggest that both of these complexes have either a more weakly coordinated CuO_4 chromophore or greater distortion toward tetrahedral. We favor the former because of the relatively high and low values of $A_\parallel$ and $g_\parallel$, respectively, when compared to published values for CuO_4 chromophores [7].

In Table V we show the covalency parameters calculated [8] from the data derived from the $CHCl_3$

solution experiments. With a few exceptions the values calculated are consistent with σ-bonded ligands [9]. What π-bonding is present is likely to be "out-of-plane' because generally $k_{\parallel} > k_{\perp}$ [8]. It is noteworthy that the TCA complexes, except for Cu(TCA)(acac), have rather high values for $k_{\parallel}$ [9] suggesting very little covalent character in their bonding.

In conclusion, TCA in its mixed ligand complexes seems to promote a distortion away from square planar towards tetrahedral with ligands of some steric bulk. A comparison of the parameters of Cu(OHAP)(SAL) with those of Cu(TCA)(SAL) and Cu(TCA)(OHAP) in Tables I through IV amply depicts this distortion. Given that steric factors will cause distortion from square planar symmetry, it has also been postulated on ligand-field grounds that increased electron density on the chelate ring increases the tendency towards a tetrahedral configuration [10]. This latter factor is most definitely the prime factor influencing the behavior of TCA in its mixed Cu(II) complexes.

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