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Metal Chelates of Heterocyclic Nitrogen-containing Ketones. XX. Temperature Dependence of Magnetic Susceptibility and Electron Spin Resonance Spectra of Halogeno–Copper(II) Complexes of Phenyl-2-picolyl Ketone Hydrazone and Phenyl Hydrazone

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Abstract

The interaction of hydrated copper(II) chloride or bromide with phenyl-2-picolyl ketone hydrazone and phenyl-2-picolyl ketone phenyl hydrazone, PPKhy and PPKPhy, respectively, have been studied employing elemental analyses, spectral studies (IR and electronic spectra) and the variable temperature magnetic susceptibility together with the electron spin resonance spectra. The complexes of the formulae $[CuLX_2]_2$, L = PPKhy or PPKPhy and X = Cl or Br, are found to be dimeric through a halide bridge while those of the stoichiometry $[CuL_2]X_2$ are monomeric in nature. The magnetic data showed that the dimeric complexes possess antiferromagnetic interaction. The mechanism of the magnetic interaction is discussed based on the variable temperature magnetic data and ESR spectra.

Introduction

The magnetic and thermal properties of many transition metal complexes have been studied either theoretically or experimentally [1–3]. The dimeric copper(II) complexes are of special interest due to the different mechanisms of the magnetic interaction. The very interesting organic ligands which form either dimeric and/or monomeric copper(II) complexes are those derived from hydrazine and its derivatives on condensation with the heterocyclic nitrogen-containing ketones which have been extensively studied in our laboratory [6–12]. These ligands can, in principle, act as bidentate and/or tridentate. Phenyl-2-picolyl ketone hydrazone, PPKhy, and phenyl-2-picolyl ketone phenyl hydrazone, PPKPhy, act as bidentate nitrogen donors with different basicity and steric effects which in turn affect the magnetic interaction between the metal ions. In the literature, no studies have appeared on these ligands. In this work we report the preparation and characterization of copper(II) complexes of these ligands. The variable temperature magnetic susceptibility and ESR spectra will be discussed in detail.

Experimental

Preparation of Ligands and their Copper(II) Complexes

Phenyl-2-picolyl ketone was prepared according to the methods given in our previous publications [6–8]. The hydrazones were prepared by mixing 0.1 mol of the ketone with 0.5 mol of the hydrazine hydrate or 0.12 mol of phenyl hydrazine in ethanol (50 ml). The reaction mixture was then refluxed on a water bath for 8–12 h and cooled to room temperature. The corresponding hydrazone was separated and filtered. The product was recrystallized from ethanol–chloroform (50%, *v*/*v*) yielding pale yellow needles.

The mono-ligand complexes, $[CuLX_2]_2$, L = PPKhy or PPKPhy and X = Cl or Br, were prepared by the addition of 0.01 mol of the corresponding ligand in ethanol (20 ml) to a 0.012 mol of copper(II) halide in ethanol (20 ml) followed by the addition of ammonia solution to raise the pH to 4–5. The reaction mixture was then stirred at room temperature for 2–3 h. During this period, the microcrystalline solid in each case was filtered off, washed several times with ethanol followed by ether and dried under vacuum over P_2O_5. The complexes of stoichiometry $[CuL_2]X_2$ were prepared by the addition of 0.1 mol of the copper(II) halide in ethanol (20 ml) to 0.24 mol of the corresponding ligand in ethanol (30 ml) followed by the same steps as described in the last preparation except

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TABLE I. Analytical Data of PPKhy, PPKPhy and their Copper(II) Complexes

Compound	Calculated		(found) (%)		
	C	H	N	X	Cu
PPKhy	73.9(73.6)	6.2(6.1)	19.9(20.0)		
$[\mathrm{Cu(PPKhy)Cl_2}]_2$	45.1(44.9)	3.8(3.8)	12.2(12.1)	20.5(20.3)	18.4(18.4)
$[\mathrm{Cu(PPKhy)Br_2}]_2$	35.9(35.4)	3.0(3.0)	9.7(9.7)	36.8(36.6)	14.6(14.5)
$[\mathrm{Cu(PPKhy)_2}]\mathrm{Cl_2}$	56.1(56.0)	4.7(4.6)	15.1(15.1)	12.8(12.9)	11.4(11.4)
$[\mathrm{Cu(PPKhy_2}]\mathrm{Br_2}$	48.3(48.0)	4.0(4.1)	13.0(13.1)	24.7(24.8)	9.8(9.7)
PPKPhy	78.9(78.6)	6.6(6.5)	14.5(14.7)		
$[\mathrm{Cu(PPKPhy)Cl_2}]_2$	54.1(53.8)	4.1(4.0)	9.9(9.8)	16.8(16.7)	15.0(15.1)
$[\mathrm{Cu(PPKPhy)Br_2}]_2$	44.7(44.3)	3.4(3.3)	8.2(8.1)	31.3(31.2)	12.4(12.5)
$[\mathrm{Cu(PPKPhy)_2}]\mathrm{Cl_2}$	64.3(64.1)	4.8(4.8)	11.8(12.0)	10.0(9.9)	8.9(9.0)
$[\mathrm{Cu(PPKPhy)_2}]\mathrm{Br_2}$	57.2(56.8)	4.3(4.3)	10.5(10.6)	20.0(19.9)	7.9(8.0)

without the addition of ammonia. If the reaction mixtures were heated, an oxidation–reduction reaction took place producing copper mirror and azo-derivatives.

The elemental analyses and physical measurements were carried out as reported before [6–12]. The elemental data are given in Table I.

Results and Discussion

Infrared Spectra

The main infrared spectral bands of PPKhy, PPKPhy and their copper(II) complexes with their tentative assignments are listed in Table II. The vibrational frequency in the 3000–3500 cm^{-1} region displayed in the spectra of the ligands is characteristic of NH and NH_2 groups in the hydrazone residue. This band is not greatly affected upon complexation. The strong to medium bands in the region of 995–1005 cm^{-1} are responsible for the ν(N–N) vibrational modes and they exhibit upward shift in the complexes, indicating its participation in coordination. The ν(C=N), azomethine, is characterized by the strong band at 1590–1600 cm^{-1}. This band was shifted to higher frequency in the spectra of all copper(II) complexes with splitting and reduction in its intensities. This indicates the participation of the azomethine group in the coordination. The pyridine ν(C=N) group is characteristic of the very strong band in the 1580–1575 cm^{-1} region which upon complex formation shifted to lower frequency with a reduction in its intensity. Furthermore, δ_{Py} appeared at 640–643 cm^{-1} in the free ligands, exhibiting a negative shift in the complexes. This indicates that pyridine ring is involved in coordination through its C=N donor. The far infrared spectra of the complexes were recorded to investigate the nature of bonding of the halide ions with copper(II) and also to verify the copper-donor bonds in the ligands. The spectra displayed bands in the 380–395 and 340–355 cm^{-1} characteristic of ν(Cu–N) vibrational frequency in case of PPKhy and PPKPhy, respectively. Also, the ν(Cu–Py) vibrational modes are traced at 240–260 cm^{-1}. The stretching vibrational modes of Cu–Cl and Cu–Br in the complexes $[\mathrm{CuLX_2}]_2$ are displayed at 230–235 and 195–205 cm^{-1} beside other bands at 275–280 and 220–230 cm^{-1}, respectively. This indicates the existence of

TABLE II. Characteristic Infrared Bands (cm^{-1}) of PPKhy, PPKPhy and their Copper(II) Complexes[a]

Compound	ν(C=N) azomethine	ν(C=N) Py	ν(NH) NH_2	ν(N–N)	ν(Cu–N)	ν(Cu–Py)	ν(Cu–X) bridging	ν(Cu–X) terminal
PPKhy	1600s	1580s	3200–3450br	995m				
$[\mathrm{Cu(PPKhy)Cl_2}]_2$	1620m	1570m	3280–3460br	1010m	390s	260m	230m	275s
$[\mathrm{Cu(PPKhy)Br_2}]_2$	1615s	1560m	3300–3460br	1015m	385s	255m	205m	225m
$[\mathrm{Cu(PPKhy)_2}]\mathrm{Cl_2}$	1620s	1570s	3290–3480br	1010s	382m	260m		
$[\mathrm{Cu(PPKhy)_2}]\mathrm{Br_2}$	1620s	1570m	3280–3490br	1015m	390m	265m		
PPKPhy	1590s	1575s	3000–3500br	1005s				
$[\mathrm{Cu(PPKPhy)Cl_2}]_2$	1615s	1565m	3200–3480br	1015m	345m	250m	235m	280s
$[\mathrm{Cu(PPKPhy)Br_2}]_2$	1620s	1560s	3100–3480br	1020m	355m	245s	195m	230m
$[\mathrm{Cu(PPKPhy)_2}]\mathrm{Cl_2}$	1615s	1555s	3210–3470br	1020m	340m	245m		
$[\mathrm{Cu(PPKPhy)_2}]\mathrm{Br_2}$	1615s	1560m	3100–3450br	1020s	350s	250m		

[a] s = strong, m = medium, br = broad.

the halide ions in the coordinate sphere as bridged and terminals [8–10].

The molar conductivity of these complexes as 10^{-3} M solutions in either nitrobenzene or chloroform was investigated. The data for the mono-ligand complexes, Table I, indicates the non-electrolytic nature of these complexes, while the bis-ligand complexes exhibit values characteristic of 1:2 electrolytes. On repeating the measurements in DMF solvent under the same conditions, the mono-ligand complexes displayed values of 50.42–75.87 ohm^{-1} cm^2 mol^{-1}. These values are still lower than those of 1:1 electrolytes [6–8], but indicate partial dissociation and/or displacement of the halide ion by the solvent molecules. On repeating the measurements after 24 h the values obtained were in the 102.65–112.35 ohm^{-1} cm^2 mol^{-1} range characteristic of 1:1 electrolytes. On measuring the last solution at 45 °C, values of 210–218.86 ohm^{-1} cm^2 mol^{-1} were obtained, indicating 1:2 electrolytes in DMF. This could be explained on the basis of:

$$[CuLX_2]_2 + DMF \xrightleftharpoons{\text{room temp.}\ 24\ h}$$

$$[Cu_2L_2X_3(DMF)]X + DMF \xrightleftharpoons{45\ ^\circ C\ 24\ h} 2[CuL(DMF)_2]X_2$$

Similar data were reported elsewhere [7, 8].

Magnetic Susceptibility

The room temperature magnetic moments of $[CuLX_2]_2$ are 1.13–1.14 and 0.87–0.97 BM for X = Cl and Br, respectively, indicating molecular association. This molecular association may be due to Cu–Cu bonding in the complexes and/or magnetic interaction through a bridge. According to the IR data, the more likely factor in this association is the bridged halide. As will be discussed later, the electronic spectra of the complexes lack any transitional band in the 26000–26670 cm^{-1} range due to Cu–Cu bonding. Another reason for the halide bridge is that when the interaction comes from direct copper–copper bonding, the magnetic moment must have values characteristic of diamagnetic. To clarify this problem, the variable temperature magnetic susceptibility of each complex was measured in the temperature range of 300–4 K. The data for some complexes are shown in Figs. (1, 2). The magnetic behaviour of all complexes is similar although the maxima are different. The susceptibilities pass through maxima at 25–35 K and then fall to very small values below 6–8 K. The small rise in the susceptibility observed was presumably due to the presence of a small amount of monomeric copper(II) complex. The reciprocal susceptibilities, Figs. (1, 2), follow very closely a Curie–Weiss behaviour with deviations especially at the temperature range of 75–80 K. The extrapolation from the range 80–300 K gave the Weiss constant, θ, for each complex. The values of the Weiss constant are −9 and −20.2 K for X = Cl and Br in case of PPKhy and −10.2 and −21 K for X = Cl and Br in case of PPKPhy, respectively, Table III. At T = 80 K, the complexes thus exhibit normal paramagnetism, although an overall antiferromagnetic interaction is observed at lower temperature. In the dimeric copper(II) complexes, the magnetic behaviour of the spin–spin coupling can be described with the help of Heisenberg Spin–Spin Exchange Hamiltonian, and since the magnetic moment is strongly reduced at room temperature and decreased further with

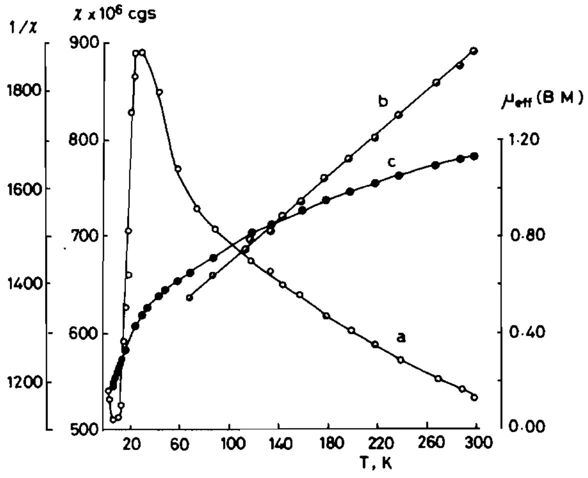

Fig. 1. Magnetic data of $[Cu(PPKhy)CuCl_2]_2$: (a) molar magnetic susceptibility; (b) reciprocal of molar magnetic susceptibility; (c) magnetic moments.

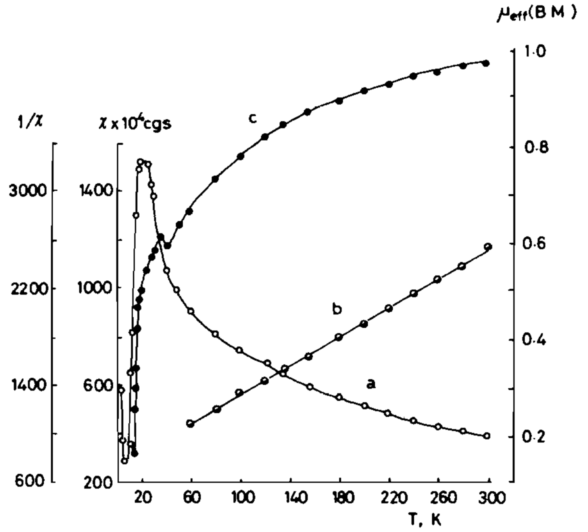

Fig. 2. Magnetic data of $[Cu(PPKPhy)Br_2]_2$: (a) molar magnetic susceptibility; (b) reciprocal of molar magnetic susceptibility; (c) magnetic moment.

TABLE III. Electronic Spectral (cm^{-1}) and Magnetic Data (BM) of Copper(II) Complexes

Compound	μ_{eff}[a]	Electronic transitional bands
$[Cu(PPKhy)Cl_2]_2$	1.13	18500, 15220, 12730
$[Cu(PPKhy)Br_2]_2$	0.87	17850, 15040, 12480
$[Cu(PPKhy)_2]Cl_2$	1.93	18580, 14770, 13700, 12750, 10700
$[Cu(PPKhy)_2]Br_2$	1.96	18600, 14800, 13580, 12550, 10900
$[Cu(PPKPhy)Cl_2]_2$	1.14	17400, 14950, 12155
$[Cu(PPKPhy)Br_2]_2$	0.97	17230, 14355, 12030
$[Cu(PPKPhy)_2]Cl_2$	1.82	16835, 15020
$[Cu(PPKPhy)_2]Br_2$	1.87	16720, 15400

[a] Measured at room temperature.

decreasing temperature, it is wise to apply the Van-Vleck equation [9]. On the basis of the isotropic Heisenberg Dirac-Van-Vleck, HDVV, model,

$$\chi_M^{corr} = \frac{N\beta^2 g^2}{3K(T-\theta)}\,[1 + (1/3)\exp^{-2J/KT}]^{-1} + N\alpha$$

where J is the spin–spin coupling constant, θ is a constant which takes into account any additional magnetic effect in the lattice, N is Avogadro's number (6.023×10^{23}), β is the Bohr magneton (0.9273×10^{-20} erg/gauss), K is Boltzman's constant (1.381×10^{-16} erg/degree) and T is the absolute temperature. $N\alpha$ is the temperature-independent paramagnetism and has the value 60×10^{-6} cm^3 mol^{-1}. Using the values of θ from the graphs and $N\alpha$, the magnetic parameters J and g (Lande' splitting factor) are calculated by means of the last equation after calculation of the correct magnetic susceptibility of the dimeric species only, using the method given before [11, 12]. The values of J are -12.3 and -23.2 cm^{-1} for chloro- and bromo-copper(II) complexes of PPKhy and -9.6 and -19.3 cm^{-1} in case of PPKPhy complexes, respectively. The Lande' splitting factor was found to have values in the range 2.13 ± 0.01. The values of J are related to the nature of the bridged anion and the basicity and steric requirements of the ligands. In all cases, the J values for chloro-complexes are more than that of the bromo-complexes. This could be attributed to the larger size and softer nature of the bromide ion, which leads to greater overlap of the bridging orbitals with the metal orbitals producing a greater antiferromagnetic interaction [13–15]. The steric effects of the ligands can also affect the magnitude of J; as the steric effects increases, the Cu–X–Cu angle will also increase leading to a decrease the Cu–X bond distance which in turn leads to the reduction of the antiferromagnetic interaction [14, 15]. This idea could be used to explain why the complexes of PPKPhy gave smaller J values than that of PPKhy, where the steric effect of the first is higher than in the latter. The mechanism of this type of magnetic interaction can be explained based on the structure of these complexes. As we will discuss later, these complexes are associated with a square-based pyramidal ligand field. In this geometry, the only occupied orbital in the metal ion is $3d_{x^2-y^2}$ and the Cu–X angle will be 90°, and the same for Cu–X–Cu, if we consider the x and y directions only, the Cu(1)–X(1) and Cu(2)–X(2), respectively. Electron transfer may be then visualized as occurring from the p_σ orbitals of each of the bridged atoms to each of the copper atoms along the pathways $p_\sigma(x)[X(1)] \rightarrow d_{x^2-y^2}[Cu(1)]$, $p_\sigma(y)[X(1)] \rightarrow d_{x^2-y^2}[Cu(2)]$, $p_\sigma(x)[X(2)] \rightarrow d_{x^2-y^2}[Cu(2)]$, $p_\sigma(y)[X(2)] \rightarrow d_{x^2-y^2}[Cu(1)]$. Such a transfer produces unpaired spins on each halide bridge which are parallel giving a strong reduction to the magnetic moment. Also, by considering the report given by Bertrand *et al.* [16] the planes formed in the title dimeric copper(II) complexes by five-coordination around the copper ion and by two-coordination around the bridged halide ions are all co-planar. Therefore, the reduction of the magnetic moments could be also attributed to the π-type super-exchange interaction in the planes between d_{xz} and d_{yz} orbitals of the two copper ions via the halide p_π-orbitals, $[Cu3d_{xz}-X(3p_\pi)-Cu(3d_{yz})]$. Therefore, both the σ- and π-interactions could be responsible for the observed antiferromagnetism in the complexes under investigation. Also, if we consider the s orbitals on the two bridged-halide ions, the coupling of the unpaired spins on the copper ions would be antiferromagnetic in nature. This picture is of course over simplified. The orbital containing the unpaired electron can not be described simply as $d_{x^2-y^2}$. In addition, the mechanism just described would predict some value of triplet–singlet separation, $2J$, for all complexes of this type provided that the environment of the copper ion is the same.

The room temperature magnetic moments of the complexes of stoichiometry $[CuL_2]X_2$, L = PPKhy or PPKphy and X = Cl or Br, are in the 1.82–1.96 BM range, indicating the presence of one unpaired electron as expected for monomeric copper(II)

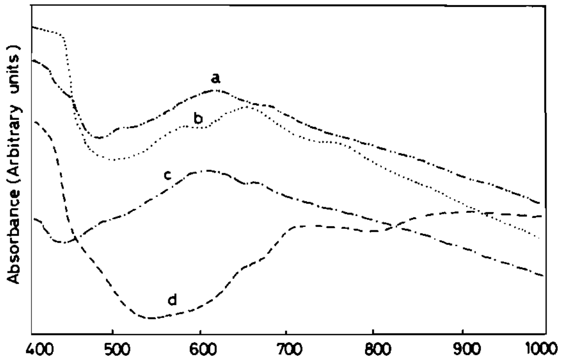

Fig. 3. Electronic spectra of: (a) $[Cu(PPKPhy)Cl_2]_2$; (b) $[Cu(PPKPhy)Br_2]_2$; (c) $[Cu(PPKhy)Cl_2]_2$; (d) $[Cu(PPKhy)Br_2]_2$.

complexes. Furthermore, these values are found to decrease very slightly with decreasing the temperature, indicating the presence of a low-lying excited term which at high temperatures is able to mix some of its orbital angular momentum of the ground state via spin–orbit coupling [17].

Electronic Spectral Data

The nujol mull and the saturated nitrobenzene solution spectra of the complexes $[CuLX_2]_2$, L = PPKhy or PPKPhy and X = Cl or Br, are similar and identical, respectively. Some representative spectra are shown in Fig. 3 and the data are collected in Table III. The spectra exhibit broad bands at 15220–15040 and 14950–14355 cm^{-1} for L = PPKhy and PPKPhy, respectively. These are beside two shoulders at 12730–12480, 18500–17855 cm^{-1} for PPKhy complexes, and 12155–12030 and 17400–17230 cm^{-1} in case of PPKPhy complexes. These spectral features are consistent with the copper(II) ion in a square based pyramidal environment rather than trigonal bipyramidal [16–18]. The latter is characterized by an intense band located in the 14000–12000 cm^{-1} region [16–21]. Furthermore, these spectral data are similar to those reported for pyridine bis(salicyl-aldiminato)copper(II) and others with known molecular structures and associated with square based pyramidal environments [22, 23]. Assuming approximately a C_{4v} symmetry for the title complexes, three bands are expected. It is tentatively found that the main bands at 15220–15040 and 14950–14335 cm^{-1} for L = PPKhy and PPKPhy, respectively, can be assigned to $^2B_1 \rightarrow {}^2B_2$ while the shoulder at the lower energy side is due to $^2B_1 \rightarrow {}^2A_1$ and that at higher energy side to $^2B_1 \rightarrow {}^2E_1$ transitions [22, 23].

The electronic spectra of the bis-ligand complexes $[CuL_2]X_2$, L = PPKhy or PPKPhy and X = Cl or Br are quite different. Representative spectra are shown in Fig. 4 and the data are depicted in Table III. The spectra of $[Cu(PPKhy)_2]X_2$ exhibit a multicomponent band covering the range 17000–14000 cm^{-1} beside a strong charge transfer band at >20000 cm^{-1}. These spectral data are consistent with that reported for many copper(II) ions in square planar ligand fields [23, 24] with bidentate and/or tridentate ligands. In the square planar field, three possible transitions are expected. Therefore, the two bands at 16835–16300 and 15400–14650 cm^{-1} are assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, in D_{4h} symmetry. The band due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition can not be identified in the spectra of these complexes, but it may be responsible for the asymmetric nature of the band at 15400–14650 cm^{-1}. The spectra of $[Cu(PPKPhy)_2]X_2$, Fig. 4, display four bands in the region of 18580–18600, 14770–14800, 13700–13580 and 10900–10700 cm^{-1}. In addition, a weak shoulder at 12750–12550 cm^{-1} was observed. The shapes as well as the band positions could not account for the square planar structure, but they are consistent with those observed for tetrahedral copper(II) complexes [22–24]. Based on the crystal field and molecular calculations for copper(II) complexes with C_{2v} point groups, the band at 13700–13580 cm^{-1} can be assigned to the $d_{xy} \rightarrow d_{xz}$ promotion and that at 10900–10700 cm^{-1} to $d_{yz} \rightarrow d_{xz}$ transition, while the remaining transitions contribute to the overall band envelope.

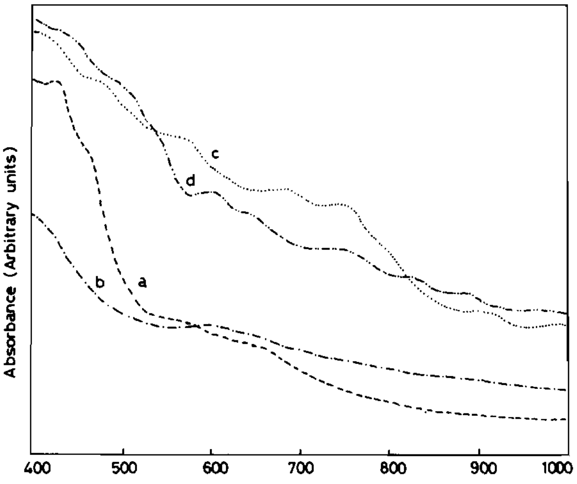

Fig. 4. Electronic spectra of: (a) $[Cu(PPKPhy)_2]Cl_2$; (b) $[Cu(PPKPhy)_2]Br_2$; (c) $[Cu(PPKhy)_2]Cl_2$; (d) $[Cu(PPKhy)_2]Br_2$.

Electron Spin Resonance Spectra

Some representative X-band ESR spectra of $CuLX_2$ at room temperature are shown in Fig. 5, and the data are given in Table IV. The bromo-complexes exhibit only one broad signal, $\Delta_{peak-peak} = 660$ and 680 gauss for L = PPKhy and PPKPhy, respectively.

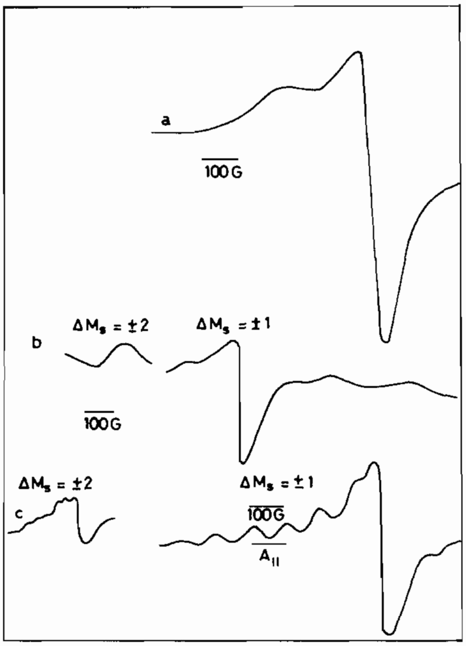

Fig. 5. X-band ESR spectra of [Cu(PPKhy)Cl$_2$]$_2$: (a) polycrystalline at room temperature; (b) dichloromethane solution at room temperature; (c) dichloromethane frozen glass.

This kind of behaviour is very common for the bromo-copper(II) complexes and can be attributed to the dipolar broadening and enhanced spin lattice relaxation of the bromide ion [25, 26]. The chloride-containing complexes exhibit a strong broad signal at 3280–3320 gauss and a very weak one at 2920–2885 gauss. The analysis of these spectra gave data listed in Table IV. More resolvable spectra were taken for the samples as dichloromethane solution either at room temperature or at 77 K, Fig. 5, and the ESR parameters are listed in Table IV. All the spectra display a broad signal at the half field region (≃1600 gauss) at room temperature which become more resolvable and well defined at 77 K, where several lines are observed. Also, the spectra exhibit strong signals at 3100–3200 gauss with two weak signals at 4380–4420 and 5830–5860 gauss. The last two signals are assigned to the parallel and perpendicular components of the singlet ($S = 0$, $M_s = 0$) to triplet ($S = 1$, $M_s = \pm 1$) transitions. The broad band at ≃ 1600 gauss is assigned to the $\Delta M_s = \pm 2$ transition. The frozen glass spectra exhibit six peaks at the low field side of the perpendicular region due to the copper(II) ion in the spin stage =1/2. From the sequence of the ESR spectra and the use of ref. 27

$$W_0 = g_{\parallel}\beta H + 2D(M_s - 1/2) + (A/N)M_I$$

where $W_0 = h\nu$ = quantum energy = 0.3065 cm^{-1}, N is the number of interacting ions (two in this case), A is the nuclear hyperfine splitting constant obtained from the splitting pattern in the low field parallel lines (156–183 × 10^{-4}), and M_s and M_I are the electronic and nuclear spins which have values of 1.0 and ±3, respectively; the parameter D was calculated to be 0.048–0.43 cm^{-1} for the chloro-complexes and 0.039–0.041 cm^{-1} for the bromo-complexes. By the use of the equations given in our previous work [7–11], the exchange parameters, D_{ex}, and the dipole–dipole interaction, D_{dd}, are calculated and given in Table IV. From the calculated values of D_{dd} and D_{ex}, one can observe that the more pronounced factor is the D_{ex}. With the use of the values of D and D_{ex} in the equation [27],

$$D = D_{ex} - (g_{\parallel}^2 - 1/2g_{\perp}^2)\beta^2/r^3$$

the separation distances between Cu–Cu in these dimeric copper(II) complexes are calculated. The

TABLE IV. Electron Spin Resonance Data of the Dimeric Copper(II) Complexes

Compound	State	T (K)	$\Delta M_s = 1$							$\Delta M_s = \pm 2$
			$g_{\parallel}$	$g_{\perp}$	g_{av}	G	$A_{\parallel}$[a]	D[b]	D_{ex}[b]	g
[Cu(PPKhy)Cl$_2$]$_2$	solid	296	2.26	2.08	2.14	3.25				
	CH$_2$Cl$_2$	296	2.25	2.08	2.14	3.13	173			4.28
	CH$_2$Cl$_2$	77	2.26	2.07	2.13	3.71	172	0.048	0.043	4.30
[Cu(PPKhy)Br$_2$]$_2$	solid	297			2.15					
	CH$_2$Cl$_2$	296	2.28	2.09	2.15	3.11	180			4.14
	CH$_2$Cl$_2$	77	2.27	2.09	2.15	3.00	183	0.039	0.034	4.13
[Cu(PPKPhy)Cl$_2$]$_2$	solid	296	2.28	2.09	2.15	3.29				
	CH$_2$Cl$_2$	296	2.29	2.09	2.16	3.22	178			4.13
	CH$_2$Cl$_2$	77	2.28	2.09	2.15	3.11	179	0.043	0.038	4.12
[Cu(PPKPhy)Br$_2$]$_2$	solid	296			2.13					
	CH$_2$Cl$_2$	296	2.26	2.07	2.13	3.71				4.20
	CH$_2$Cl$_2$	77	2.26	2.07	2.13	3.71	156	0.041	0.037	4.18

[a] $A_{\parallel}$ values are given in cm^{-1} multiplied by 10^4; [b] D and D_{ex} are given in cm^{-1}.

values were found to be in the range of 3.48–4.12 Å, Table IV. The obtained values are used to interpret the appearance of the $\Delta M_s = \pm 2$ transition as well as the resolved signals. This transition appears when the Cu–Cu separation is between 3 and 5 Å, and its intensity decreases and disappears when the distance becomes more than 5 Å, where the zero-field splitting becomes very small [28, 29]. Accordingly, the magnetism as a function of temperature and the variable ESR data are used to proove the presence of intramolecular exchange in these dimers.

The room temperature X-band ESR spectra of the polycrystalline samples $[Cu(PPKPhy)_2]X_2$, X = Cl or Br, are of the axial type giving two g-values, $g_\parallel$ = 2.26, 2.25 and $g_\perp$ = 2.05, 2.04, for X = Cl and Br, respectively, and g_{av} = 2.19 and 2.11, respectively. In these spectra we could observe the hyperfine lines for copper ions with a separation of 180×10^{-4} for X = Cl and 185×10^{-4} cm^{-1} for X = Br, but the nitrogen hyperfine lines could not be observed. On recording the spectra of the polycrystalline samples at 77 K, the nitrogen lines were detected and found to be 11×10^{-4} and 14×10^{-4} cm^{-1}, respectively. The extensive analyses of these spectra gave the values of $A_\parallel$ and $A_\perp$ to be 180×10^{-4}, 15×10^{-4} cm^{-1} in case of chloro-complexes and 185×10^{-4}, 15×10^{-4} cm^{-1} for bromo-complexes. The resolution of Cu^{2+} hyperfines in these complexes could be attributed to a decrease in the dipolar interaction. This reduction in the dipolar interaction could be due to the orientation of the bulky NH–Ph group in a manner so as to increase the separation between successive planes containing the planar CuN_4 units. This has been reported in the crystal structure of hexakis(imidazole)-copper(II)nitrate, and it resulted in the partial resolution of the copper lines.

The X-band ESR spectra of the polycrystalline sample $[Cu(PPKhy)_2]X_2$, X = Cl or Br, at room temperature are typical tetragonal spectra, Fig. 6.

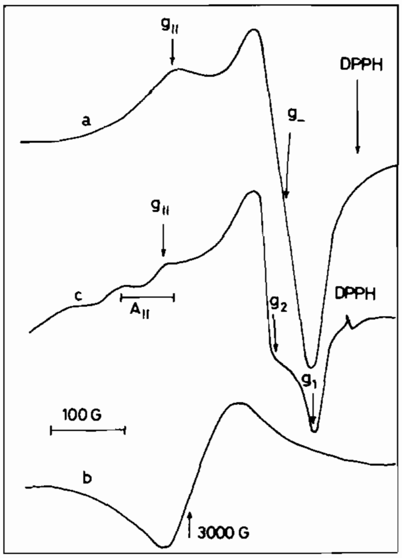

Fig. 6. X-band ESR spectra of $[Cu(PPKhy)_2]Cl_2$: (a) polycrystalline sample at room temperature; (b) dichloromethane solution at room temperature; (c) dichloromethane frozen glass.

The analysis of these spectra gave $g_\parallel$ = 2.26, 2.28 and $g_\perp$ = 2.06 and 2.07 for X = Cl and Br, respectively. The G factor was calculated by using $G = g_\parallel - 2/g_\perp - 2$, giving values of more than four, indicating the absence of super-exchange interaction between the copper centers and that the local tetragonal axes are aligned parallel or slightly misaligned. The improved resolution of g and the hyperfine anisotropy of the copper ion are obtained as frozen glass samples. In all cases the nitrogen lines are not observed, but the anisotropic hyperfine coupling could be estimated to be 60×10^{-4} and 61×10^{-4} cm^{-1} for chloro- and bromo-complexes, respectively; such values are uncommon for copper(II) complexes, especially those not containing sulphur donor ligands.

TABLE V. Electron Spin Resonance Spectra of the Monomeric Copper(II) Complexes

Compound	State	T (K)	$g_\parallel$	$g_\perp$	g_{av}	G	$A_\parallel$	$A_\perp$	A_{av}[a]
$[Cu(PPKhy)_2]Cl_2$	solid	296	2.26	2.06	2.13	4.33			
	CH_2Cl_2	296			2.14				
	CH_2Cl_2	77	2.31	2.12 2.06	2.16		60.0		
$[Cu(PPKhy)_2]Br_2$	solid	296	2.28	2.07	2.14	4.10			
	CH_2Cl_2	296	2.30		2.13				
	CH_2Cl_2	77	2.30	2.11 2.05	2.15		61.0		
$[Cu(PPKPhy)_2]Cl_2$	solid	296	2.26	2.05	2.12	5.20	180.0		
	solid	77	2.23	2.04	2.10	5.75	182.0	15	70
$[Cu(PPKPhy)_2]Br_2$	solid	296	2.25	2.05	2.11	5.00	185.0		
	solid	77	2.28	2.07	2.14	4.00	185.0	15	72

[a] $A_\parallel$, $A_\perp$ and A_{av} values multiplied by 10^4 cm^{-1}.

The origin of the small hyperfine coupling constant in these pseudo tetrahedral copper(II) complexes is associated with a metal 4s and 4p orbital admixture in the ground state. On repeating the measurements on CH_2Cl_2 solutions at room temperature, only single line spectra are observed. This could be attributed to the small anisotropic super-exchange coupling [30, 31].

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