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The Copper(II) Complexes of 1-Allyl-3-(*o*-, *m*- and *p*-carboxyphenyl)-2-thiourea

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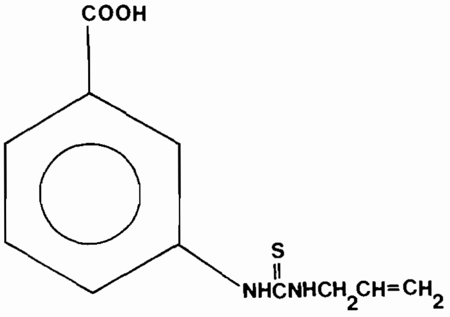
Abstract

The copper(II) complexes of 1-allyl-3-(2-, 3- and 4-carboxyphenyl)-2-thiourea have been isolated and characterized by elemental analysis, infrared, EPR, and UV–Vis studies. The *ortho* and *para* ligands form complexes of stoichiometry CuL_2 while the *meta* ligand forms complexes of stoichiometry CuL and CuL_4. All ligands form additional bridges resulting in polymeric solid-state structures. The *ortho* ligands coordinate to the metal through a carboxylate oxygen and the aryl nitrogen to form a tetrahedrally-distorted tetragonal geometry about the copper, whereas the *para* ligands coordinate only through the aryl nitrogen atom, with the remaining cooper coordination sites being occupied by two water molecules. In the 1:1 *meta* complex the carboxylate binds as a unidentate ligand to the copper, while the 1:4 *meta* complex has a tetragonally-elongated octahedral copper geometry with coordination by four nitrogen atoms from four different ligands.

Introduction

In recent years there has been considerable interest in the role of copper in antiinflammatory action [1–6]. One of the earliest uses of a copper compound as an antiinflammatory drug was the use of allocupreide sodium as an antiarthritic. This was studied extensively from 1940 to 1955, when interest shifted to the copper salicylates. Although allocupreide sodium is a copper(I) complex, the ease of oxidation of Cu(I) to Cu(II) makes it quite possible that the *in vivo* agent is a Cu(II) species [7]. We have investigated the interaction of Cu(II) with the ligand component of allocupreide, 1-allyl-3-(3-carboxyphenyl)-2-thiourea, *m*-ACT, and with the *ortho*, *o*-ACT, and *para*, *p*-ACT, analogues, which have all been studied as growth inhibitors [8–11]. We herein report the results of EPR, infrared, and UV–Vis absorption spectroscopic studies of the copper(II) complexes in solution and in the solid state.



m-ACT

Experimental

IR spectra of KBr disks of the parent ligands and the copper complexes were obtained in the 4000 to 200 cm^{-1} region with a Perkin-Elmer 1330 spectrophotometer. To assist in band assignments, IR spectra of the deuterated analogues were obtained after the ligands were dissolved in D_2O by raising the pH with NaOD, reprecipitated by adding DCl, collected and dried. This process was repeated twice. UV–Vis spectra of chloroform and DMSO solutions and of fluorocarbon mulls were recorded in the 200–750 nm region with a Cary 210 spectrophotometer. EPR spectra were obtained with a Varian E-9 spectrometer operating at 9.1 GHz with 100 kHz modulation. The microwave frequency was measured using a Hewlett-Packard microwave frequency counter and the magnetic field was calibrated using a Magnion NMR-type gaussmeter. ^1H and ^{13}C NMR spectra of DMSO-d_6 solutions of the ligands were obtained using a WM-250 NMR spectrometer. Chemical shifts are referenced to TMS. NMR resonance assignments were made by comparison with reference compounds and by application of chemical shift additivity rules [12]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

The ligands were prepared by reaction of allylisothiocyanate with the appropriate aminobenzoic acid in ethanol solution according to published procedures [13]. See also 'Supplementary Material'.

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Copper(II) Bis(1-allyl-3-(2-carboxyphenyl)-2-thiourea), Cu(o-ACT)$_2$

The complex was prepared by dissolving 2 g ligand in the minimum amount of dry ethanol (40 ml) and adding 0.55 equivalents of copper perchlorate in 10 ml dry ethanol. The pea green precipitate that immediately formed was collected and washed with ethanol and ether. The *ortho* complex was also prepared in aqueous solution by the procedure described below. *Anal.* Calc. for ($CuC_{22}H_{22}N_4O_4S_2$): C, 49.47; H, 4.15; N, 10.49; O, 11.98; S, 12.01; Cu, 11.90. Found: C, 50.19; H, 4.09; N, 10.52; O, 10.16; S, 12.41; Cu, 12.63%.

Copper(II) (1-Allyl-3-(3-carboxyphenyl)-2-thiourea), Cu(m-ACT)

No *meta* and *para* copper complexes could be obtained in pure form from ethanol solution and therefore aqueous solutions were used. To a solution of 2.0 g ligand in 40 ml ethanol, was added an aqueous solution of 0.55 equivalents of copper perchlorate or copper chloride. The pH of the resulting solution was raised to 3.5 by the addition of sodium hydroxide. The dark green precipitate that formed was collected, washed with water and ethanol and dried over $MgSO_4$. Microanalysis of the solids so produced gave variable results best interpreted as Cu(*m*-ACT) contaminated with additional amounts of Cu, Cl, and O.

Copper(II) Tetra(1-allyl-3-(3-carboxyphenyl)-2-thiourea), Cu(m-ACT)$_4$

This light green solid was prepared in the same way as the Cu(*m*-ACT) complex except that the solution was stirred with gentle heating at 45 °C for 30 min. Heating at higher temperatures caused loss of sulfur from the product. *Anal.* Calc. for ($CuC_{44}H_{44}N_8O_8S_4 \cdot 4H_2O$): C, 49.08; H, 4.87; N, 10.41; S, 11.91; Cu, 5.90. Found: C, 48.85; H, 4.56; N, 10.04; S, 11.88; Cu, 5.98%.

Copper(II) Bis(1-allyl-3-(4-carboxyphenyl)-2-thiourea), Cu(p-ACT)$_2$

The light green *para* complex was prepared by the same method as Cu(*m*-ACT). *Anal.* Calc. for ($CuC_{22}H_{22}N_4O_4S_2 \cdot 4H_2O$): C, 43.59; H, 4.99; N, 9.24; S, 10.58; Cu, 10.48. Found: C, 44.01; H, 4.24; N, 9.21; S, 10.39; Cu, 10.08%.

Results and Discussion

Infrared Results

o-ACT

Infrared absorption spectra of the *ortho* ligand, *o*-ACT, have no water or carboxyl O–H bands in the 2500–3500 cm^{-1} region which indicates that the ligand exists in the carboxylate form. This conclusion is confirmed by the ^1H NMR data (see 'Supplementary Material') which show a deficiency of two protons (assigned as the COOH and NH-allyl protons) from the number expected for the ligand. Since no inorganic cations are present, the corresponding cation is presumably the protonated amine adjacent to the allyl group; proton NMR resonances for $NH_2RR'^+$ species are frequently extremely broad. This is supported by the observation that the chemical shifts for the NCH_2 and CH protons and carbon atoms of the allyl group for the ortho ligand are quite different to those of the *meta* or *para* ligands. The C=S and COOH ^{13}C NMR chemical shifts are also significantly different for the *ortho* ligand and we attribute this to the strong intramolecular hydrogen bonding between the *ortho* ϕNH and COO$^-$ groups.

The strong N–H stretch at 3262 cm^{-1} in the infrared spectrum of *o*-ACT is completely lost on complexation to Cu(II) showing that the copper binds to the nitrogen atoms. The only other bands above 1800 cm^{-1} in the infrated spectrum of the copper complex are weak aromatic and vinyl C–H bands which suggests that no O–H bonds are present in the complex.

The antisymmetric carboxylate stretch occurs at 1660 cm^{-1} in the ligand; the frequency is higher than usual [14], approaching the value expected for a free carboxylic acid C=O stretch. This is probably because of strong intramolecular hydrogen bonding to the amine. The symmetric carboxylate stretch occurs at 1420 cm^{-1}. After complexation, $\nu_a(COO^-)$ increases, as expected for coordination of one oxygen to the copper, to 1702 cm^{-1}; and $\nu_s(COO^-)$ decreases to 1376 cm^{-1}, which is similar to the frequencies reported for copper(II) aminobenzoate complexes [15] and to $\nu_s(COO^-)$ for the Cu(*m*-ACT) derivative (see below). Thus we believe that the COO$^-$ binds to Cu(II) as an unidentate ligand. This is supported by the lack of O–H modes.

Small bands at 1970, 1890, and 1850 cm^{-1} indicating *ortho* substitution are lost on coordination to copper. The weak C–H bands near 3000 cm^{-1} are unaltered and the allyl C=C band at 1628 [16] moves slightly to 1612 cm^{-1}. The C_{aryl}–N absorption at 1495 moves to 1480 in the copper complex, while the C_{alkyl}–N absorption at 1128 cm^{-1} is not appreciably affected.

The infrared absorptions of thioureas have been assigned by Jensen and Neilsen [17]. Of the NHC(=S)NH bands, the primarily N–C–N modes are band B at 1535 cm^{-1} which moves to 1520 and weakens, and band C at 1325 cm^{-1} which moves to 1332 with a large decrease in intensity. A strong absorption at 1190 cm^{-1} attributed to the NH_2^+ group, since it moves by the expected factor of 1.36 to 878 cm^{-1} on deuteration, is lost. Sharp bands at 1000 and 930 cm^{-1} sensitive to deuteration are

TABLE I. Infrared Absorption Bands

o-ACT	m-ACT	p-ACT	Cu(o-ACT)$_2$	Cu(m-ACT)	Cu(p-ACT)$_2$	
3262s	3240sb	3366s			3300b	N–H
	3050sb	3202s			3050b	N–H
	3300–2200vb			3400vb	3300–2200vb	O–H
	2640wb	2660mb			2660w	COO–H
	2550wb	2540mb			2540w	COO–H
1660sb			1702s	1565sb		$\nu_a(COO^-)$
	1685s	1690sb			1700s	C=O
1628m		1610m	1612m		1610	C=C
				1610sh		HOH
1593w	1594m	1594w	1590w		1594	C=C
1535sb	1545s	1535sb	1520m		1565sb	band B
1495m	1460m	1428sb	1480m		1420m	C_{ar}–N
1420s			1376s	1390sb		$\nu_s(COO^-)$
	1340s	1340m			1340m	CO–OH
1325s	1310sb	1300s	1332w		1270mb	band C
1190s	1265s	1128m			1100sb	N–H band D
1128m	1218m	1175m	1130m		1180w	C_{alk}–N
1000m	795m	786m				band F
930m	754m	761m				band F
				760w		HOH

s: strong, m: medium, w: weak, b: broad.

probably band F which is chiefly due to N–H vibrations. The absorptions with strong C=S contributions that occur below 800 cm^{-1} could not be unambiguously assigned since the two strongest bands, at 757 and 692 cm^{-1} do not shift on deuteration or on complex formation and are apparently due to ring CH vibrations. The number of bands in the low frequency region below 600 cm^{-1} decreases on copper complexation; leaving two unassigned bands at 345 and 322 cm^{-1} as possible Cu–ligand modes.

The large changes in the thiourea vibrations indicate copper binding to this moiety and the loss of identifiable N–H vibrations indicates copper coordination to both nitrogen atoms of the ligand. The carboxylate group also binds to the copper.

m-ACT

The infrared absorption spectra of the *meta* ligand has two broad absorptions at 3240 and 3050 cm^{-1} which shift to 2350 cm^{-1} and 2060 upon deuteration, as expected for N–H vibrations. There are two copper(II) complexes of *m*-ACT, but in both the N–H bands are very broad indicating formation of copper–nitrogen bonds.

The complex formed from aqueous solutions without heat could not be prepared in a pure form but apparently has a Cu(*m*-ACT) stoichiometry. It has a broad featureless EPR spectrum, and an infrared spectrum with only five major bands. The carboxylic acid C=O stretch which occurs at 1685 cm^{-1} in the ligand is lost and is replaced by the antisymmetric COO$^-$ stretch at 1565 cm^{-1}. The ligand C–OH stretch at 1340 cm^{-1} is replaced by the symmetric carboxylate stretch at 1390 cm^{-1}. The loss of the C=O absorption, and the occurrence of COO$^-$ stretches separated by 175 cm^{-1} shows that the carboxylate binds to copper through a single oxygen atom [18]. The thiourea bands occur at 1545, 1310, 795 and 754 cm^{-1} in the ligand but are not clearly observed in the copper complex, apparently lying under the carboxylate bands. Water modes are observed at 3400 and 1610 cm^{-1}, and a perchlorate mode (confirmed by chloride substitution) occurs at 1100 cm^{-1}. Other weak absorptions due to the ligand are present, but all are very broad and assignments could not be made. Microanalyses gave variable amounts of copper and perchlorate for different preparations; the amount of perchlorate being inversely proportional to purity. We therefore consider the pure Cu(*m*-ACT) complex to be uncharged.

The second *meta* complex, which is formed from aqueous solutions that have been heated, has a Cu(*m*-ACT)$_4$ stoichiometry and a well resolved EPR spectrum with parallel copper hyperfine structure. The microanalytical results show four water molecules per copper. On grinding, Cu(*m*-ACT)$_4$ turned brown and the infrared spectrum appeared to be a mixture of ligand bands and bands of the Cu(*m*-ACT) complex so that no deductions about structure could be made. The Cu(*m*-ACT)$_4$ complex is, however, insoluble in solvents that dissolve the ligand and therefore is not a mixture of unbound ligand and Cu(*m*-ACT). It has been noted for other copper carboxylate complexes that grinding can cause changes from bridged to nonbridged structures [19].

p-ACT

The ***para*** ligand has a very strong, broad O–H absorption in the infrared spectrum between 2000 and 3400 cm^{-1} which is retained on copper binding. A sharp N–H absorption occurs at 3366 cm^{-1} and a broader one at 3202 cm^{-1}. Upon deuteration these move by the expected factor of 1.37 to 2490 and 2340 cm^{-1}. Both absorptions are broadened substantially on copper binding and move to 3300 and 3050 cm^{-1} respectively. The strong carboxylic acid C=O stretch at 1690 cm^{-1} moves to 1700 cm^{-1} which suggests that the carboxylate does not coordinate to the copper. The C–O stretch [14] occurs at 1340 cm^{-1} in the ligand and does not change on complex formation.

The stretch at 1535 cm^{-1} has been ascribed to band B, a predominantly N–C–N stretch of the –NC(=S)N– moiety [17], and this moves to 1565 cm^{-1}. The broad absorption near 1300 cm^{-1} identified as band C which is chiefly due to a NCN vibration [17], shifts to 1270 cm^{-1} on copper coordination and weakens. The bands at 786 and 761 cm^{-1} due to band F which is mainly a NH mode [17] are lost on complex formation. The strong C_{aryl}–N absorption at 1428 cm^{-1} moves to 1420 cm^{-1}. The C_{alkyl}–N band occurs at 1175 cm^{-1} in the ligand and shifts to 1180 cm^{-1}.

A band at 1128 assigned to N–H modes moves to 1100 cm^{-1} on complexation to copper. To ensure that this was not due to perchlorate, the complex was prepared with copper chloride which resulted in the same spectrum. The bands at 1610 and 1594 cm^{-1} attributed to C=C stretches of the allyl [16] and ring groups are unaffected by complex formation. Many unidentified ligand bands at frequencies below 960 cm^{-1} are lost or substantially broadened in the copper complex. In the low frequency region several bands are lost and weak broad bands grow in at 540 and 620 cm^{-1}.

The preservation of the C–O and C=O stretches, the shifts in O–H, N–H, and NC(=S)N band positions, and the extensive broadening of the N–H bands indicate binding of the copper to the thiourea group and not to the carboxylate. Since both N–H stretching vibrations are affected, both nitrogen atoms bind to the copper.

EPR Results

o-ACT

EPR spectra of Cu(o-ACT)$_2$, in the solid state, Fig. 1a, indicate a $d_{x^2-y^2}$ ground state since $g_\parallel = 2.145 > g_\perp = 2.035$. The observation of a weak signal near $g = 4$, Fig. 1d, and the fact that resolution is poor but increases as the temperature increases, indicates that dipolar interactions between copper atoms of neighbouring molecules are strong. This, together with the insolubility of the complex in most solvents, suggests a polymeric structure.

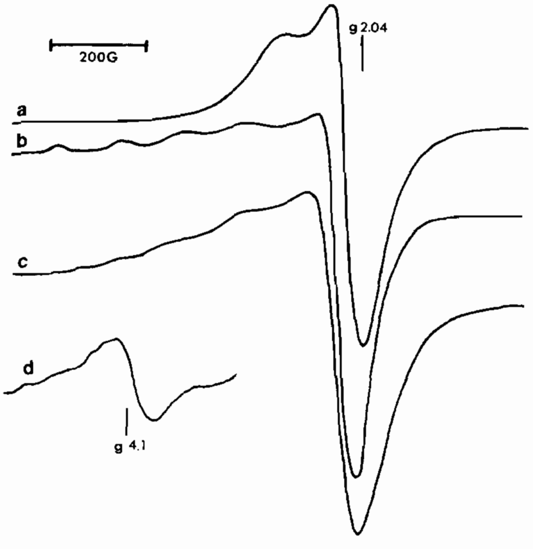

Fig. 1. X-band spectra of the copper complexes in the solid state at 300 K. (a) Cu(o-ACT)$_2$, (b) Cu(m-ACT)$_4$, (c) Cu(p-ACT)$_2$. The $g = 4$ region of Cu(o-ACT)$_2$ with a scale expansion of ×800 is shown in (d).

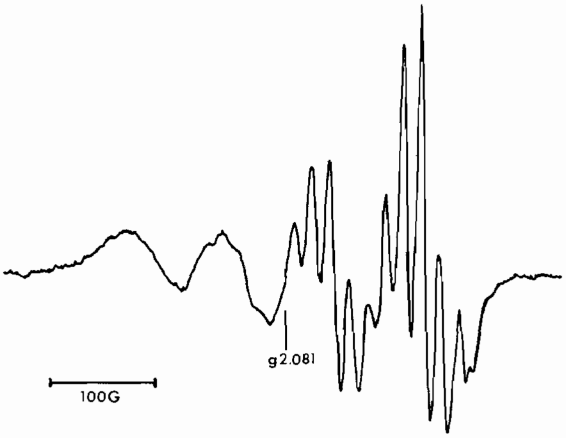

Fig. 2. X-band EPR spectrum of Cu(o-ACT)$_2$ in chloroform solution at 300 K.

In liquid (300 K), Fig. 2, and frozen (110 K), Fig. 3b, chloroform solutions the EPR spectrum of Cu(o-ACT)$_2$ shows well resolved superhyperfine structure due to two equivalent nitrogen atoms. The EPR parameters ($g_\parallel = 2.191$, $g_\perp = 2.033$, $A_\parallel$(Cu) = 0.0145 cm^{-1}, $A_\perp$(N) = 0.00168 cm^{-1}, $g_{iso} = 2.081$, A_{iso}(Cu) = 0.0084 cm^{-1}) could be explained by a square planar coordination by two sulfur and two nitrogen atoms with a +2 charge on the CuN_2S_2 moiety [20]. However, the microanalytical data show that no counteranions are present. Furthermore, sulfur and

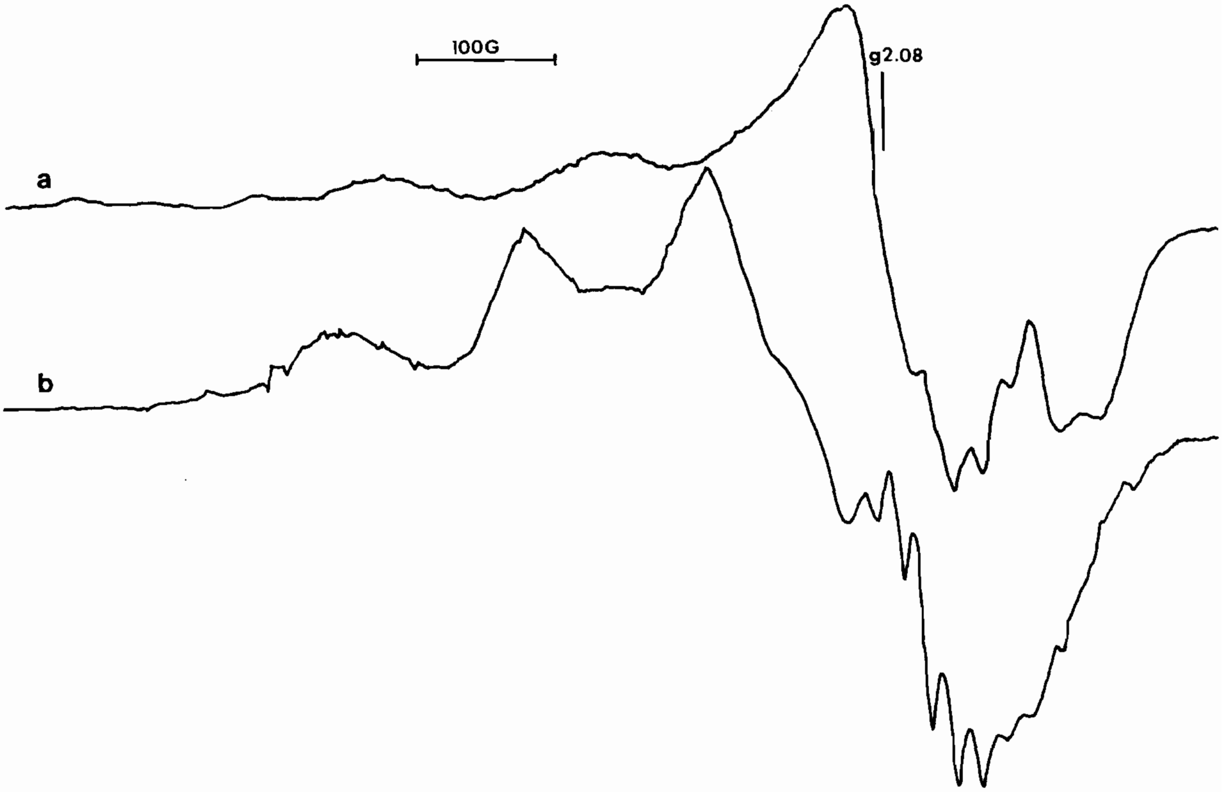

Fig. 3. X-band EPR spectra of frozen solutions at 110 K of (a) Cu(*m*-ACT)$_4$ in DMSO, and (b) Cu(*o*-ACT)$_2$ in CHCl$_3$.

nitrogen from the same ligand are sterically prohibited from both binding to a copper atom, thus a S_2N_2 coordination would require a Cu(*o*-ACT)$_4$ stoichiometry. A more likely explanation is N_2O_2 coordination with a significant tetrahedral distortion from planarity [20]. In DMSO and DMF solutions the complex rapidly decomposes to give the solvated Cu(II) ion.

m-ACT and p-ACT

The solid-state EPR spectra of Cu(*m*-ACT)$_4$ and Cu(*p*-ACT)$_2$ show well resolved parallel copper hyperfine structure in the $g = 2$ region (Fig. 1b, 1c), indicating that the copper atoms are well separated. There are no major changes between 100 K and 300 K except that resolution increases at the lower temperature. These features are characteristic of monomeric copper(II) species. The EPR parameters (*meta*: $g_{\parallel} = 2.347$, *para*: $g_{\parallel} = 2.340$, both: $g_m = 2.075$, $A_{\parallel}(\mathrm{Cu}) = 0.0151$ cm^{-1}) suggest a tetragonally-elongated octahedral copper environment [20] with at least two nitrogen atoms. EPR spectra of Cu(II) complexes are insensitive to the axial ligands. The EPR spectrum of Cu(*m*-ACT) consisted of a single broad line with no resolved copper hyperfine structure.

Spectra recorded between 0 and 8000 G (Fig. 4), however, show that small amounts of a triplet state species are also present in all three samples. The absorptions at 4605 G, 5960 G and at very low field can be interpreted in terms of the axial spin Hamiltonian

$$\mathcal{H} = g\beta HS + D(S_z^2 - 2/3)$$

where $S = 1$ and the other symbols have their usual meaning. The value of D is calculated to be 0.380 ± 0.005 cm^{-1}, which is typical of dimeric copper(II) benzoate complexes [18]. The EPR results suggest that although the major species is monomeric in the *meta* and *para* complexes, small amounts of dimeric compounds are also present. This helps explain the somewhat variable stoichiometries we obtained from different preparations. It seems probable that the dimeric species has the typical carboxylate bridged structure since the zero field splitting parameter, D, is similar to that found in other benzoate compounds [18].

In DMSO solution the *para* complex rapidly dissociates whereas the 1:4 *meta* derivative dissociates more slowly enabling an EPR spectrum to be obtained by rapidly freezing freshly prepared solutions. The EPR parameters for the *meta* complex in DMSO solution, ($g_{\parallel} = 2.163$, $g_m = 2.077$, $A_{\parallel}(\mathrm{Cu}) = 0.0169$ cm^{-1}, $A_{\perp}(\mathrm{N}) = 0.0016$ cm^{-1}) like those for the *ortho* complex, indicate a significant tetrahedral distortion from planarity. Nitrogen hyperfine splitting is clearly

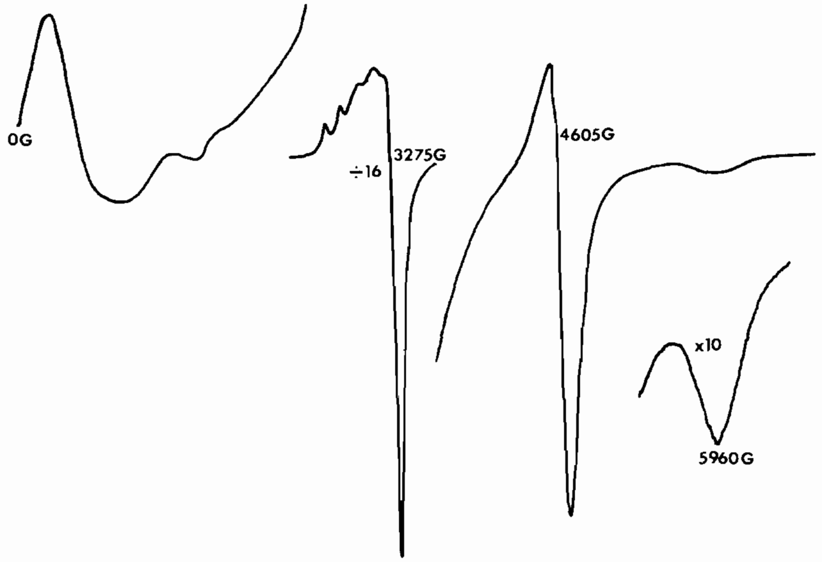

Fig. 4. X-band EPR spectrum of Cu(m-ACT)$_4$ solid at 300 K showing triplet transitions.

resolved in the perpendicular region of the spectrum (Fig. 3b) but could not be resolved well enough to determine the number of nitrogen atoms surrounding the copper.

Absorption Spectra

The electronic spectra for the *ortho* complex in chloroform solution exhibits absorption bands at 24 400, 17 250 and 16 000 cm^{-1}. Because of the limited solubility, extinction coefficients were not determined. The latter two bands are attributed to copper d-d transitions. This split d-d band has been observed in many monomeric carboxylate–pyridine complexes of copper [21, 22]. The average wavelength of 602 nm is consistent with a tetrahedrally-distorted square planar N_2O_2 geometry [23]. In a fluorocarbon mull a weak broad absorption occurs at about 16 700 cm^{-1}, confirming that the solid-state and solution species have the same copper environment.

DMSO solutions of Cu(m-ACT)$_4$ had an absorption maximum at 14 700 cm^{-1}. Reflectance spectra of the solids in fluorocarbon mulls show maxima at 14 800 cm^{-1} for Cu(m-ACT)$_4$ and Cu(p-ACT)$_2$. These wavelengths are typical of square planar N_2O_2 copper(II) complexes [23]. No bands could be resolved for Cu(m-ACT).

Conclusions

All of the copper complexes are quite insoluble in water and non-polar solvents but dissolve in DMSO and DMF by undergoing ligand exchange. The insolubility indicates polymeric solid-state structures for all the complexes, similar to those found for the copper aminocarboxylate complexes [24, 25].

The results for Cu(o-ACT)$_2$ suggest a tetragonally-elongated octahedral geometry about the copper with an additional tetrahedral distortion. The strongly bound ligands are two carboxylate oxygen atoms and two nitrogen atoms. Which nitrogen coordinates to the copper is difficult to establish since the NCSN group vibrations are affected similarly by coordination to either nitrogen atom. However, the aryl C–N stretch is affected more than the alkyl C–N stretch, and on the basis of the chelate effect, which would favor coordination of the nitrogen atom *ortho* to the carboxylate group, it seems probable that the nitrogen attached to the ring binds to copper, as is found for o-aminobenzoic acid [24]. The observation of a $g = 4$ EPR signal indicates that neighbouring copper(II) ions are relatively close, and the great insolubility of the complex indicates a polymeric structure. Either the other nitrogen or the second carboxylate oxygen could be involved in bonding to another copper atom as a bridging ligand, although the lack of any observable N–H infrared stretching mode suggests nitrogen–copper bridging.

The fact that both Cu(m-ACT)$_4$ and Cu(p-ACT)$_2$ complexes have well resolved solid-state EPR spectra indicates that the copper(II) ions are well separated. Both complexes have strongly bound water molecules which are probably coordinated to the copper. The EPR results indicate tetragonally elongated octahedral copper sites with at least two nitrogen ligands. Both complexes have free carboxylic acid groups. In Cu(m-ACT)$_4$ four nitrogen atoms from four different ligands coordinate to the copper. The ligands apparently bridge copper sites producing a polymeric structure. The axial ligands are probably water molecules. In Cu(p-ACT)$_2$, the ligands forming the equatorial plane are the aryl nitrogen atoms of two ligands, and two water molecules. The polymeric structure is completed by coordination of the alkyl nitrogen atoms to the axial sites of neighbouring coppers.

The Cu(*m*-ACT) complex has unidentate carboxylate and water ligands. The polymeric structure is completed by weak bridging interactions probably with the carboxylate moieties.

The results of these studies show that all three ligands form very stable, water-insoluble complexes with copper(II). Although the structural details can probably only be determined by crystallographic studies, we have characterized the essential structural features of all stable species that form.

Supplementary Material

Because the ligands have not been previously well documented, preparative and NMR data are given as supplementary information which is available from the authors.

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