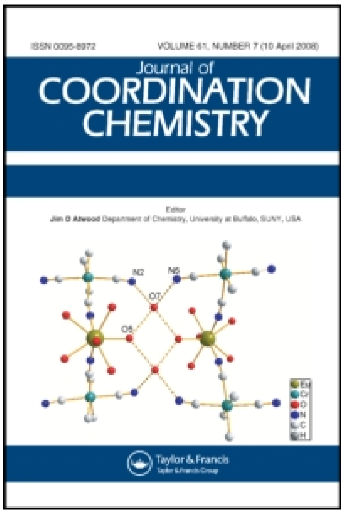

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METAL COMPLEXES FOR SUBSTITUTED 3-PHENYL-HYDRAZO ACETYLACETONES. PART 1, SPECTROSCOPIC STUDIES OF COPPER COMPLEXES OF PHENYL HYDRAZO ACETYLACETONE AND OF ITS ORTHO-, META- AND PARA-CARBOXYLIC ACID DERIVATIVES

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METAL COMPLEXES FOR SUBSTITUTED 3-PHENYL-HYDRAZO ACETYLACETONES. PART 1, SPECTROSCOPIC STUDIES OF COPPER COMPLEXES OF PHENYL HYDRAZO ACETYLACETONE AND OF ITS ORTHO-, META- AND PARA-CARBOXYLIC ACID DERIVATIVES

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Copper complexes of 3-phenyl-hydrazo acetylacetone and its ortho, meta and para carboxy derivatives have been prepared. These complexes have been studied using electron spin resonance, infra red and u.v. spectroscopic techniques. All these ligands form 2:1 (ligand:copper) complexes and in the case of the ortho derivative a 1:1 complex is also formed.

The 3-phenyl-hydrazo acetylacetone forms a 2:1 complex in which the copper atom is co-ordinated with the hydrazo nitrogen and the C=O oxygen from each ligand.

In the case of the ortho compound a 1:1 complex can also be formed. The co-ordination requirements of the copper being satisfied through the hydrazo nitrogen, one C=O oxygen, and the O^- of the ortho-carboxy ion together with a solvent molecule.

The 2:1 complex of the ortho compound (in which the co-ordination requirements of copper are satisfied by one hydrazo nitrogen and one C=O from each ligand) is not as stable as the 2:1 complex for the unsubstituted ligand because the ortho group introduces very large steric hinderance which results in this 2:1 complex being rapidly converted into the 1:1 complex.

For the para complex there is no 1:1 complex because the carboxylic acid group is too far from the copper to co-ordinate with it. In the meta compound for the same reasons the stable complex is the 2:1 type.

INTRODUCTION

Copper complexes of 3-phenyl-hydrazo acetylacetone, and its ortho carboxy derivative have been prepared previously, and studied using infra red, polarography, and u.v./visible spectrometry.[1] In this paper we have extended this study to the m- and p-carboxy derivatives, and also used electron spin resonance technique to examine the structures of all these compounds.

EXPERIMENTAL

Materials

Preparation of organic ligands

i) 3-phenyl-hydrazo acetylacetone, (3-PAA). The parent ligand was synthesised by coupling the diazotized aniline with acetylacetone,[2–4] and the crude product was recrystallised several times from ethanol to give yellow needles m.p. 88° (Lit.[2–4] m.p. 88°).

ii) Ortho-, meta-, and para-carboxy-3-phenyl-hydrazo acetylacetone, (o-, m-, p-CPAA). The three derivatives were prepared by coupling the corresponding diazonium salts of aminobenzoic acid and acetylacetone in sodium acetate solution.[1a,1b] The crude compounds were recrystallized several times from aqueous acetic acid to give yellow, reddish yellow and yellow needle-like crystals with m.p. 228°, 176° and 267° for ortho-, meta-, and para-carboxy-3-phenyl-hydrazo acetylacetone respectively.

The acids are sparingly soluble in water, but soluble in organic solvents. They are not hygroscopic and the crystalline form contains no water of crystallization as shown by quantitative analysis.[1a,1c]

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Preparation of Copper Complexes

a) Copper-bis-3-phenyl-hydrazo acetylacetone, (3-PAA)$_2$–Cu(II). This was prepared as described previously.[1a] The complex is insoluble in water, sparingly soluble in common organic solvents and soluble in dimethylformamide. Analytical data of the complex indicates 1:2 (metal:ligand) stoichiometry.[1a]

b) Copper-3-o-carboxy phenyl-hydrazo acetylacetone, o-CPAA–Cu(II). The complex was prepared as previously using copper acetate.[1a]

c) Copper-3-o-carboxyphenyl-hydrazo acetylacetone, (o-CPAA)$_2$–Cu(II). An aqueous solution of *copper nitrate* was added to aqueous solutions of the potassium salt of o-CPAA with continuous stirring at 60°C, and pH 4.2. Green fine crystals were formed which decomposed at 310°C. Analysis: found:– C, 52.1; H, 3.83; N, 10.16; Cu, 11.26; Calc. for $Cu(C_{12}H_{11}N_2O_4)_2$:– C, 51.66; H, 3.55; N, 10.04; Cu, 11.4.

d) Copper-bis-3-m-carboxyphenyl-hydrazo acetylacetone, (m-CPAA)$_2$–Cu(II). This was prepared as described previously.[1a]

e) Copper-bis-3-p-carboxyphenyl-hydrazo acetylacetone, (p-CPAA)$_2$–Cu(II). This complex was prepared using the same method as for the (m-CPAA)$_2$–Cu(II). It decomposed at 310°C. Analysis: Found:– C, 51.49; H, 4.15; N, 9.89; Cu, 11.7. Calc. for $Cu(C_{12}H_{11}N_2O_4)_2$:– C, 51.66; H, 3.95; N, 10.04; Cu, 11.4.

Preparation of Zinc and Nickel Complexes

Zinc and nickel complexes of the ligands were prepared by mixing aqueous solutions of the potassium salt of the ligand and zinc or nickel sulphate at 80°C within the pH range 5–6 with continuous stirring. Fine yellow crystals were formed.

Preparation of Solid Solutions

A dilute solid solution of the copper complex in the zinc, or nickel complex of Zn/Cu, or Ni/Cu ratio of 100/1 was prepared by mixing the appropriate solutions and allowing the mixture to crystallise.

Spectral Measurements

U.v. measurements were carried out on DMF solutions of the complexes at room temperature using a Unicam SP 800 Spectrometer.

Infra-red measurements were made on the complexes in potassium bromide discs using a Perkin Elmer 437 Spectrometer. E.s.r. measurements were made on DMF solutions of the copper complexes at room temperature, and at 77 K using a Varian E-109 Spectrometer. Solid solutions were run at 77 K.

RESULTS AND DISCUSSION

The u.v. and e.s.r. results are given in Tables I and II. The infra-red data are discussed in the text.

(3-PPA)$_2$–Cu(II)

DMF Solution

At room temperature The values for the u.v. absorptions given for the free ligand in Table I, 267 and 363 nm, are associated with the C=O[5] and hydrazo groups.[6,7] The fact that in the complex these maxima have undergone a shift to higher wavelength indicates that the oxygen and nitrogen atoms are involved in the chelating process. The e.s.r. results show that we have copper in the complex. The solution at room temperature shows a typical e.s.r. spectrum for the copper complex with typical line width variation indicative of strong anisotropy. The

TABLE I
Principal U.V. and visible absorption maxima for ligands and their copper complexes in DMF at room temperature

Complex	λmax./nm			
	Copper complex		Free ligand	
	–C=O	=N–NH	–C=O	=N–NH
(3-PAA)$_2$–Cu(II)	272	368	267	363
(o-CPAA)$_2$–Cu(II)	270	376	266	372
o-CPAA-Cu(II)	274	404	266	372
(m-CPAA)$_2$–Cu(II)	268	368	267	366
(p-CPAA)$_2$–Cu(II)	267	374	269	368

TABLE II
E.S.R. results for copper complexes (A values in mT, solutions 10^{-2} M)

Sample	g_{iso}	A_{iso}^{Cu}	A_{iso}^{N}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cu}$	$A_{\parallel}^{N}$	No. of N atoms observed	$\Delta g_{\parallel}/\Delta g_{\perp}$
$(3\text{-PAA})_2\text{-Cu(II)}$									
In DMF at room temp.	2.115	6.0	1.2					2	
In DMF at 77 K				2.230		16.0^{a}	1.1	2	
Doped in Zn at 77 K				2.1995		17.9^{a}	1.2	2	
Doped in Ni at 77K				2.199		18.0^{a}	1.2	2	
Pure solid at 77 K				2.218	2.054				4.04
$(o\text{-CPAA})_2\text{-Cu(II)}$									
In DMF at 77 K				2.259		$17.6\,\mathrm{Av}^{b}$	~1.0	2^{c}	
Pure solid at 77 K				2.321	2.076				4.21
$(o\text{-CPAA})\text{-Cu(II)}$									
In DMF at room temp.	2.125	7.0	1.5					1	
In DMF at 77 K				2.273		$16.7\,\mathrm{Av}^{b}$	1.5	1	
Doped in Zn at 77 K				2.313		19.0^{a}	1.4	1	
Pure solid at 77 K				2.177	2.063				2.81
$(m\text{-CPAA})_2\text{-Cu(II)}$									
In DMF at 77 K				2.280		$15.5\,\mathrm{Av}^{b}$			
Doped in Ni at 77 K				2.360	2.070				
Pure solid at 77 K				2.360	2.070				5.15
$(p\text{-CPAA})_2\text{-Cu(II)}$									
Doped in Ni at 77 K				2.344		$15.3\,\mathrm{Av}^{b}$			
Pure solid at room temp.	2.074								
Pure solid at 77 K				2.260^{d}	2.062^{d} 2.011	$16.7\,\mathrm{Av}^{b}$			

[a] Cu^{63} isotope.

[b] Av means the weighted average of the two isotopic splitting constants.

[c] Although the spectrum is not fully resolved, the results are compatible with two nitrogen atoms.

[d] $g_x = 2.011$, $g_y = 2.062$, $g_z = 2.260$.

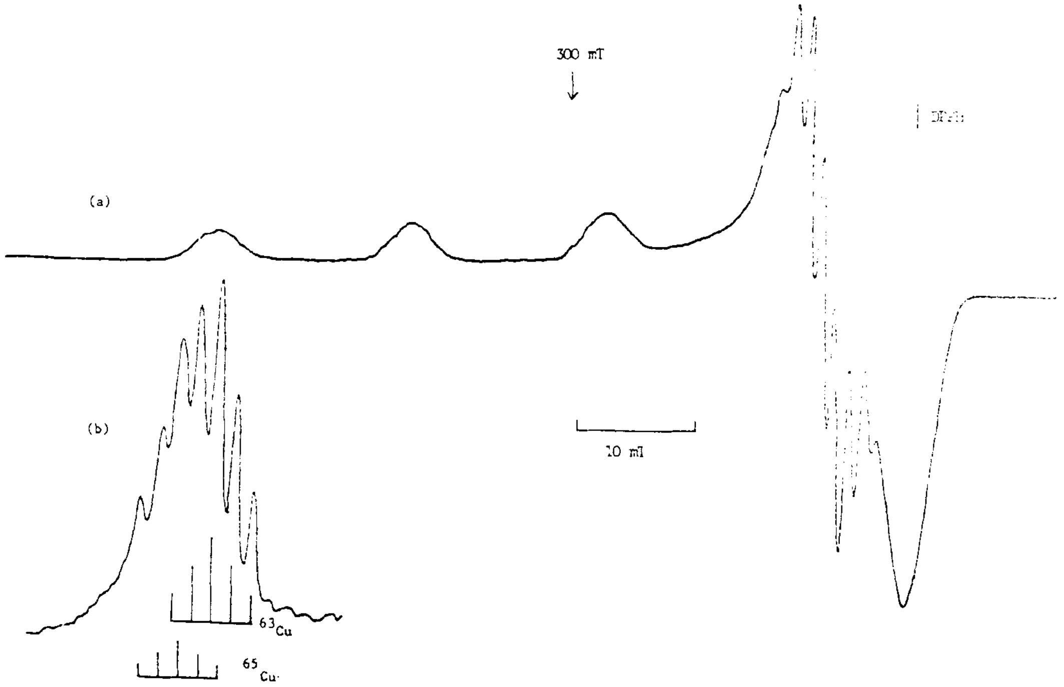


FIGURE 1 (a) E.S.R. spectrum of frozen solution of $(3\text{-PAA})_2\text{-Cu(II)}$ in DMF at 77 K; (b) shows detail of first parallel line for the above.

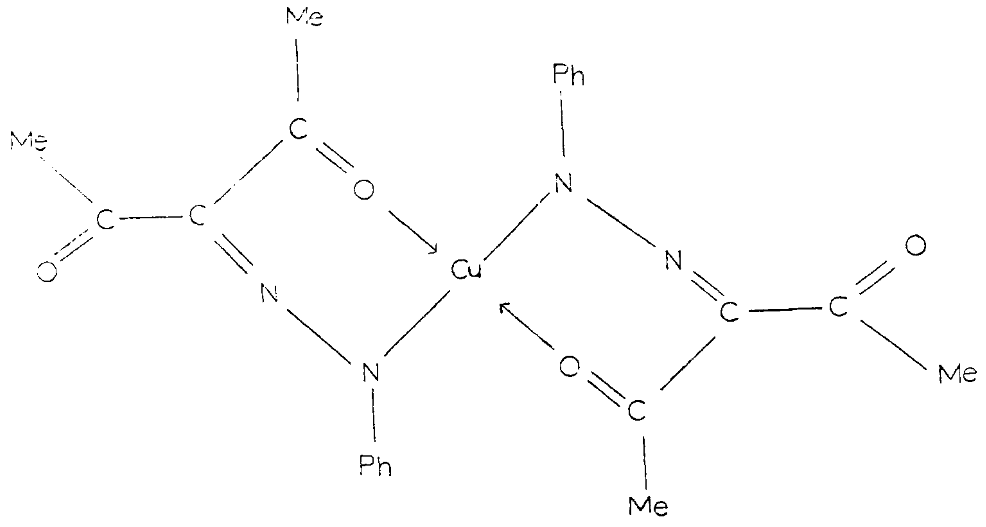


FIGURE 2 Schematic structure of complex for $(3\text{-PAA})_2\text{-Cu(II)}$.

g_{iso} value is 2.115 and the A_{iso}^{Cu} is 6.0 mT. There is nitrogen superhyperfine structure in the spectrum A_{iso}^{N} = 1.2 mT, and an indication that there are two nitrogen atoms involved, (see Table II).

At 77 K The hyperfine structure on the perpendicular feature of the frozen solution spectrum, (Figure 1(a)), cannot be analysed completely, but the parallel features are fully resolved, (as shown in Figure 1(b) for the first parallel line), demonstrating that there are two equivalent nitrogen atoms associated with Cu^{63} and Cu^{65}. The spectrum is nearly axial which fits in well with the idea that in the plane of the ligands we have a slightly distorted square planar copper structure, (Figure 2). It is impossible to tell whether the nitrogen atoms lie upon the same axis, or upon different axes.

Since only two nitrogen atoms are involved with the copper in this complex, which contains two ligands for each copper ion, the two nitrogen atoms must be on different ligands. From our e.s.r. results, we are not able to decide which of the two nitrogen atoms in each ligand is involved in the chelation, but since the complex is neutral,[1a] the Cu^{2+} ion must have replaced the protons. Since at the pH (4.6) at which the complex was prepared, the most stable tautomer of the ligand is the hydrazo form, we believe that the copper is co-ordinated to that nitrogen atom adjacent to the phenyl group.[1a,1c] We can detect no splitting due to the second nitrogen atom on the ligand, and this confims that the ligand is in the form of the hydrazo tautomer.

From the e.s.r. spectrum, (Figure 1), it can be deduced that the electron resides predominantly in a $d_{x^2-y^2}$ orbital typical of elongated tetragonal-octahedral copper complexes, (see Hathaway and Billing).[8]

Doped Solid Solution at 77 K

We have also prepared doped samples in the corresponding Zn^{2+} and Ni^{2+} complexes and obtained fully resolved spectra showing the presence of the copper isotopes in these doped systems. Again we find that there are two equivalent nitrogen atoms associated with the copper, the nitrogen splitting shows that there is anisotropy in the nitrogen tensors, and the electron is predominantly in the $d_{x^2-y^2}$ orbital. In spite of these similarities, there is an important difference between the structure of the complex in the doped solid solution and that in DMF solution at 77 K (see changes in $g_{\parallel}$ and $A_{\parallel}^{Cu}$ parameters, given in Table II), showing that the crystal lattice, or solvation is exerting a considerable influence on the arrangement of the ligands around the copper.

Pure Solid at 77 K

In the infra-red spectrum of the ligand there is a weak vibrational band at 3100–2900 cm^{-1} which can be attributed to the NH group.[9] This band disappeared in the spectrum of the solid complex indicating that the hydrogen atom of the hydrazo group in the ligand is replaced by copper on complex formation. This is confirmed by the fact that a medium band appears in the complex at 549 cm^{-1} which can be assigned to the Cu–N bond.[1,10,11] There is also a very strong band at 1675 cm^{-1} in the ligand which can be attributed to the C=O stretching frequency[12] and this band moves to 1635 cm^{-1} in the complex, indicating that the oxygen of the C=O group is associated with copper in the complex. This is confirmed by the presence of bands at 415 and 428 cm^{-1} which are associated with the Cu–O stretching frequency.[12,13] The e.s.r. spectrum of this solid shows a typical axial spectrum with two g-values,

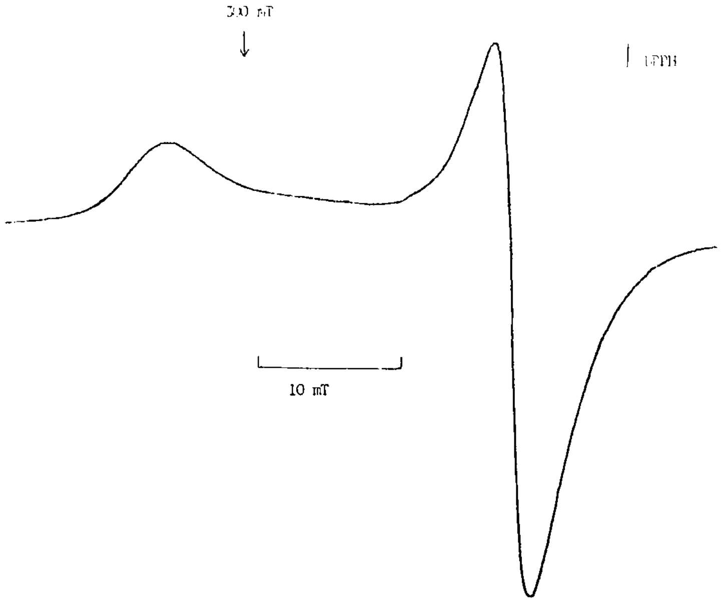


FIGURE 3 E.S.R. spectrum of pure solid of $(3\text{-PAA})_2$–Cu(II) at 77 K.

(see Table II and Figure 3), which indicates a $d_{x^2-y^2}$ ground state, and a square planar arrangement, about the copper.

Since the e.s.r. spectrum shows no hyperfine splitting for nitrogen and copper, there must be some interaction between the copper atoms. Hathaway and Billing[8] have shown that for pure copper complexes, the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ for axial spectra can be related to the exchange between neighbouring copper ions. If $\Delta g_{\parallel}/\Delta g_{\perp}$ is > 4, there is no exchange interaction, and the copper axis is aligned with the crystal axis. If the value is < 4, there is misalignment and exchange interaction. The value of $\Delta g_{\parallel}/\Delta g_{\perp}$ for $(3\text{-PAA})_2$–Cu(II) in the pure solid is 4.04, showing that the interaction between the copper ions is not exchange, but dipolar.

$(o\text{-CPAA})_2$–Cu(II)

DMF Solution

At room temperature The 2:1 complex is unstable in THF, DMF and ethanol. The relative stability being THF > DMF > ethanol. In these solvents, the 2:1 complex quickly changes to the 1:1 species. In spite of this, we were able to obtain reliable $\lambda_{max.}$ data by extrapolation to zero time. The C=O and the hydrazo absorptions show a red shift when the ligand is complexed with copper (Table I), again indicating the association of these groups with copper in the complex. The solution was too unstable to obtain e.s.r. solution spectra.

At 77 K We were able to obtain good spectra for the frozen solution, (Table II, Figures 4a and 4b), which were compatible with the association of two nitrogen atoms with the copper, and a square planar arrangement. We believe that the structure of the complex is similar to that given in Figure 2 for $(3\text{-PAA})_2$–Cu(II) complex.

In Figure 4c is given the frozen solution spectrum of a solution which has stood for twenty-four hours at room temperature together with the frozen solution spectrum of the (o-CPAA)–Cu(II) complex for comparison (Figure 4d), and it is seen that these two spectra are identical.

The THF frozen solution spectrum shows a single spectrum of the 2:1 species. The DMF frozen solution spectrum, (Figure 4b), shows the presence of a small amount of second species, which is not the final 1:1 complex, (Figure 4d), (the 2:1 species is not as stable in DMF as it is in THF). This second species has one nitrogen atom associated with the copper, (see enlargement of parallel features in Figure 4b), and the parameters are:– $g_{\parallel}$ 2.209, $A_{\parallel}^{Cu^{63}}$ 19.4, $A_{\parallel}^{N}$ 1.5. It could be that this second species is an intermediate consisting of two ligands and one copper atom, the copper being associated with one

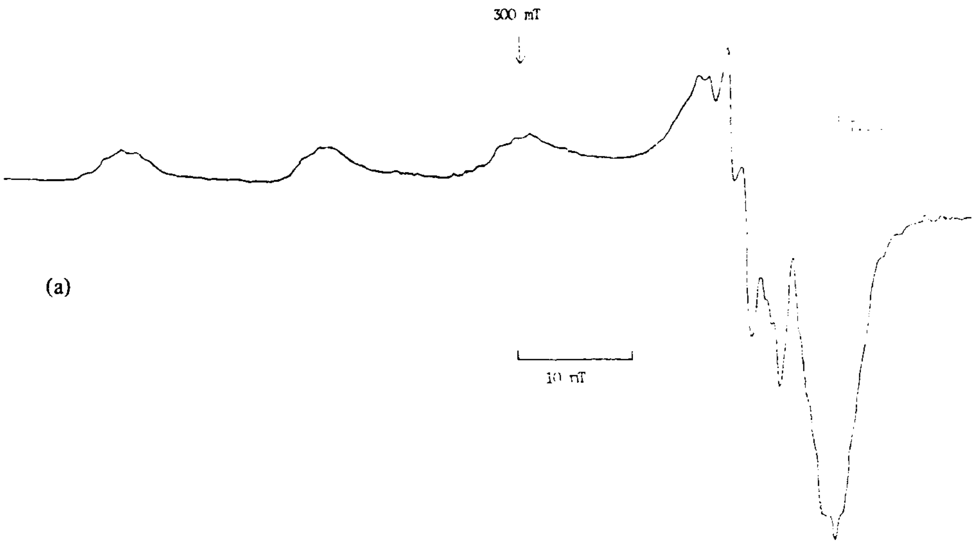
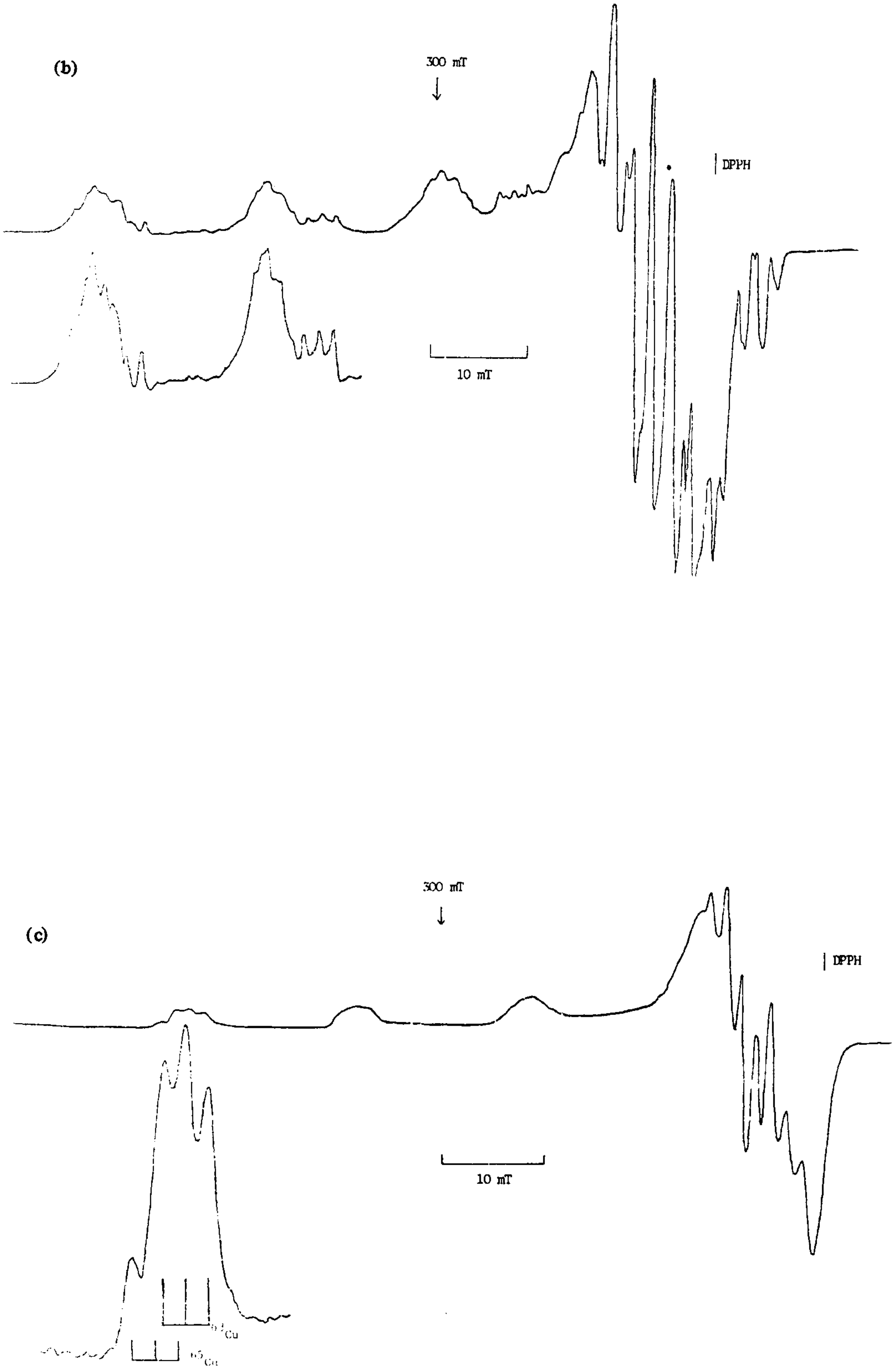
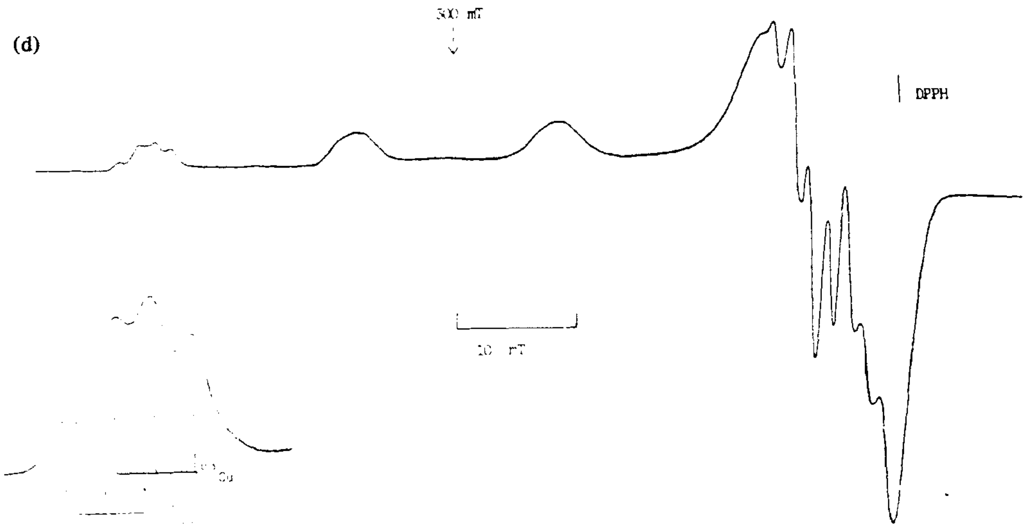


FIGURE 4 (a) E.S.R. spectrum of frozen solution of $(o\text{-CPAA})_2$–Cu(II) in THF at 77 K; (b) E.S.R. spectrum of frozen solution of $(o\text{-CPAA})_2$–Cu(II) in DMF at 77 K; at time zero, including an enlargement of the first two parallel lines; (c) E.S.R. spectrum of (b) after warming to room temperature for 24 hours and cooling to 77 K, including an enlargement of the first parallel line; (d) E.S.R. spectrum of frozen solution of (o-CPAA)–Cu(II) in DMF at 77 K including an enlargement of the first parallel line.


(b)
300 mT
DPPH
10 mT
(c)
300 mT
DPPH
10 mT
^{63}Cu
^{65}Cu



nitrogen and one oxygen from one ligand, one oxygen from the other ligand, and a solvent molecule in the fourth position instead of the second nitrogen atom.

Pure Solid at 77 K

The infra-red spectrum shows the presence of copper-oxygen (450 cm^{-1}) and copper-nitrogen (535 cm^{-1}) bands in the complex. Accompanying complex formation there is a change in the infra-red absorption associated with the hydrazo group from 3100–2500 cm^{-1} in the ligand to 3100–2800 cm^{-1} in the complex. We believe this means that the OH of the carboxylic acid group is unaffected by the copper, but that the hydrogen atom of the NH group is replaced by copper. Confirmation of the fact that the carboxylic acid group is not involved with copper in the complex is given by the observation that the absorption at 1680 cm^{-1} attributed to the C=O of a carboxylic acid group[9] is present in both the ligand and the complex. The peak at 1650 cm^{-1} due to C=O in the ligand, however, disappears in the complex indicating that the carbonyl group is again involved with copper in the complex. There is a suggestion of a new peak appearing at 1595 cm^{-1} in the complex which is not fully resolved.

The e.s.r. data for the solid at 77 K shows a typical axial structure consistent with a $d_{x^2-y^2}$ ground state for the unpaired electron.

The $\Delta g_{\parallel}/\Delta g_{\perp}$ value for this species is 4.21 which is similar to the value obtained for the $(3\text{-PAA})_2$-–Cu(II) complex.

(o-CPAA)–Cu(II)

DMF Solution

The C=O (266 nm) and hydrazo (372 nm) u.v. bands in the ligand change to 274 nm and 404 nm in the complex, (Table I), indicating that the C=O and hydrazo groups are involved with copper in the complex. The very large change in the hydrazo absorption is, we believe, due to the fact that since only one ligand is involved in the complex, the bonding between the nitrogen and the copper is very much stronger in the 1:1 than in the 2:1 complex due to the absence of steric interference between the two ligand molecules.

The e.s.r. results at room temperature and at 77 K, (Table II and Figure 4d), show that only one nitrogen atom is associated with copper, and that this nitrogen has a high splitting constant confirming the point made in the previous paragraph. It is interesting that the visible $\lambda_{max.}$ of 580 nm for the 2:1 complex is changed to 645 nm for the 1:1 complex which shows that the change has been associated with a decrease in the ligand field. By analogy with Freeman's work on peptide complexes[14] this suggests that one of the two nitrogen atoms associated with the copper in the 2:1 complex has now been replaced by oxygen. A molecular model shows that it is not possible for the NH, OH and two C=O groups of one ligand to be involved with the copper atom. In solution we have only the u.v. evidence available to show that the C=O and hydrazo groups are involved, so it could well be that the other position is taken up by a solvent DMF molecule.

Doped Solid Solution

At 77 K The doped sample shows the presence of one nitrogen atom. The parameters are different from those for the frozen DMF solution. The fact that these parameters are very different from each other shows that the environment can have a very marked effect on the arrangement of the atoms in the complex. This complex, therefore, is more flexible than 2:1 complexes due, we believe, to its asymmetry.

Pure Solid at 77 K

The 3100–2500 cm^{-1} (NH and OH) absorption in the ligand disappears completely in the solid complex showing that not only is the hydrazo group involved in chelation, but also the OH of the carboxylic acid group. The infra-red C=O band at 1650 cm^{-1} is moved to 1593 cm^{-1} in the complex indicating that the C=O group is chelating with copper. The C=O of the carboxylic acid group, however, at 1675 cm^{-1} remains unchanged. This is confirmed by the presence of a Cu–N band at 535 cm^{-1} and a Cu–O band at 452 cm^{-1}. This would suggest that the hydrogen atoms of the hydrazo and the carboxylic acid groups are replaced by copper and that the third chelating group is an oxygen atom of a carbonyl group. As discussed above, because of steric requirements, the fourth position will be occupied by a solvent molecule, which, in this case, would be water. There is a very weak band in the infra-red at 3450 cm^{-1} which could be assigned to water of crystallization. Further work[15] shows that in the analogous 1:1 complex of ortho-carboxyphenyl-hydrazo diethylmalonate with Cu(II) there is a medium band at 3450 cm^{-1} giving definite evidence for the presence of one molecule of water of crystallization co-ordinated to the copper atom. This suggests that when the COOH group is in the ortho-position, the steric hinderance between the two ligands is very great, and this leads to the instability of the 2:1 complex which breaks down easily into the 1:1 complex. In the 1:1 complex the copper bonds to carboxylic acid oxygen, and a solvent molecule takes up the fourth co-ordination position. This steric effect would explain why the interaction of copper with the nitrogen is much stronger in the 1:1 complex, and also why this complex is so stable.

The e.s.r. data on the pure solid indicate that considerable exchange is taking place between Cu(II) ions, since the $\Delta g_{\parallel}/\Delta_{\perp}$ is very low, 2.81.[8,16] This indicates that the complex molecules are arranged in a polymeric structure in which ligand molecules act as bridges between the copper atoms to give a polymer with the stoichiometric ratio of 1:1.

(m-CPAA)$_2$–Cu(II)

DMF Solution

The u.v. absorptions due to the C=O and hydrazo groups do not change much from ligand to complex (Table I), suggesting that the chelation with copper in this complex is weak. The complex precipitates within six hours from DMF solution, suggesting some change in structure which increases the interaction between the complexes, and leads to a polymeric structure. This interaction between the complexes may be the reason why a good e.s.r. spectrum in solution is not obtained.

Doped Solid Solution at 77 K

There is considerable broadening in this spectrum. The results for the solution doped in nickel gave $g_{\parallel} = 2.360$ and $g_{\perp} = 2.070$ which are identical with those for the pure solid, (Table II), suggesting that this system is not a true solid solution. The doped solution in zinc is too poorly resolved to analyse, but it gives a typical axial spectrum for $s = 1/2$ with no hyperfine, or superhyperfine structure.

Pure Solid

The absorption at 1720 cm^{-1} (C=O) in the ligand moves to 1670 cm^{-1} in the complex indicating that the carbonyl groups are involved in chelation. This is confirmed by the appearance of a Cu–O band (445 cm^{-1}) in the complex.

Our infra-red results also show that on complex formation a new band appears at 3500 cm^{-1} which, we believe, is due to water of crystallization. We also find that the absorption due to the OH of the carboxylic acid group (3200–2850 cm^{-1}) is present in the complex showing that this group is not involved with the copper atom. Because of the appearance of the new broad band at 3500 cm^{-1} in the complex, we are not able to see the disappearance of the NH absorption. There is, however, a Cu–N band at 553 cm^{-1} in the complex which is definite evidence that the hydrogen atom of the hydrazo group has been replaced by copper.

The e.s.r. results for the solid complex at 77 K show an axial spectrum typical of $d_{x^2-y^2}$ ground state for the unpaired electron. There is no evidence for exchange between neighbouring cupric ions. (The ratio of $\Delta g_{\parallel}/\Delta g_{\perp}$ is high (5.15)).

$(p\text{-CPPA})_2-Cu(II)$

DMF Solution

The u.v. band for C=O shows practically no change on complex formation. The hydrazo absorption, however, changes from 368 to 374 nm (Table I) indicating that nitrogen is involved with copper in the complex. The e.s.r. spectrum of the solution was very poorly resolved.

Doped Solid Solution

The doped solid solution in the nickel compound gave a poorly resolved e.s.r. spectrum.

Pure Solid

The presence of Cu–N bond in the solid is confirmed by the appearance of a band at 550 cm^{-1}. The only evidence that C=O is associated with the copper in the complex is the disappearance of the absorption at 1630 cm^{-1} on complex formation. There is no band corresponding to Cu–O. The C=O absorption at 1680 cm^{-1} in the ligand remains at the same frequency on complexation, although it becomes less sharp. There is a very strong band at 3450 cm^{-1} in the complex which we attribute to water of crystallisation. (The analytical results would accommodate one water of crystallisation).

The solid sample has virtually no resolvable e.s.r. spectrum at room temperature saving a very broad line giving $g = 2.074$. On cooling to 77 K, a very well resolved spectrum is found having the parameters given in Table II. There are three g values, ($g_x = 2.011$, $g_y = 2.062$, $g_z = 2.260$) showing that we have rhombic distortion in this case. Resolution of the copper hyperfine interaction implies that the copper ions are quite well removed from each other. This is the only one of the five complexes in which a value $A_{\parallel}^{Cu}$ can be obtained for the pure solid sample.

CONCLUSIONS

The 3-PAA ligand has four possible coordination sites, i.e. two C=O groups and two nitrogen atoms. Molecular models show that only one of the C=O groups, and one of the nitrogen atoms can be simultaneously co-ordinated to the copper. Of the two nitrogen atoms, the hydrazo nitrogen, by loss of its proton, is the more probable coordination site.[7, 1a] Since one ligand can provide only two possible co-ordinating sites, the complex must be of the 2:1 variety, which is what we find (see Figure 2).

When an ortho carboxylic acid group is present, the co-ordination requirements of the copper can be satisfied by one ligand through the hydrazo nitrogen, one C=O oxygen, and the O^- of the ortho-carboxylate ion together with a solvent molecule. This gives a stable 1:1 complex with a strong nitrogen-copper interaction as shown by the u.v. and e.s.r. results.

The ortho compound can also form a 2:1 complex in which the co-ordination requirements of copper are satisfied by one hydrazo nitrogen from each ligand, and one C=O from each ligand. This complex, however, is not as stable as the 2:1 complex for 3-PAA, because the ortho-group introduces very large steric hinderance, which results in this 2:1 complex being rapidly converted into the 1:1 complex. This drive to form the 1:1 complex not only results from the presence of steric hinderance in the 2:1 complex, but is also assisted by the fact that in the 1:1 complex the carboxylate ion co-ordinates with the copper. This is confirmed by results[15] which show that if we have Cl, Br or MeO as ortho substituents, the 2:1 complex is stable, and does not break down into the 1:1 complex, although the steric effect of these ortho groups will be quite large. This is because these ortho groups cannot co-ordinate to the copper in the 1:1 complex in the same way that the carboxylate ion can.

For the p-compound, there is no 1:1 complex, because the carboxylic acid group is too far from the copper to coordinate with it. In the m-compound, for the same reason, the stable complex is the 2:1 type.

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