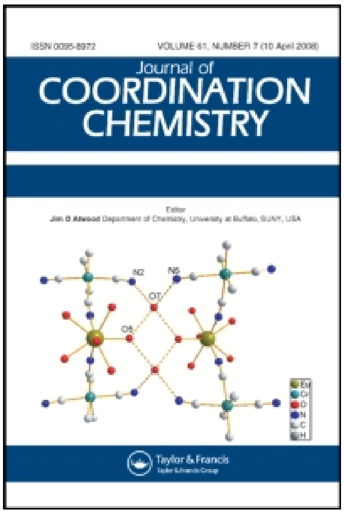

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF Cu(II) COMPLEXES OF SOME LIGANDS CONTAINING THE AMIDE GROUP

Bhagwan S. Garg[a]; Malladi J. Reddy[a]; Vinod Kumar[a]
[a] Department of Chemistry, University of Delhi, Delhi, India

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF Cu(II) COMPLEXES OF SOME LIGANDS CONTAINING THE AMIDE GROUP

BHAGWAN S. GARG,* MALLADI J. REDDY and VINOD KUMAR

Department of Chemistry, University of Delhi, Delhi-110007, India

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Complexes of Cu(II) with *N*-(2′-carboxyphenyl)benzamide (CPBH), 2-amino-*N*-(2′-carboxyphenyl)benzamide (ACPBH), isoxazolylbenzamine (IB), *N*-anilinobenzamide (AB), *N*-(2-pyridyl)-3-carboxypropanamide (PCPAH) and *N*-(2-pyridyl)-2-carboxybenzamide (PCBAH) have been prepared and characterized by analyses, magnetic susceptibility measurements, thermal studies and I.R., electronic and EPR studies. Visible and E.P.R. spectra indicate that the complexes are monomeric, having either square planar or distorted octahedral geometry. Interesting amide bonding patterns have been observed and various E.P.R. parameters have been evaluated.

KEY WORDS: Copper(II), amides, structures, covalency.

INTRODUCTION

The coordination chemistry of the amide group has received much attention due to its diverse coordinating behaviour and the role it plays in biological processes.[1-4] Weirsema and Windle,[5] on the basis of EPR spectra of Cu(II) salicylamide complexes, have reported that salicylamide coordinates through the nitrogen of the amide group. On the other hand, Pannu *et al.*[6] have proposed a structure for this complex with oxygen coordinating. The majority of amide ligands form monomeric complexes with Cu(II) (doublet state). However, ESR spectra of Cu(II) cyclic and pendant acid amide complexes with other anchoring groups are dimeric, with the two metal ions exchange coupled (triplet state).[7] In view of these differences, further investigation of the coordination behaviour of the amide group is worthwhile.

In our continuing studies of metal-amide interactions, we report the syntheses and spectroscopic studies of complexes of Cu(II) with *N*-(2′-carboxyphenyl)benzamide (CPBH), 2-amino-*N*-(2′-carboxyphenyl)benzamide (ACPBH), *N*-isoxazolylbenzamide (IB), *N*-anilinobenzamide (AB), *N*-(2-pyridyl)-3-3carboxypropanamide (PCPAH) and *N*-(2-pyridyl)-2-carboxybenzamide (PCBAH) (Figure 1).

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification.

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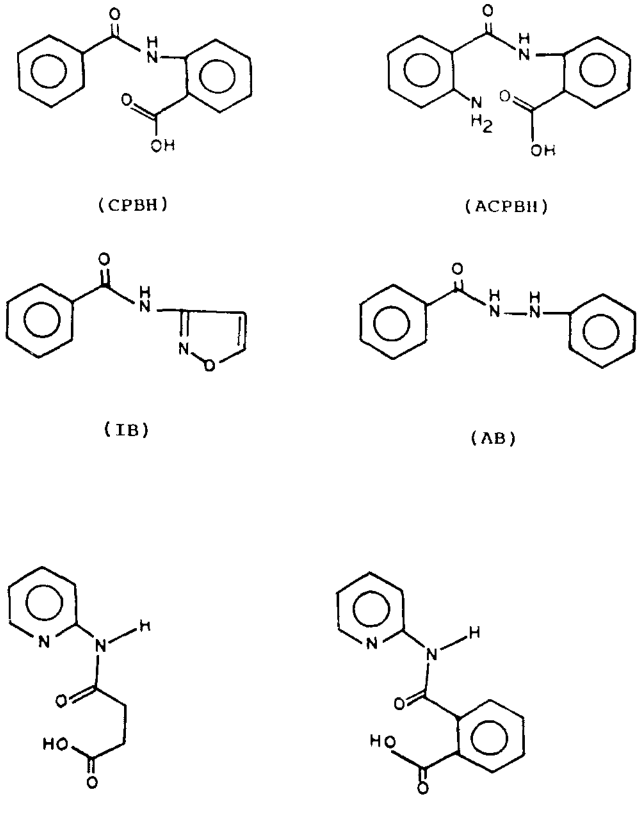
* Author for correspondence.



(CPBH) (ACPBH) (IB) (AB) (PCPAH) (PCBAH)

Figure 1 Structures of the ligands.

Synthesis of Ligands

All ligands were prepared and purified according to reported procedures with slight modifications.[8-10] Ligands were characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy. AB, PCPAH and PCBAH were synthesized as reported elsewhere.[11]

Elemental analysis were obtained using a Perkin Elmer CHN analyser or by atomic absorption spectroscopy. Spectra were recorded as follows: IR spectra in the 4000–200 cm^{-1} region in KBr and Cs I pellets on a Perkin Elmer 18D spectrophotometer; electronic spectra in the 900–200 nm region on Beckman DU-64 spectrophotometer in methanol; x-band EPR spectra on a JEOL JES-3XG ESR spectrometer with a variable temperature cryostat. Magnetic susceptibilities were measured at room temperature by the Faraday method using a Cahn-Ventrol RM-2 balance; mercuric tetrathiocyanato cobaltate(II) was used as standard. Susceptibilities were corrected for diamagnetic ligand contributions.

Synthesis of Complexes

$Cu(CPB)_2(H_2O)_2$ *and* $Cu(ACPB)(OAc).H_2O$

In a typical preparation, 2 mmol CPBH or ACPBH was suspended in 25 cm^3 of water to which was added a calculated volume of standard Na_2CO_3 solution with constant stirring. To the clear NaL solution thus obtained 1 mmol of copper acetate dissolved in 10 cm^3 of H_2O was added. The green solids which separated were filtered under suction, washed with warm water several times, and then with acetone, and air dried.

$Cu(IB)_2$, $Cu(IB)(OAc)_2$ *and* $Cu(IB)(SO_4)$

Some 20 cm^3 of the methanolic solution of *N*-isoxozalylbenzamide (10 mmol) was added to copper acetate (5 mmol) in 50 cm^3 of methanol. On refluxing the reaction mixture, the initially formed pale violet precipitate became darker in colour and the green filtrate on evaporation gave compounds with other compositions, e.g., $Cu(IB)(OAc)_2$. If copper sulphate was used instead of acetate, a green compound separated. All complexes were washed thoroughly with warm water and acetone, and air dried.

$Cu(AB)(SO_4)$

Some 25 cm^3 of a methanolic solution of *N*-anilinobenzamide (4 mmol) was added to a copper sulphate solution (2 mmol in 10 cm^3 of distilled water) with constant stirring. A green complex immediately separated; this was washed with warm water and acetone, and air dried.

$Cu(PCPAH)_2X_2$ *and* $Cu(PCBAH)_2$ $(X = Cl^-, Br^-, NO_3^-, ClO_4^-)$

In a typical preparation, 2 mmol of ligand was suspended in dry ethanol and a 1 mmol solution of copper salt added to it, dropwise. The clear solution obtained was stirred for one hour. When a coloured precipitate formed, it was filtered and washed with ethanol and ether, and dried *in vacuo* over P_2O_5. In some cases it was necessary to precipitate the complexes with ether (e.g., ClO_4^-).

$Cu(PCPAH)_2Cl.N_3$ *and* $Cu(PCBAH)_2Cl.N_3$

Some 2 mmol of the ligand was suspended in ethanol and 1 mmol of $CuCl_2$ in ethanol was added to it. The mixture was stirred for 10 minutes and 2 mmol of sodium azide was added. A fast change of colour from green to brown was observed and the resulting solution was stirred for 5 hrs. The coloured precipitate formed was filtered and washed with ethanol and ether, and dried *in vacuo* over P_2O_5.

RESULTS AND DISCUSSION

All the complexes are blue or green crystalline substances. They are non-hygroscopic and insoluble in non-polar solvents, but freely soluble in alcohols, DMF and DMSO. All decompose in the range 190–268°C, and by dilute mineral acids.

Analytical data and other related details for the complexes are presented in Table 1.

Table 1 Physical and analytical data for the complexes

	Complex	Colour	Decomp. Temp. (°C)	Elemental Analysis Found (Calcd.) % C	H	N	M
1	$Cu(CPB)_2(H_2O)_2$	Green	523	57.80 (57.98)	4.02 (4.17)	4.92 (4.83)	10.72 (10.96)
2	$Cu(ACPB)(OAc).H_2O$	Green	541	49.11 (48.54)	4.20 (4.06)	7.76 (7.07)	15.75 (16.05)
3	$Cu(IB)_2$	Violet	518	54.92 (54.86)	3.01 (3.22)	12.17 (12.79)	13.98 (14.51)
4	$Cu(IB)(OAc)_2$	Green	513	45.05 (45.47)	3.68 (3.82)	7.43 (7.57)	17.02 (17.18)
5	$Cu(IB)CSO_4)$	Green	519	34.48 (34.54)	2.14 (2.32)	7.92 (8.05)	18.06 (18.27)
6	$Cu(AB)(SO_4)\cdot 2H_2O$	Bluish green	531	39.08 (38.27)	3.62 (3.95)	6.61 (6.87)	15.23 (15.50)
7	$Cu(PCPA\underline{H})_2Cl_2$	Bluish green	463	41.28 (41.37)	3.79 (3.83)	10.58 (10.72)	12.02 (12.17)
8	$Cu(PCPA\underline{H})_2Br_2$	Bluish green	471	35.29 (35.35)	3.18 (3.27)	9.14 (9.16)	
9	$Cu(PCPA\underline{H})_2(NO_3)_2$	Blue		37.44 (37.56)	3.42 (3.47)	14.59 (14.60)	
10	$Cu(PCPA\underline{H})_2Cl.N_3$	Light brown		40.81 (40.87)	3.62 (3.78)	18.49 (18.54)	11.94 (12.02)
11	$Cu(PCPA\underline{H})_2(ClO_4)_2$	Blue		33.18 (33.23)	3.02 (3.07)	8.56 (8.61)	
12	$Cu(PCBA\underline{H})_2Cl_2$	Light green	475	50.41 (50.48)	3.20 (3.23)	9.00 (9.06)	10.16 (10.28)
13	$Cu(PCBA\underline{H})_2Br_2$	Bluish green	498	44.11 (44.14)	2.79 (2.82)	7.81 (7.92)	
14	$Cu(PCBA\underline{H})_2(NO_3)_2$	Blue		46.42 (46.49)	2.89 (2.98)	12.49 (12.51)	
15	$Cu(PCBA\underline{H})_2Cl.N_3$	Greenish brown		49.43 (49.48)	3.09 (3.17)	8.56 (8.61)	10.02 (10.07)
16	$Cu(PCBA\underline{H})_2(ClO_4)_2$	Light blue		41.67 (41.82)	2.56 (2.68)	7.43 (7.50)	

Vibrational Spectra

Table 2 gives diagnostic IR bands for the compounds. The C=O and C—O stretching frequencies at *ca* 1620 and 1350 cm^{-1} in the free ligands containing carboxylic groups are shifted to *ca* 1550 and 1380 cm^{-1} in the complexes and are assigned to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ modes, respectively.[12,13] The ν_{O-H} and $\nu_{C=O}$ modes of the carboxylic group at 2600 and 1700 cm^{-1} in the free ligands disappear in the IR spectra of the complexes.

The amine ν_{N-H} frequency in ACPBH centred at ~3490 cm^{-1} shifts to lower frequency by ~100 cm^{-1} in the complexes, thus indicating that nitrogen is coordinated.[14] A band at ~1640 cm^{-1} in ACPBH and CPBH assignable to $\nu_{C=O}$ of the amide group shows no appreciable shift in the complexes, thus ruling out coordination through the amide oxygen atom.

However in IB, PCPAH and PCBAH complexes, the amide ν_{N-H} band shifts towards higher frequencies, thus indicating non-participation of the nitrogen atom in coordination. On the other hand, the $\nu_{C=O}$ (amide I) frequency undergoes a negative shift in the complexes, indicating coordination through oxygen.[15] In complex

Table 2 Diagnostic IR bands (cm^{-1}) for the compounds

	V_{N-H} amide, amine (ν_{O-H})	Amide I	Amide II	ν_{COO^-}		ν_{M-N}	ν_{M-O}
				Asym.	Sym.		
CPBH	3240	1635	1520	1680	1375		
1	3265 (3400)	1640	1500	1510	1380	460	360
ACPBH	3260 3490	1640	1580	1690	1390		
2	3270, 3400 (3410)	1635	1490	1500	1360	450	350
IB	3230	1680	1480				
3			1490			445	360
4	3270	1635	1500			440	365
5	3265	1640	1480			450	370
AB	3240	1640	1500				
6	3210 (3425)	1645	1490			460	360
PCPAH	3120	1690	1440	1540	1380		
7	3140	1640	1480	1540	1380	435	338
8	3165	1645	1470	1542	1380	435	340
9	3150	1630	1480	1530	1370	434	300
10		1620	1460	1536	1380	436	332
11	3140	1690	1434	1530	1375		
PCBAH	3140	1690	1444	1535	1378		
12	3140	1620	1480	1528		435	320
13	3160	1640	1475	1530		438	324
14	3200	1620	1475	1545		432	315
15		1610	1450	1540	1382	436	332
16	3200	1618	1455	1530	1380	435	336

3, $\nu_{C=O}$ disappears clearly indicating iminol formation and replacement of the H-atom by Cu(II); this increases the ligand field strength and favours a square planar arrangement. This is further confirmed by the disappearance of the ν_{N-H} peak. In the $\nu_{(O-H)}$ water region, spectra of complex 1 show two sharp bands attributed to the presence of coordinated water. Characteristic stretching bands of other coordinating groups such as sulphate, nitrate and perchlorate were also observed in expected regions. Bands corresponding to ν_{M-O} and ν_{M-N} vibrations are also evident.

All complexes of PCPAH and PCBAH exhibit sharp maxima in the 1610–1590 cm^{-1} region attributed to coupled stretching modes of the pyridyl C—C and C—N bonds, which have been shown to give rise to small frequency shifts and a marked intensity increase on coordination of the pyridyl N-atom. The in-plane and out-of-plane deformation modes of the pyridine ring occur at *ca* 620 and 405 cm^{-1}, respectively, for the free ligands. For compounds 13–22 the δ(py) modes shift to higher frequencies, indicating the coordination of the pyridyl N-atom.[16]

Magnetic moments and electronic spectra

Magnetic moments at room temperature and visible absorption bands are given in Table 3. The Cu(II) complexes are all paramagnetic, μ_{eff} values corresponding to the presence of one unpaired electron (1.80–2.02 BM). The relatively higher values for the azido complexes can be rationalized in terms of decreased 3d–4p orbital mixing.

Table 3 Magnetic moments and electronic spectra data for the complexes

	Complex	μ_{eff} (B.M.)	Electronic spectral bands, λ_{max} (cm^{-1})	Tentative assignments	Comments
1	$Cu(CPB)_2(H_2O)_2$	1.84	13210 17132	$^2T_{2g}\leftarrow{}^2E_g$ MLCT	Distorted O_h Cu(II) environment
2	$Cu(ACPB)(OAc).H_2O$	1.80	15625 19230	$^2B_{2g}\leftarrow{}^2E_{1g}$ $^2E_g\leftarrow{}^2B_{1g}$	Square planar Cu(II)
3	$Cu(IB)_2$	1.86	15151 20200	$^2B_{2g}\leftarrow{}^2B_{1g}$ $^2E_g\leftarrow{}^2B_{1g}$	Square planar Cu(II)
4	$Cu(IB)(OAc)_2$	1.90	14285 19120	$^2B_{2g}\leftarrow{}^2B_{1g}$ $^2E_g\leftarrow{}^2B_{1g}$	Square planar Cu(II)
5	$Cu(IB)(SO_4)$	1.82	14820 19182	$^2B_{2g}\leftarrow{}^2B_{1g}$ $^2E_g\leftarrow{}^2B_{1g}$	Square planar Cu(II)
6	$Cu(AB)(SO_4).2H_2O$	1.84	14705 18866	$^2B_{2g}\leftarrow{}^2B_{1g}$ $^2E_g\leftarrow{}^2B_{1g}$	Square planar Cu(II)
7	$Cu(PCPA\underline{H})_2Cl_2$	1.93	13158	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
8	$Cu(PCPA\underline{H})_2Br_2$	1.88	13021	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
9	$Cu(PCPA\underline{H})_2(NO_3)_2$	1.97	14286	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
10	$Cu(PCPA\underline{H})_2Cl.N_3$	2.02	13513	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
11	$Cu(PCPA\underline{H})_2(ClO_4)_2$	1.80	14832	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
12	$Cu(PCBA\underline{H})_2Cl_2$	1.99	12820	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
13	$Cu(PCBA\underline{H})_2Br_2$	1.90	12682	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
14	$Cu(PCBA\underline{H})_2(NO_3)_2$	1.96	13333	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
15	$Cu(PCBA\underline{H})_2Cl.N_3$	1.98	13312	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment
16	$Cu(PCBA\underline{H})_2(ClO_4)_2$	1.82	14126	$^2T_{2g}\leftarrow{}^2E_g$	Distorted O_h Cu(II) environment

The visible spectra of complexes 2–6 show absorption bands in the ranges 14285–15625 cm^{-1} and 18866–20,200 cm^{-1}, assignable respectively to transitions $^2B_{2g}\leftarrow{}^2B_{1g}$ and $^2E_g\leftarrow{}^2B_{1g}$ of a square planar structure.[17] All other complexes showed only one broad band ranging from 12682–14832 cm^{-1}, thus suggesting a distorted octahedral geometry. This band is considerably blue shifted as compared with the first maxima of corresponding Ni(II) complexes, with $\lambda(Cu)/\lambda_{(Ni)} \sim 1.40$. This also suggests appreciable distortion from octahedral geometry.[18] In the cases of 10 and 15, a band at ~25000 cm^{-1} has been observed, and which can be assigned to charge transfer.

E.P.R. spectra

E.P.R. spectra of all complexes in the polycrystalline state have been recorded and bonding parameters calculated using Knebhul's approximation.[18] Typical spectra are shown in Figures 2, 3 and 4, and relevant data is given in Table 4.

The spectra of all Cu(II) complexes show two peaks at room temperature, an intense absorption at high field and less intense one at low field, from which $g_\parallel$, $g_\perp$ $\langle g \rangle$ and $A_\parallel$ have been calculated. The trend $g_\parallel > g_\perp > 2.0023$ observed for all complexes indicates that the unpaired electron most likely resides in the $d_{x^2-y^2}$ orbital, thus implying a $^2B_{1g}$ ground state.[19]

Kivelson and Nieman[20] have shown that $g_\parallel$ is a moderately sensitive function for indicating covalency. Relatively speaking, $g_\parallel > 2.3$ is characteristic of an ionic environment and $g_\parallel < 2.3$ of a covalent environment in metal-ligand bonding. Values of $g_\parallel > 2.3$ were observed for complexes 7, 8, 10, 12, 13 and 15. Based on the values

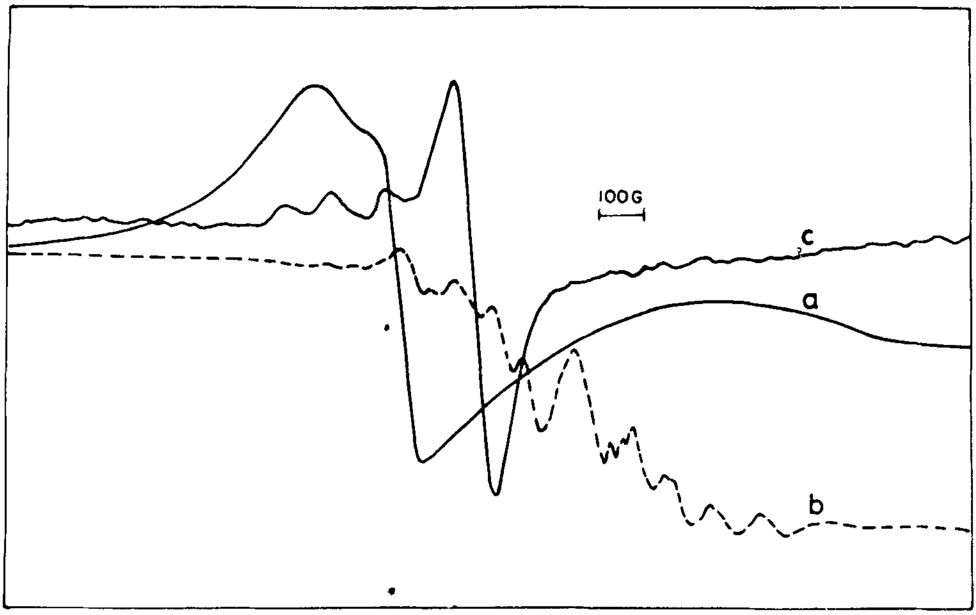


Figure 2 X-band EPR spectra of [Cu(ACPB)(OAc)]. H_2O: (a) at RT (polycrystalline); (b) at LNT (polycrystalline); (c) at 140°K (solution in DMF).

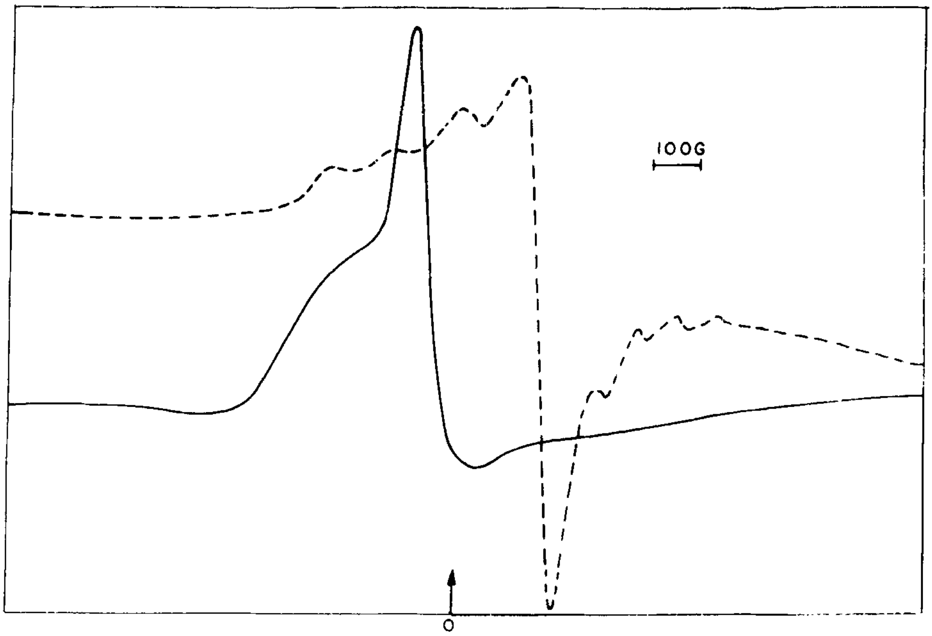


Figure 3 X-band EPR spectra of $(Cu(IB)_2)$ at RT (full line) and LNT.

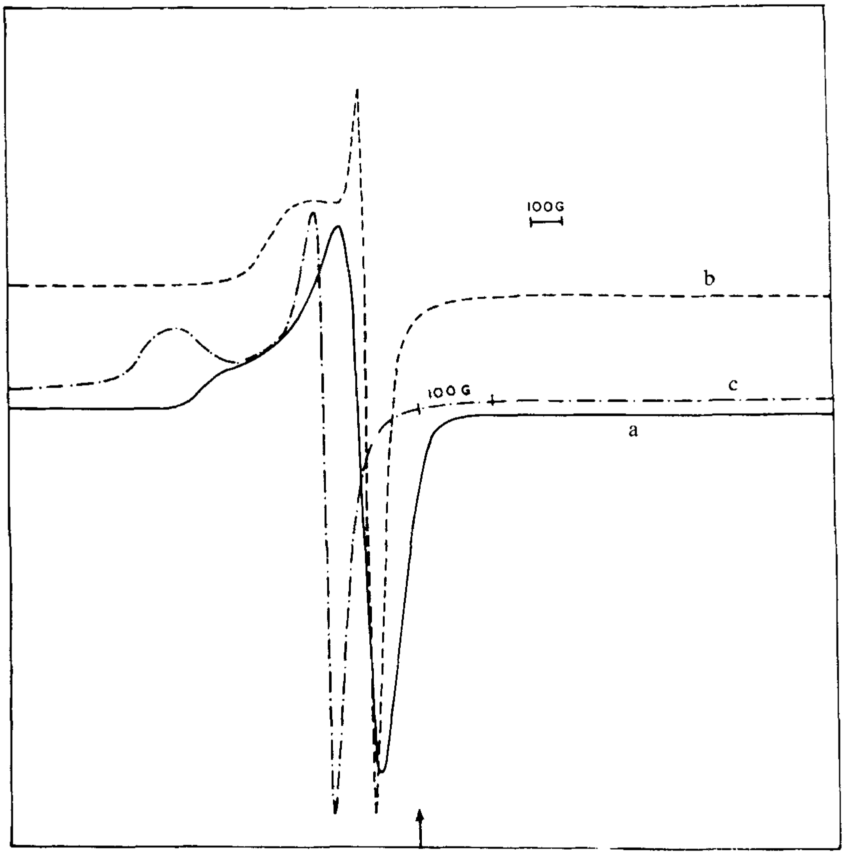


Figure 4 X-band EPR spectra of (a) $(Cu(PCPAH)_2Cl_2$; (b) $(Cu(PCBAH)_2Cl_2)$; (c) $(Cu(PCBAH)_2(ClO_4)_2)$.

Table 4 EPR parameters for the Cu(II) complexes

S.No.	Temp. (°C)	$g_\parallel$	$g_\perp$	$\langle g \rangle$	$A_\parallel$	G	α^2	$K_\parallel$	$K_\perp$	$-\lambda$
1	120	2.214	2.068	2.12	124	2.56		0.49	0.77	418
2	120	2.210	2.050	2.10	160	4.20		0.40	0.51	346
3	120	2.192	2.034	2.09	120	5.65		0.36	0.40	304
4	298	2.186	2.042	2.09		4.43				
5	298	2.198	2.056	2.10		3.54				
6	298	2.220	2.068	2.12		3.24				
7	298	2.390	2.135	2.22	207	2.88	0.76			
8	298	2.325	2.114	2.18	192	2.85	0.63			
9	298	2.214	2.095	2.13	193	2.25				
10	298	2.538	2.156	2.28	167	3.45				
11	298	2.237	2.088	2.14	120	2.69	0.52			
12	298	2.815	2.114	2.18	200	2.76	0.60			
13	298	2.310	2.112	2.18	198	2.86	0.61			
14	298	2.213	2.062	2.11	207	3.44				
15	298	2.598	2.158	2.30	172	3.78				
16	298	2.200	2.095	2.13	193	2.11				

of $g_{\parallel}$, the extent of covalency of the M—L bond follows the order, IB > ACPBH > AB > PCBAH > PCPAH. In terms of other coordinating groups, the covalency order may be $OAc^- > SO_4^{-2} > NO_3^- > ClO_4^- > Br^- > Cl^- > N_3^- > H_2O$ (*vide supra*). The $\langle g \rangle$ values in the range of 2.09–2.30 are in agreement with an orbitally non-degenerate ground state.[21]

It is noteworthy that the ESR spectrum of complex 2 recorded at liquid nitrogen temperatures in the polycrystalline state shows a multiple line spectra which is thought to be due to non-equivalent nitrogens bonded to Cu(II).[22] However, solution spectra do not give any such information.

In compexes having D_{4h} symmetry, g values for the Cu(II) ion with a $^2B_{1g}$ ground state are given by the expressions[23]

$$g_{\parallel} = 2 - \frac{K_{\parallel}^2 \lambda}{(^2B_{2g} \leftarrow {}^2B_{1g})} \tag{1}$$

$$g_{\perp} = 2 - \frac{K_{\perp}^2 \lambda}{(^2E_g \leftarrow {}^2B_{1g})} \tag{2}$$

where K is the orbital reduction factor and λ the spin orbit coupling constant. Equation (3) follows.

$$\frac{g_{\parallel} - 2}{g_{\perp} - 2} = G = \frac{K_{\parallel}^2}{K_{\perp}^2} \cdot \frac{(^2E_g \leftarrow {}^2B_{1g})}{(^2B_{2g} \leftarrow {}^2B_{1g})} \tag{3}$$

In view of the close similarity of the spectra, it is worth checking the g values obtained from the EPR spectra used to evaluate $K_{\parallel}$ and $K_{\perp}$ by the above expressions for complexes 1, 2 and 3. In all the complexes, $K_{\perp} > K_{\parallel}$. If the assignment of the electronic energy levels, $^2B_{1g} < {}^2B_{2g} < {}^2A_{1g} < {}^2E_g$ was used, lower numerical values of $^2B_{2g} < {}^2E_g$ were used. Lower numerical values of the $^2B_{2g} \leftarrow {}^2B_{1g}$ transition would significantly reduce the values of $K_{\parallel}$ such that $K_{\perp} > K_{\parallel}$. This is another reason why the assignment $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$ is preferred.

The spin-orbit coupling constant, λ, is reduced in all the complexes from the free ion value of $-828\ \text{cm}^{-1}$, signifying the extent of mixing of metal and ligand orbitals. It is pertinent to state that the g values obtained by Knebhul's approximation are subject to inaccuracies in as much as they ignore the effect of hyperfine coupling constants. However, in the present systems, the effect is likely to be the same in all the complexes. Thus the relative g values may be same although absolute values may be substantially in error.

In axial symmetry, G is a measure of the exchange interaction between Cu(II) centres in a polycrystalline solid.[24] According to Hathaway,[25] if the value of $G > 4$, exchange interaction is negligible, while $G < 4$ indicates considerable exchange interaction in solid complexes. Following this criterion, only complexes 2, 3 and 4 exclude any exchange interaction. Much reliance however can not be placed on this criterion since many planar Cu(II) complexes are known to have $G < 4$ even in the magnetically dilute state.[5,20]

We have calculated α^2 by using simple relationship[26] (4).

$$g = 2.0023 - \frac{8\lambda\alpha^2}{\Delta xy} \tag{4}$$

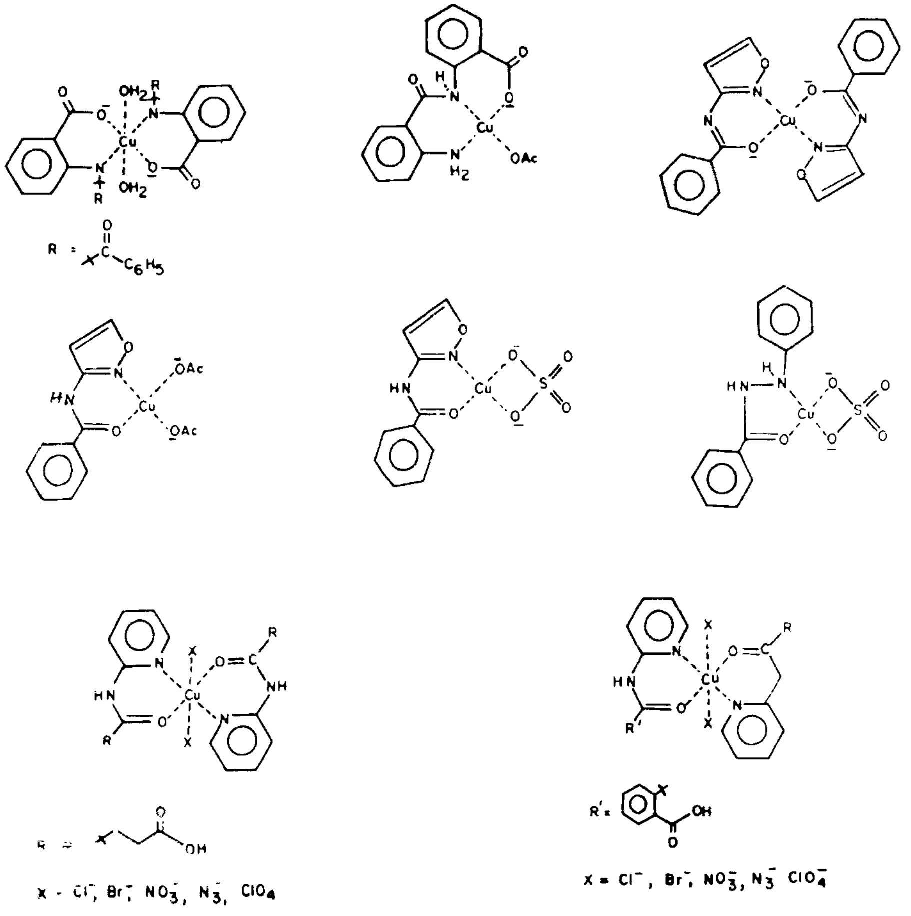


Figure 5 Proposed structures of the Cu(II) complexes.

The quantity α^2 is a function which depends on the nature of the copper-ligand bond, decreasing with increasing covalency from 1.0 to a minimum theoretical value of 0.50. All complexes are seen to be fairly covalent, α^2 varying from 0.52 to 0.76.

The most probable structural arrangements are given in Figure 5. In the absence of detailed structural studies, modes of coordination in all the complexes remain somewhat speculative; we are trying to obtain crystals suitable for X-ray analysis but have not so far been successful.

The free acid amide groups have planar configurations with large resonance stabilization energies. Amide nitrogen coordination without deprotonation will lead to a loss of planar configuration and stabilisation energy. While amide oxygen coordination requires no loss of resonance energy. Hence, the latter is expected for non-deprotonated complexes. Interestingly, iminol coordination in complex 3 is suggested on the basis of IR results. This arrangement seems to be an intermediate for deprotonated nitrogen coordination. However, deprotonation of the amide N atom is not ruled out at neutral pH values.

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