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Molecular magnetic properties of two-copper(II) containing complexes $[Cu(II)\ (1\text{-phenylamidino-}O\text{-}n\text{-butylurea})\ en\ (H_2O)]_2^{2+}$ and $[Cu(II)\ sulphato\text{-}mono\ (1\text{-phenylamidino-}O\text{-methylurea})]_2$ An EPR study

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Abstract

Electron paramagnetic resonance (EPR) investigations were conducted on [Cu(II) (1-phenylamidino-*O*-*n*-butylurea) en $(H_2O)]_2^{2+}$ (1) and [Cu(II) sulphato-mono (1-phenylamidino-*O*-methylurea)$]_2$ (2) respectively, in the temperature range 300–77 K. Fine structure characteristics of $S = 1$ system, was observed in both complexes with zero field splitting of 0.0525 and 0.0225 cm^{-1}, respectively, suggesting the formation of dimeric complexes. The presence of the half-field signal ($\Delta M_s = \pm 2$), in the complex 1, further confirmed the formation of dimer. The temperature dependence of EPR signal intensity has given evidence for the ferromagnetic (FM) coupling between the two Cu^{2+} ions. The isotropic exchange interaction constants J, were evaluated from this and were found out to be ∼57 and ∼27 cm^{-1}, respectively, for the complexes 1 and 2. The photoacoustic spectra of these complexes had shown a band around 26,400 cm^{-1} characteristic of metal–metal bonding giving an independent support for the existence of dimeric Cu^{2+} species. The high magnetic moment values at room temperature for complex 1 ($2.68\mu_B$) and complex 2 ($2.00\mu_B$), obtained from the magnetic susceptibility measurements, support the formation of ferromagnetically coupled Cu^{2+} dimers.

Keywords: Copper(II) complexes; Phenyldicyandiamide; EPR; PAS; FM coupling; Dimer

1. Introduction

Metal–metal interactions in organometallic complexes particularly those of transition metals have been the subject of many investigations for a long time [1–5]. This has been extensively reviewed even two decades ago by Smith and Pilbrow [1] and Eaton and Zaw [6]. The main interest of such investigations is to elucidate metal-metal interaction among d electron systems and also to get insight into the structural aspects by electron paramagnetic resonance (EPR), with special reference to investigate the nature of magnetic coupling in dimeric complexes.

In majority of the cases, where the site symmetry at the paramagnetic ions is identical and the exchange interaction is mediated through a shared ligand, there is a greater possibility of formation of antiferromagnetically coupled dimers resulting in localized $S = 0$ singlet state. On the other hand, the ferromagnetic interaction which can arise due to interaction of unpaired spins at different site symmetries in bimetallic systems, offers greater variety and richness of magnetic order at low temperatures. Therefore, the systems containing two strongly coupled unpaired electrons (with effective spin $S = 1$) are attracting considerable attention. Although there are many reports on EPR of antiferromagnetically coupled dimers, relatively few systems with ferromagnetically coupled dimers are reported [7,8]. Some

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of these aspects are being currently refocused due to the possibility of manipulating magnetic ordering in molecular magnets at very low temperatures [9,10] and possibility of manipulating magnetic order by external means, e.g. by optical excitation [11]. We have recently observed magnetic ordering below 40 K in $(NBu_4)_2Co_2[Cu(opba)]_3$. S [opba is *ortho*-phenylenebis (oxamato) and S is 3 $DMSO{\cdot}3H_2O$ or $2H_2O$], a weakly interacting systems, exibiting well resolved ^{14}N hyperfine structure (shfs) on the EPR spectrum of Cu(II). In these complexes, pseudo-triplet magnetic excited state formed by antiferromagnetic spin pairing between Cu^{2+} and Co^{2+} linked together in two or three dimensional network resulted in long range magnetic ordering at lower temperatures [12].

In our earlier paper on the EPR studies of dichloro-mono (1-phenylamidino-*O*-alkylurea) Cu(II) (alkyl: Me, Et, Pr, Bu or Pe), we have shown that in these complexes, copper(II) ions exist as monomers having square planar geometry. Furthermore, we obtained evidence for the magnetic field induced “partial molecular alignment” in some of these field cooled (10 KG) complexes at 77 K [13]. As part of these investigations we have synthesized two types of copper complexes, viz. [Cu(II) (1-phenylamidino-*O*-alkylurea) en $(H_2O)]_2{}^{2+}$ (type I complex), and Cu(II) sulphato-mono(1-phenylamidino-*O*-methylurea) (type II complex) where alkyl: Me, Et, Pr, Bu and Pe. EPR investigations of these complexes down to 77 K had shown that except for R: Bu in type I and R: Me in type II other complexes basically exist as Cu-monomers. Thus more interesting complexes are the butyl one in type I and methyl one in type II class which exhibited dimeric EPR spectra. Investigations on these complexes are presented in this paper. Further, the results of electronic absorption studies on the complexes 1 and 2 are also presented.

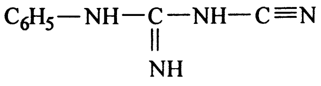
2. Experimental

2.1. Materials and instrumentation

All the chemicals used were of reagent grade. Phenyldicyandiamide (PD) (I) was synthesised by the earlier reported method [14]. The purity of the samples was checked by IR spectra.

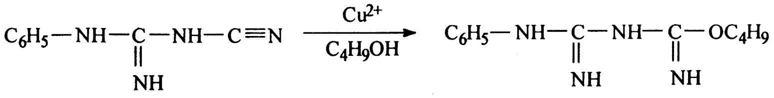
2.2. Preparation of complexes (see Table 1)

(A) Dichloro-mono (1-phenylamidino-*O*-*n*-butylurea) copper(II) (DPB) was prepared recently by refluxing cupric chloride (0.01 mol) and phenyldicyandiamide (0.01 mol) in *n*-butanol on a steam bath for 1 h. The complex was filtered off immediately and washed several times with *n*-butanol and dried in air [13]. Blue crystals (80%, mp 192 °C).



$C_6H_5-NH-\underset{\underset{NH}{\|}}{C}-NH-C\equiv N$

(I)



$C_6H_5-NH-\underset{\underset{NH}{\|}}{C}-NH-C\equiv N \xrightarrow[C_4H_9OH]{Cu^{2+}} C_6H_5-NH-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-OC_4H_9$

(II)

(B) The mixed ligand complex 1 was prepared by dissolving 20 mmol of compound (DPB) in hot aqueous ethylenediamine solution (20 cm^3; 20.1 mmol) and adding 95% hot ethanol (50 cm^3) with constant stirring for 30 min. The mixture was slowly cooled and kept in a refrigerator overnight. Pale pink crystals separated out were collected and washed repeatedly with ethanol and dried in air (60%, mp 53 °C).

(C) Complex 2 was synthesized by slight modification of the published method [15]. Bluish green crystals separated out by refluxing phenyldicyandiamide (0.01 mol)

Table 1
Analytical data and magnetic moment in different complexes

Code	Colour	Empirical formula	Calculated (%)				μ^a (B.M.)
			Found (%)				
			C	H	N	Cu	
PD	Colourless	$C_8N_4H_8$	60.6	5.0	35.0		
			59.8	4.9	34.9		
DPB	Blue	$C_{12}N_4OH_{18}CuCl_2$	39.1	4.9	15.2	17.2	1.86
			39.2	4.9	15.4	17.1	
1	Pale pink	$C_{14}N_6O_2H_{28}CuCl_2$	37.62	6.27	18.81	14.22	2.68
			37.81	6.24	18.79	14.32	
2	Blue	$C_9N_4O_7H_{16}CuCl_2$	27.87	4.12	14.45	16.38	2.00
			27.65	4.11	14.42	16.41	

PD: phenyldicyandiamide; DPB: dichloro-mono(1-phenylamidino-*O*-*n*-butylurea) copper(II).

[a] Susceptibility values of the respective complexes were measured at 298 K.

and cupric sulphate (0.01 mol) in methanol on a steam bath for 3 h, were collected immediately, washed by methanol and finally by acetone. It was dried in air (75%, dp 205 °C).

2.3. Physical measurements

Photoacoustic spectra (PAS) on solid samples were recorded using homemade spectrometer in 350–800 nm range using Tungsten halogen lamp as a source [16] whereas solution spectra were recorded on a Beckmann DU-640 spectrophotometer. IR spectra were recorded on a Bruker IFS-66V in KBr disc and far IR spectra using polyethylene pellets over the range 500–50 cm^{-1}. EPR experiments were conducted using Bruker ESP-300 spectrometer operated at X-band frequency (9–10 GHz) with 100 KHz field modulation. DPPH was used as field marker. Temperature was varied in the range 77–350 K using Bruker variable temperature accessory. The room temperature magnetic moments (μ_{eff}) were measured using PAR vibrating sample magnetometer (VSM) Model 155. C, H and N contents were determined microanalytically on a C, H, N analyzer Perkin-Elmer 240C model. The amount of copper was determined by fusing the complex with $KHSO_4$, then extracting with a mixture of HNO_3 and H_2SO_4 and finally by performing an iodometric titration. Molar conductances in MeOH were measured at room temperature on an Elico conductivity bridge type CM-82T.

3. Result and discussion

3.1. Electronic spectra

The photoacoustic (PA) signals of complexes I (Fig. 1b) and II showed a broad band ca. 15,552 cm^{-1} due to d–d transitions. It also showed a weak absorption band around 26,400 cm^{-1} indicating the possibility of metal–metal bonding [17]. The PA spectrum of well known antiferromagnetically coupled copper acetate ($S = 0$ ground state) is also included for comparison. This exhibited an absorption around 26,500 cm^{-1} typical of metal-metal bonding (Fig. 1a) in addition to a broad d–d band around 16,400 cm^{-1}. The optical absorption spectrum of complex 1 in methanol (where complex 1 dissociates into Cu^{2+} monomers), showing d → d transitions around 19,000 cm^{-1}. The highly intense absorption around 26,000 cm^{-1} or 384 nm is due to charge transfer band [18].

3.2. IR spectra

IR spectrum of phenyldicyandiamide shows a band at 2167 cm^{-1}, $\nu_{C{=}N}$ band at 1656 cm^{-1} and $\nu_{C{-}N}$ at 1396 and 1301 cm^{-1} [19]. The absence of a band at 2167 cm^{-1} in the IR spectra of the complexes I and II suggests the absence of a nitrile group in these complexes. Lowering of $\nu_{C{=}N}$ band in the range 1590–1600 cm^{-1} and appearance of $\nu_{C{-}N}$ band at 1350 and 1251 cm^{-1} indicates the coordination through C=N group of phenylamidine part. The fragment N=C–O–C of 1-phenylamidino-*O*-*n*-butylurea (II) is more delocalized and the bond order of the =C–O– group is raised which gives a new $\nu_{C{=}N}$ band at 1681 cm^{-1} after co-ordination [13,20,21]. These complexes show ν_a (C–O–C) stretch at 1188 cm^{-1} and ν_s (C–O–C) at 962 cm^{-1} [21]. The weak bands in the 920–940, 751–760 and 637–651 cm^{-1} ranges may be assigned due to co-ordinated water [17]. In the IR spectrum of complex 1, broad and strong absorption and strong band at 3231 cm^{-1} is assigned to $\nu_{N{-}H}$ of the primary amine [22,23]. Two bands at 1060 and 1392 cm^{-1} are due to $\nu_{C{-}C}$ and $\nu_{C{-}N}$ of ethylenediamine [24]. The IR spectrum of complex 2 shows bands at 961, 1002, 1096 and 1184 cm^{-1}, suggesting the presence of a bidentate bridged sulphate in the complex [15,17]. The bands in the 471–480 and 555–571 cm^{-1} ranges have been assigned to $\nu_{(M{-}N)}$ and to $\nu_{(M{-}O)}$ modes [17,24,25].

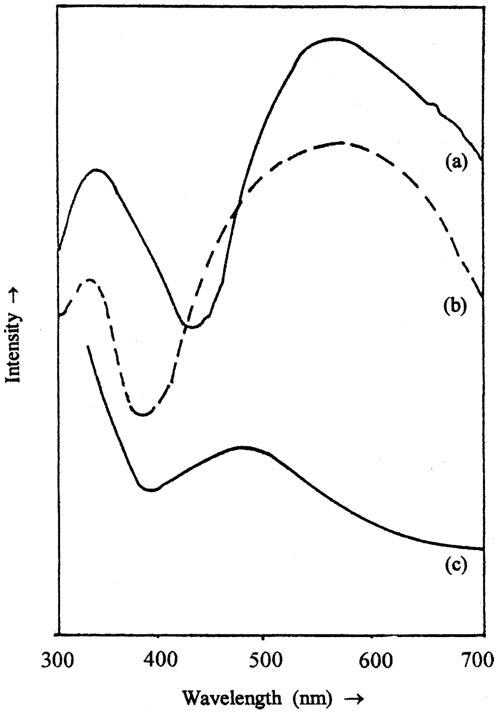


Fig. 1. Absorption spectrum of (a) copper acetate (b) complex 1 in solid state using PAS and (c) complex 1 in methanol solution using Beckman DU-6 spectrophotometer.

3.3. EPR spectra

The EPR spectra were obtained on polycrystalline samples in the temperature range 300–77 K using 2 mW power and saturation of EPR signals was not observed at this microwave power level. Fig. 2b and d shows the EPR spectra for complex 1 at 300 K and at 77 K. To resolve the copper hyperfine structure on the parallel components the EPR spectra were also recorded in the second harmonic presentation (not

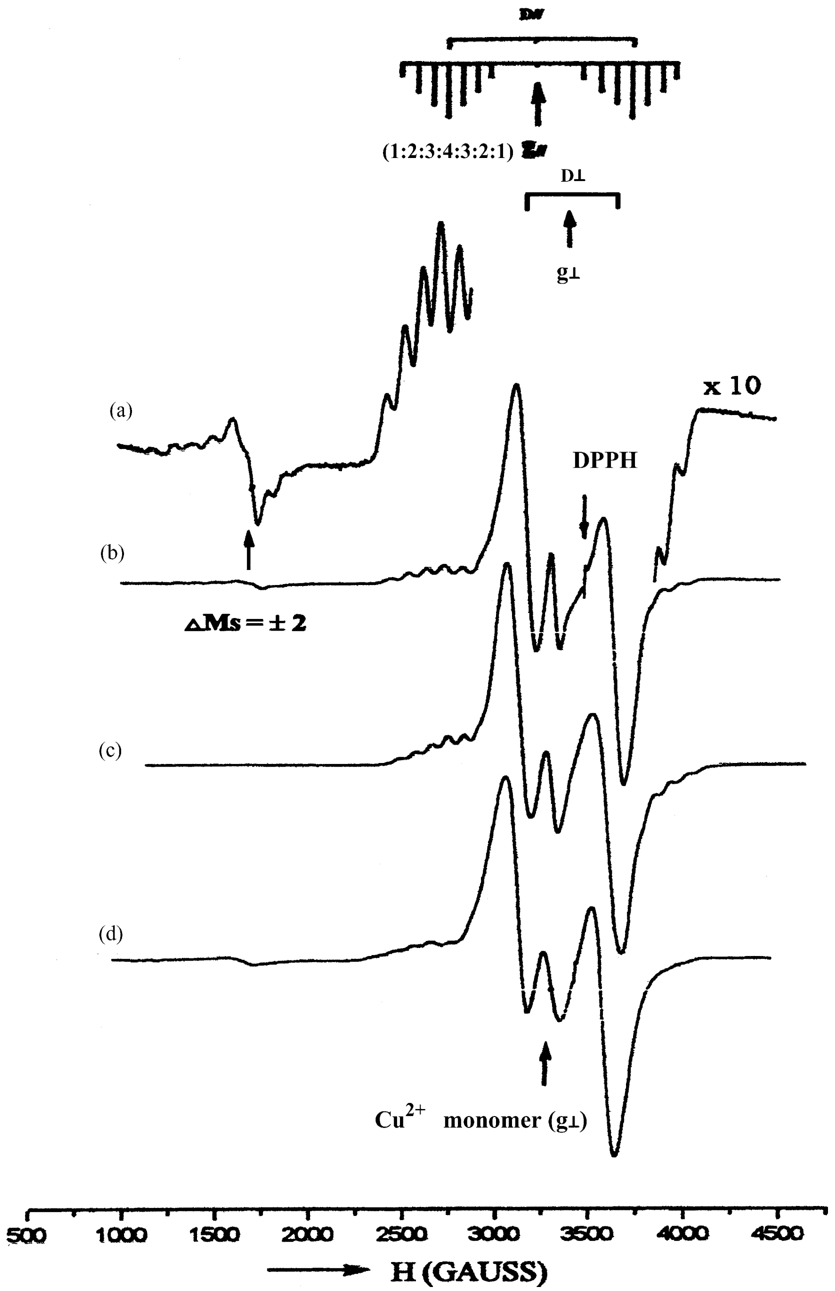


Fig. 2. EPR spectrum of complex 1 at X-band (a) at 300 K higher gain, (b) at 300 K at lower gain, (c) simulated spectrum of copper dimers using the parameters as given in Table 2 and (d) at 77 K.

shown in figure). The spectrum consists of two intense lines with features of perpendicular components having a separation of nearly 400 G. On either side of perpendicular spectrum, a signal composed of several narrow lines with nearly double the separation (790 G) as that of perpendicular separation were observed. The seven line structure on the parallel component with the relative intensities 1:2:3:4:3:2:1 of the hyperfine splitting (clearly visible on the low field // component) is due to hyperfine interaction between two Cu^{2+} ($I = 3/2$) nuclei. This signal is assigned to Cu^{2+} pairs. The most interesting feature in the EPR spectrum of the complex 1 is the resolved hyperfine structure on parallel components inspite of the fact that intermolecular dipolar interaction is expected to cause appreciable line broadening in such concentrated paramagnetic complexes. In addition, a weak signal at $g = 3.9000$, with unresolved hyperfine coupling was observed at half the resonance field ($H = 1600$ G) of that of the copper monomer. The weak signal corresponds to the forbidden transition ($\Delta M_S = \pm 2$) among the $S = 1$ coupled states, whereas, the signals observed around $g = 2.0000$ region correspond to the allowed fine structure transitions ($\Delta M_S = \pm 1$).

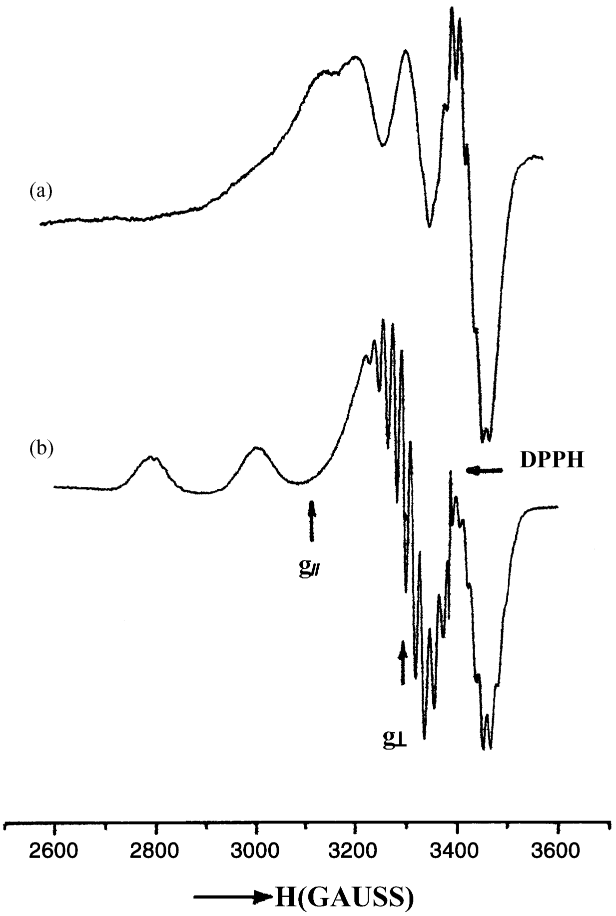


Fig. 3. EPR spectrum of complex 1 in methanol solution (a) at room temperature and (b) at 77 K.

The EPR spectrum of complex 1 (Fig. 3) dissolved in DMF and methanol at 77 K (frozen complex) showed axially symmetric spectrum. This is shown in Fig. 3. It may be noted that $(g_\perp)_{\mathrm{dimer}} \approx (g_\perp)_{\mathrm{monomer}}$ whereas $(g_{//})_{\mathrm{monomer}} > (g_{//})_{\mathrm{dimer}}$. A substantial differences in $g_{//}$ values of that of the monomer may be noted (Table 2). On dissolution in DMF and methanol in addition to breaking of a dimer into monomers which is supported conductance value in methanol ($\Lambda_M = 158\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$ for bi-univalent electrolyte) [26], there can be a change in ligation in axial position (ligand molecules get attached to complex at axial position in solution) [18]. The observed g-values, i.e. $g_{//} > g_\perp > 2.000$ for monomer and dimer are suggestive of the $d_{x^2-y^2}$ character of the unpaired electrons.

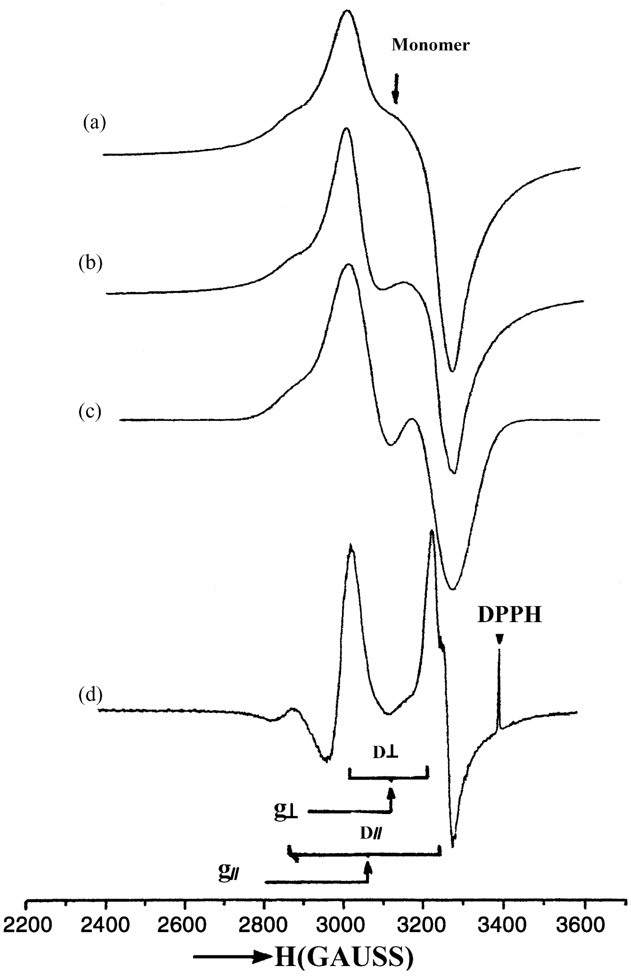


Fig. 4. EPR spectrum of complex 2 (a) at room temperature, (b) at 77 K, (c) simulated spectrum using parameters given in Table 2 and (d) second derivative spectrum at 77 K.

The EPR spectrum of the complex 2 at 300 K was very different compared to that of complex 1. The EPR spectrum showed a composite signal, viz. a weak perpendicular doublet (dimer signal) superimposed on perpendicular component of copper monomers (that is the coexistence of both copper monomers and dimer). This is shown in Fig. 4a. On

Table 2
EPR parameters of copper monomers and dimers in various matrices

Matrix	$g_{//}$	$g_\perp$	g_{iso}	$A_{//}$	A_1	A_{iso}	D (cm^{-1})	J (cm^{-1})
1. Cu^{2+} in complex 1/MeOH	2.1943	2.0530	2.1013	611.74	81.76	258.40	–	–
2. $(Cu^{2+})_2$ in complex 1	2.1200	2.0525	2.0750	254.12	–	–	0.0525	57
3. $(Cu^{2+})_2$in complex 2	2.2383	2.1773	2.1976	–	–	–	0.0225	27
4. $(Cu^{2+})_2$ in CeO_2	2.2079	2.0403	2.0962	498.77	79.22	220	–	–
5. $(Cu^{2+})_2$ in CeO_2 [30]	2.2079	2.0403	2.0962	249.40	39.60	109.44	0.066	−52
6. $(Cu^{2+})_2$ in Y zeolite [31]	2.3450	2.0660	2.1590	453.30	Unres.	–	0.048	–

Conversion factor $1\,\mathrm{G} = 2.8025 g/g_e$ MHz. Error in g is ±0.0001 and in A is ±2.8 MHz.

lowering the temperature to 77 K, and intense doublet, characteristic of fine structure emerged having $g_{//} = 2.2383$, $g_{\perp} = 2.1773$, $g_{\mathrm{iso}} = 2.1976$, $D = 225\,\mathrm{G}$ with the simultaneous disappearance of the monomer signal (Fig. 4b). These results indicate that Cu^{2+} ions are predominantly in dimeric form at 77 K, whereas at room temperature there are indications of some monomeric species of Cu^{2+}. This implies that $S = 1$ lies lower getting more populated with lowering of temperature. The EPR spectrum in the second derivative presentation is shown in Fig. 4b. The EPR spectrum was simulated using the EPR parameters given in Table 2 and is shown in Fig. 4c. The most contrasting feature in the EPR spectrum of complex 2 is the absence of any hyperfine structure arising from two equivalent coppers and also absence of half field signal due to ($\Delta \mathrm{M_S} = \pm 2$) transition between 77 and 300 K. However, room temperature magnetic moment of complex 2 is $2.0\mu_{\equiv}$ which suggests weak coupling between two copper ions. Since the complex 2 was insoluble in organic solvents, and hence was not investigated in the dissolved form.

The isotropic exchange interaction constant J or the separation between the singlet and a triplet, was calculated from the temperature dependence of the intensity of dimer signal. The population of the triplet state is governed by Boltzman distribution and the Curie law following the equation $N = N_0 3/T \exp(-J/k\beta T)$. The increase in the intensity of EPR signal with lowering of temperature suggested ferromagnetically coupled copper dimers in complex 1 and complex 2. J was estimated to be ~57 and ~27 cm^{-1} in the respective samples.

The average metal–metal distance in the $S = 1$ dimer was calculated by using the equation $D = 3g^2\beta^2/2r^3 = 1.39 \times 10^4 (g/r^3)$ [26]. The distance between the two unpaired electrons [Cu(II)–Cu(II)] in the dimers was estimated to be 3.7 and 4.7 Å, respectively, for complexes 1 and 2 (this method does not give accurate estimate of r when dipolar coupling is of the order of nuclear hyperfine coupling). Alternatively the metal–metal distance r was estimated for complex 1 from the relative intensity ratio of the forbidden half-field transition ($\Delta M_{\mathrm{s}} = \pm 2$) to that of total intensity of the normal transition ($\Delta M_{\mathrm{s}} = \pm 1$) using the following equation [27]. Relative intensity = intensity of $\Delta M_{\mathrm{s}} = \pm 2$/total intensity of $\Delta M_{\mathrm{s}} = \pm 1 = \mathrm{A}/r^6 (9.1/\nu)^2$, where υ is the operating frequency of the EPR spectrometer in GHz and A is constant and it depends on nature of paramagnetic ion [$A = 19.5 + 10.9\,\Delta g (\Delta g = |g_{//} - g_{\perp}|)$]. This method has advantage that the metal–metal distance estimated is independent of the value of exchange coupling J. The metal–metal distance estimated to be 4 Å is consistent with that of 3.7 Å obtained from the observed zero field splitting.

The EPR, magnetic susceptibility, IR and PAS data on complexes 1 and 2 are presented above clearly established Cu dimerization in both compounds. The Cu^{2+}–Cu^{2+} interaction appears to be ferromagnetic in nature as the intensity of dimer signal increases with the lowering of the temperature. And this observation is also supported by the high values of magnetic moments. The formation of dimeric copper complexes, as mentioned in the introduction, in itself is not a very new aspect as extensive literature exists. The important aspect of this investigation, however, is the existence of ferromagnetic coupling in the copper complexes and its implications in the possible modeling of the structure of these complexes. It should be reemphasized that the ferromagnetic coupling between two copper ions, in a dimer, implies that they have different local coordinations around the paramagnetic ions (that is the nature of unpaired electron is quite different with symmetry prohibiting direct overlap of electronic wavefunctions) [28] or relative orientation of monomer complexes in the crystalline matrix is such that the metal orbital in the neighboring monomer sites would be nearly orthogonal to each other. From the g-values given in Table 2, the structure of monomer species of complex 1 would be elongated octahedron with unpaired electron in $\mathrm{d}_{x^2-y^2}$ orbital under the assumption that at least one metal ion of the dimer, retained its original structure (i.e. as in complex 1 in MeOH/DMF, the g-values of other complex have been estimated to be $g_{//} = 2.0457$ and $g_{\perp} = 2.0525$).

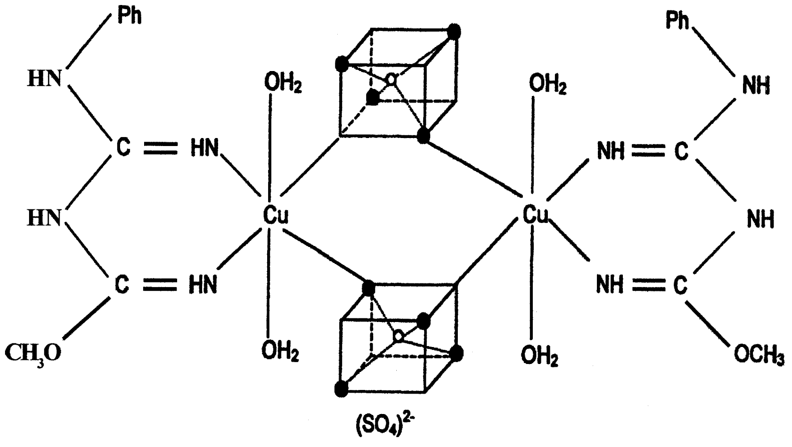


Fig. 5. Proposed structure of [sulphato mono (1-phenylamidino-*O*-methylurea) copper(II)]$_2$.

This has very small anisotrophy with $g_{\perp} > g_{//} > 2.0000$. Thus the unpaired electron has larger $3z^2$–r^2 character in this complex. If the dimerization is of two identical monomers, the *g*-values of monomer and dimer would have been the same. From the *g*-values of dimer and monomer of copper complex 1 in MeOH/DMF, it can be inferred as a possible case of dissimilar ions [29]. The coupling between two copper monomers one with $d_{x^2-y^2}$ and the other with $3z^2$–r^2 character would result in ferromagnetic coupling as observed. It is not clear why the site symmetries at two copper monomers are slightly different. This work only points to this possibility and the models given by us are purely suggestive and the structure can possibly be confirmed by other independent experiment such as X-ray diffraction. For the complex 2 also, essentially a similar senario appears to be valid, as the $d_{x^2-y^2}$ orbitals at neighboring Cu^{2+} sites will be directed in different directions due to tetrahedral nature of ${SO_4}^{2-}$ ions. The proposed structure of complex 2 is shown in Fig. 5.

4. Conclusions

In summary, this work has given clear evidence for the formation of ferromagnetically coupled dimers in copper complexes 1 and 2 having the formula [Cu(II) (1-phenylamidino-*O*-*n*-butylurea) en $(H_2O)]_2$ $(Cl_2)_2$ and [Cu(II) sulphato-mono(1-phenylamidino-*O*-methylurea)$]_2$. *J* was estimated to be ∼57 and $\sim 27\,\mathrm{cm}^{-1}$ for the complexes 1 and 2.

5. Supplementary material (for review purpose only)

There are a large number of papers published in India and International Journals regarding the synthesis of metal complexes of dicyanamide and substituted dicyanamides. But very few spectroscopic (EPR) studies [1–3] appeared dealing with bonding properties and field induced alignment in some of the copper(II) complexes.

To the best of our knowledge this will be the first spectroscopic report of the compounds derived from these ligands which tries to rationalize the magnetic properties of two-Cu(II)-containing complexes in terms of molecular structures. As our attempts to synthesize single crystal of these complexes under study are not fruitful till date, we are not in a position to add crystallographic results. We should leave it by the description of the magnetic interactions in the copper pairs deduced from the spectra with a request for a rapid publication. We think that the structures which are deduced from the EPR parameters are highly speculative. On the other hand, without giving the structural formulae of the complexes under study, we think that most readers will certainly not be able to identify the complexes from the information presented without a significant effort. So we have included one suggestive/tentative structure of complex 2 in the text and the other as supplementary material (for review purpose only).

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