

Synthesis, magnetic and electrochemical properties of binuclear copper(II) complexes of pyridoxal hydrazones

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Abstract

Some new binuclear copper(II) complexes with pyridoxal benzoylhydrazone (PBH), pyridoxal *o*-hydroxybenzoylhydrazone (PHBH), pyridoxal picolinoylhydrazone (PPH), pyridoxal nicotinoylhydrazone (PNH), and pyridoxal isonicotinoylhydrazone (PINH) have been synthesized and characterized by analytical, magnetic, spectral, ESR and electrochemical methods. All the complexes exhibit normal magnetic moments at room temperature. The variable temperature magnetic moments, however, indicate the presence of very weak intramolecular antiferromagnetic interactions ($-2J \approx 90 \text{ cm}^{-1}$) in between the copper(II) centers in the complexes. The ESR spectral data at 77 K are characteristic of binuclear Cu–Cu complexes and exhibit a seven-line pattern in the low field g_{\parallel} region. The cyclic voltammograms of each complex showed two oxidation waves attributed to $\text{Cu}_2^{\text{II,II}} \rightarrow \text{Cu}_2^{\text{II,III}}$ and $\text{Cu}_2^{\text{II,III}} \rightarrow \text{Cu}_2^{\text{III,III}}$ processes at significantly low potentials.

Introduction

The study of binuclear copper(II) complexes is a subject of considerable current interest because of their structural, magnetic, ESR and electrochemical properties and also as potential models for a number of important biological systems containing couple sites [1–13]. In general, systems of this sort are strongly antiferromagnetically coupled and mixed-valence copper(I,II) complexes are generated by one-electron reduction steps at negative potentials [5, 6] or copper(I,I) species by the transfer of two electrons at the same negative potential [8, 12]. In a few cases, the electron delocalization over a pair of copper ions was evidenced by ESR spectroscopy [14].

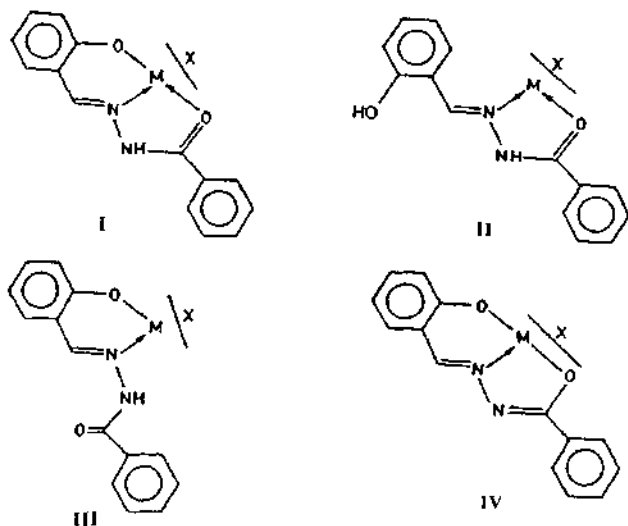
Although the oxidation of copper(II) to copper(III) is known in many mononuclear tri- and tetrapeptide complexes [15, 16], the characterization of binuclear

copper(II,III) and -(III,III) is still very limited. Mandal *et al.* have reported that the dicopper(II,II) complex of a saturated macrocyclic ligand can be oxidized stepwise to dicopper(II,III) and then to (III,III) [9]. The mixed valence species has been 'spin-trapped' even at room temperature by ESR spectroscopy. One-electron oxidation of the trinuclear copper(II) complex of pyridine 2-carboxaldehyde oxime or isonitrosoketimines to tricopper(II,II,III) species is also known [17]. Recently, Koikawa *et al.* have reported the stepwise formation of binuclear copper(II,III) and -(III,III) species from binuclear complexes of *N*-(2-hydroxyphenyl)salicylamide and homologues with a substituent on the '2-hydroxyphenyl' moiety by one-electron oxidation steps at positive potentials [18]. Except for these, no examples of synthetic binuclear copper(II) complexes with one-electron oxidation steps are known.

Hydrazones formed by condensation of substituted acid hydrazides with aromatic 2-hydroxyaldehydes, β -diketones, and keto acids of the pyruvic acid type are well known chelating agents [19]. The most studied among them are the benzoylhydrazones of 2-hydroxy-

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aldehyde, which can form four types of coordination with transition metal ions (I-IV).



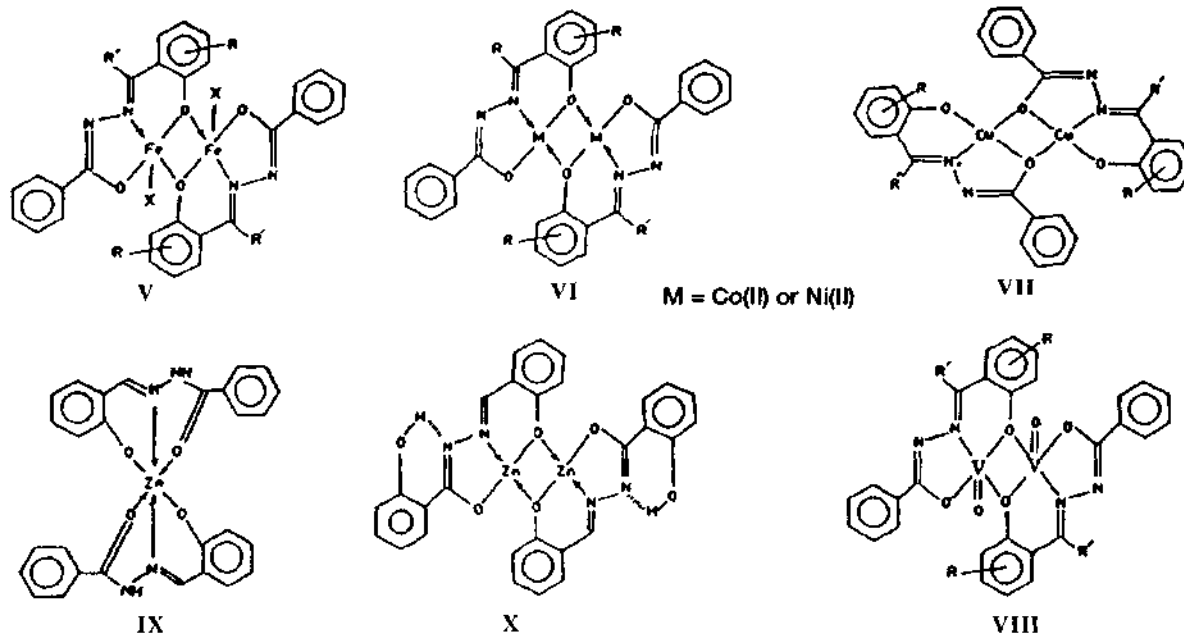
The reaction of VO(IV), Mn(II), Fe(III), Fe(II), Co(II), Ni(II) and Cu(II) transition metal ions with the benzoylhydrazones of salicylaldehyde, *o*-hydroxyacetophenone, *o*-hydroxypropionophenone, *o*-hydroxybutyrophenone and 2-hydroxynaphth-1-aldehyde in neutral or weakly alkaline solution affords mainly complexes containing the enol form of the ligands [20-23]. The variable-temperature magnetic properties of the complexes containing the deprotonated enol form of benzoylhydrazones indicate the presence of antiferromagnetic exchange interactions between the paramagnetic metal ions [22, 23]. On the basis of IR and magnetic studies, a dimeric structure V was suggested for Fe(III), VI for

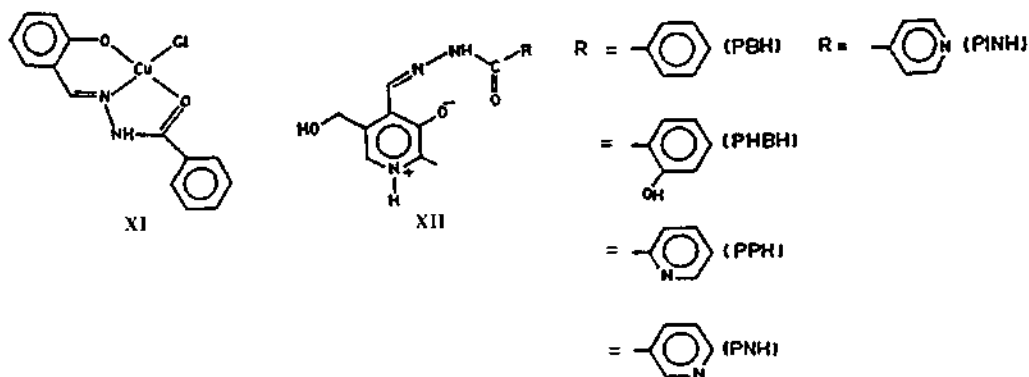
Co(II) and Ni(II), VII for Cu(II) and VIII for VO(IV) complexes.

The reaction of Ni(II) and Zn(II) acetate with salicylaldehyde benzoylhydrazones yields the complexes containing the enol form (I) and also the keto form (IV) of the aroylhydrazones. The Zn(II) ion can form octahedral complexes (IX) with salicylaldehyde benzoylhydrazone and a dinuclear complex with salicylaldehyde *o*-hydroxybenzoylhydrazones [24]. The dinuclear structure X is stabilized due to the formation of an intramolecular H bonding in the enol form of the benzoylhydrazones.

The coordination of aroylhydrazones in the keto form has also been reported [22, 23]. The Mn(II) salt on reaction with salicylaldehyde benzoylhydrazones and salicylaldehyde *o*-hydroxybenzoylhydrazones in ethanol affords the octahedral complexes with structure IX.

The reaction of copper(II) chloride with salicylaldehyde benzoylhydrazones affords the mononuclear copper(II) complex XI. The salicyloylhydrazones of salicylaldehyde and *o*-hydroxyacetophenone also react with copper(II) chloride to form complexes of the type $\text{Cu}(\text{HL})\text{Cl} \cdot n\text{H}_2\text{O}$ ($n = 0, 1$) [24, 25]; an interesting point is that the hydroxyl group in the benzene ring of the hydroxyl part is not involved in the coordination of the metal. This paper describes, for the first time, the characterization and electrochemical properties of binuclear copper(II) complexes of pyridoxal hydrazones (XII) undergoing two successive Cu(II) \rightarrow Cu(III) oxidation-reduction processes.





Experimental

Physical measurement

The variable-temperature magnetic susceptibility data were obtained in the temperature range 5–300 K by using a vibrating sample magnetometer, operated at 5 kG. The magnetometer was calibrated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and a calibrated GaAs diode was used for measuring the sample temperature and temperature control. For all data, diamagnetic corrections were used in the calculation of molar paramagnetic susceptibility [26].

X-band electron paramagnetic resonance spectra ($\nu = 9.1$ GHz) in DMSO at liquid nitrogen temperature were obtained with a Varian E-109 Century Series X-band spectrometer located at the University of Wisconsin, MI, USA. DPPH was used as a reference material. Electronic absorption spectra were recorded on a Cary model 14 spectrophotometer in DMF and the IR spectra (Csl disk, $4000\text{--}200\text{ cm}^{-1}$) on a Perkin-Elmer 1430 spectrophotometer.

All electrochemical measurements were carried out at room temperature in acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte under a dinitrogen atmosphere with use of a PAR model 175 universal programmer, model 377A cell system. A three-electrode system (cyclic voltammetry) was used in which the working electrode was a platinum disk and the auxiliary electrode a platinum wire, with a saturated calomel electrode (SCE) as a reference. Constant-potential coulometry was performed with a platinum mesh 'flag' working electrode, a platinum mesh auxiliary electrode, and SCE reference electrode using a PAR model 173 potentiostat and a PAR model 179 digital coulometer. Dilute solutions (*c.* 10^{-3} M) of the complexes were used and potentials are referenced to the saturated calomel electrode. Potentials are uncorrected for the junction contributions.

Elemental analysis for C, H and N were carried out on a Perkin-Elmer model 240C automatic instrument. The metal was estimated according to a standard procedure.

Materials

Pyridoxal hydrochloride was purchased from Aldrich Chemical Co., USA and used without further purification. The other starting materials were purchased from Sigma Chemical Company, St. Louis, USA and also used without further purification. Organic solvents were purified according to the published procedure [27]. Benzoyl hydrazide, 2-hydroxybenzoyl hydrazide, pyridinoyl hydrazide, nicotinoyl hydrazide and isonicotinoyl hydrazide were synthesized according to the reported methods [22–24].

Preparation of pyridoxal hydrazones

A solution of pyridoxal hydrochloride (1 mmol), in its neutral form, in 30 ml of ethanol was heated under reflux with constant stirring with a solution of appropriate hydrazide (1 mmol) in 20 ml of ethanol for about 30 min. After cooling, a yellow microcrystalline product was obtained, which was filtered and washed with ether and dried *in vacuo* over P_2O_5 .

Preparation of copper(II) complexes

A solution of $\text{Cu(II)Cl}_2 \cdot 2\text{H}_2\text{O}$ (5 mmol) in ethanol (25 ml) was added to a hot solution of appropriate pyridoxal hydrazone (5 mmol) and heated under reflux for about 30 min. The resulting green solution was concentrated on a rotary evaporator to 30 ml and cooled. The microcrystals of the compound, which separated from the solution, were filtered, washed with ethanol and ether, and dried *in vacuo* over P_2O_5 .

Results and discussion

The IR spectra of solid pyridoxal benzoylhydrazone (PBH), pyridoxal *o*-hydroxybenzoylhydrazone (PHBH), pyridoxal picolinoylhydrazone (PPH), pyridoxal nicotinoylhydrazone (PNH) and pyridoxal isonicotinoylhydrazone (PINH) exhibit $\nu(\text{N-H})$ and $\nu(\text{N-H}^+)$ of the pyridine ring absorption bands at *c.* 3350s and 3130m, and 2800mb cm^{-1} , respectively, whose protonation has occurred due to the migration of the phenolic OH group to the pyridine nitrogen, indicating that the

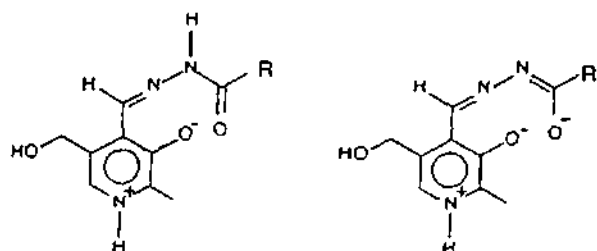
TABLE 1. Analytical data of pyridoxal hydrazones and their copper(II) complexes

Compound	Color	Found (%)			Calc. (%)		
		C	H	N	C	H	N
PBH	yellow	63.32	5.20	14.78	63.15	5.26	14.73
PHBH	yellow	59.78	5.00	13.98	59.80	4.98	13.95
PPH	yellow	58.77	4.91	19.55	58.74	4.89	19.58
PNH	yellow	58.72	4.90	19.61	58.74	4.89	19.58
PINH	yellow	58.79	4.87	19.60	58.74	4.89	19.58
Cu ₂ (PBH) ₂ Cl ₂	green	46.94	3.67	10.89	46.99	3.65	10.96
Cu ₂ (PHBH) ₂ Cl ₂	brown	45.04	3.47	10.54	45.11	3.50	10.52
Cu ₂ (PPH) ₂ Cl ₂	green	43.77	3.40	14.55	43.75	3.38	14.58
Cu ₂ (PNH) ₂ Cl ₂	green	43.80	3.36	14.60	43.75	3.38	14.58
Cu ₂ (PINH) ₂ Cl ₂	green	43.73	3.38	14.62	43.75	3.38	14.58

TABLE 2. Selected IR spectral data of pyridoxal hydrazones and their copper(II) complexes

Compound	$\nu_{as}(\text{NH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{Cu}-\text{O}-\text{Cu})$	$\nu(\text{Cu}-\text{O})$ phenolic	$\nu(\text{Cu}-\text{O})$ enolic	$\nu(\text{Cu}-\text{N})$
PBH	3350s	3130m	1630vs	1520s, 1280s				
PHBH	3350s	3130w	1630vs	1518s, 1280s				
PPH	3345s	3132w	1630s	1520m, 1280s				
PNH	3345s	3130m	1625s	1515m, 1280s				
PINH	3350s	3130m	1625vs	1520m, 1280s				
Cu ₂ (PBH) ₂ Cl ₂			1590s	1540s, 1300m	725m	440m	340m	410m
Cu ₂ (PHBH) ₂ Cl ₂			1590s	1540s, 1300m	725m	435s	340m	410m
Cu ₂ (PPH) ₂ Cl ₂			1585s	1540m, 1300m	730s	435m	340m	415m
Cu ₂ (PNH) ₂ Cl ₂			1585s	1545m, 1308m	725m	445m	340m	415m
Cu ₂ (PINH) ₂ Cl ₂			1580s	1540s, 1310m	730s	440m	340m	410m

ligands exist in the keto form (I) in the solid state. However, in solution and in the presence of some metal ions the ligands may exist in equilibrium with the tautomeric enol form (II). The tautomer II by the loss of enolic proton may act as a charged tridentate ligand coordinating through the phenolic oxygen, the azo-



methine nitrogen and the carbonyl oxygen atoms. When a hot ethanolic solution of the free ligands is heated

under reflux with a solution of copper(II) chloride in ethanol in a 1:1 ratio, green microcrystalline solids of the general formula Cu₂(HL)₂Cl₂ (HL = anion of PBH, PHBH, PPH, PNH or PINH) are obtained. The analytical data are reported in Table 1. The complexes are soluble in moderate polar and polar solvents but decompose in water. The molar conductance of the complexes in acetonitrile at *c.* 10⁻³ M at 27 °C are in the range 230–250 ohm⁻¹ cm² mol⁻¹ indicating their bi-univalent behavior in solution [30].

The assignment of some important IR bands of the free ligands and their copper(II) complexes is reported in Table 2. The phenolic $\nu(\text{C}-\text{O})$ stretching and bending vibrations observed at *c.* 1520 and 1280 cm⁻¹ in the free ligands are displaced to higher frequency by *c.* 20 cm⁻¹ in copper(II) complexes. The upward shift of the

TABLE 3. Magnetic susceptibility data of the complexes

$\text{Cu}_2(\text{PBH})_2\text{Cl}_2$ $-2J = 97 \text{ cm}^{-1}$ $\rho = 0.0039$	T (K)	297.5	275.0	250.0	230.0	197.5	150.0	115.0
	μ_{eff} (μ_{B})	1.73	1.72	1.71	1.70	1.67	1.60	1.49
	$\chi_{\text{m}} \times 10^6$	1257	1345	1462	1571	1765	2133	2413
	T (K)	90.0	75.0	62.5	50.0	38.8	25.0	20.0
	μ_{eff} (μ_{B})	1.38	1.22	1.10	0.94	0.80	0.60	0.50
	$\chi_{\text{m}} \times 10^6$	2745	2481	2420	2210	2602	1800	1562
$\text{Cu}_2(\text{PHBH})_2\text{Cl}_2$ $-2J = 85 \text{ cm}^{-1}$ $\rho = 0.0042$	T (K)	295.0	250.0	195.0	150.0	107.0	90.0	67.5
	μ_{eff} (μ_{B})	1.78	1.76	1.70	1.64	1.53	1.42	1.22
	$\chi_{\text{m}} \times 10^6$	1342	1549	1853	2241	2616	2722	2756
	T (K)	47.5	35.0	22.5	12.5	7.5	4.2	
	μ_{eff} (μ_{B})	1.07	0.80	0.60	0.41	0.25	0.12	
	$\chi_{\text{m}} \times 10^6$	3013	2287	2007	1681	1042	428	
$\text{Cu}_2(\text{PPH})_2\text{Cl}_2$ $-2J = 94 \text{ cm}^{-1}$ $\rho = 0.0038$	T (K)	297.5	262.5	225.0	195.0	177.6	150.0	140.0
	μ_{eff} (μ_{B})	1.77	1.74	1.72	1.69	1.67	1.61	1.58
	$\chi_{\text{m}} \times 10^6$	1316	1442	1644	1831	1964	2160	2230
	T (K)	122.5	105.0	92.5	80.0	65.0	47.5	37.5
	μ_{eff} (μ_{B})	1.51	1.42	1.33	1.21	1.07	0.91	0.78
	$\chi_{\text{m}} \times 10^6$	2327	2400	2390	2033	2200	2131	2028
$\text{Cu}_2(\text{PNH})_2\text{Cl}_2$ $-2J = 80 \text{ cm}^{-1}$ $\rho = 0.004$	T (K)	297.5	255.0	205.0	165.0	112.5	90.0	67.5
	μ_{eff} (μ_{B})	1.82	1.78	1.73	1.68	1.60	1.46	1.27
	$\chi_{\text{m}} \times 10^6$	1392	1554	1825	2138	2844	2960	2987
	T (K)	45.0	32.5	20.0	12.5	10.0	7.5	4.2
	μ_{eff} (μ_{B})	1.06	0.8	0.60	0.32	0.20	0.12	0.13
	$\chi_{\text{m}} \times 10^6$	3000	2461	2250	1600	1280	666	430
$\text{Cu}_2(\text{PINH})_2\text{Cl}_2$ $-2J = 78 \text{ cm}^{-1}$ $\rho = 0.0045$	T (K)	300.0	250.0	200.0	155.0	112.5	92.5	67.5
	μ_{eff} (μ_{B})	2.04	1.93	1.83	1.71	1.57	1.47	1.24
	$\chi_{\text{m}} \times 10^6$	1734	1862	2093	2358	2738	2920	2847
	T (K)	47.5	35.0	27.5	15.0	10.0	4.2	
	μ_{eff} (μ_{B})	1.01	0.85	0.69	0.49	0.34	0.13	
	$\chi_{\text{m}} \times 10^6$	2630	2580	2164	2000	1445	430	

bands suggests the dimeric structure for the complexes involving phenoxide bridging [31, 32]. The shift of the bands towards higher frequency sides is probably consistent with the increase in C–O bond strength for extended delocalization of the π -system of the azine moiety [33]. The dimeric nature of the Cu(II) complexes is further confirmed by the appearance of a

$\text{M} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{M}$ ring vibration at $c. 730 \text{ cm}^{-1}$ [34, 35]. A

broad band, observed at 2600 cm^{-1} in the $\text{Cu}_2(\text{PHBH})_2\text{Cl}_2$ complex is assigned to the $\nu(\text{OH})$ stretching vibration of the 2-hydroxybenzoyl moiety which is involved in an intramolecular H bonding with the azomethine nitrogen atom, stabilizing further the dimeric structure. The Cu(II) complexes do not show any characteristic bands of amino and amide groups, indicating that the ligands are coordinating in the enolic form [23].

The coordination of the azomethine nitrogen atom to the Cu(II) ion is indicated by the displacement of

the bands chiefly assigned to the $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{N})$ stretching vibrations [36]. The spectra of the complexes exhibit a downward displacement of $\nu(\text{C}=\text{N})$ from $c. 1630 \text{ cm}^{-1}$ for ligands to $c. 1590 \text{ cm}^{-1}$ and $\nu(\text{N}-\text{N})$ from $c. 980 \text{ cm}^{-1}$ to $c. 960 \text{ cm}^{-1}$. The changes are indicative of the coordination of the azomethine nitrogen atom to the copper(II) ion [37].

In the far-IR spectra, the Cu(II) complexes show bands at $c. 440$, $c. 415$ and $c. 345 \text{ cm}^{-1}$ which are assigned to $\nu(\text{Cu}-\text{O})$ phenolic, $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cu}-\text{O})$ enolic vibrations, respectively [38].

In the UV region, the free ligands exhibit two multiple bands, the first of which shows an absorption maximum at $c. 44.0 \text{ kK}$ ($\log \epsilon \approx 4.75$) with a shoulder at $c. 42.5 \text{ kK}$ and the second maximum at $c. 33.2 \text{ kK}$ ($\log \epsilon \approx 4.58$) with shoulders at $c. 34.7$ and $c. 32.0 \text{ kK}$. The high energy absorption bands are assigned to $\pi \rightarrow \sigma^*$ transitions and the three absorption bands are attributed to $\pi \rightarrow \pi^*$ transitions [33]. The high absorption by the ligands masks any splitting of the bands and only slight wavelength variations are observed in all copper(II)

complexes. The spectra of the complexes are dominated by the ligand absorption bands. In the visible region, the complexes exhibit three absorption bands at *c.* 29.0, *c.* 22.0 and *c.* 14.7 kK. The intense absorption band at *c.* 29.0 kK ($\log \epsilon \approx 4.52$) is assigned to the Cu(II) \rightarrow ligand* charge transfer transition, while the bands at 14.7 kK ($\log \epsilon \approx 2.62$) and at *c.* 22.0 kK ($\log \epsilon \approx 2.53$) are assigned to d-d transitions in a square planar geometry [24]. The splitting of d orbitals in square planar complexes has been discussed comprehensively by Nishida and Kida [39] in terms of the effect of π -bonding with ligands. In general, the copper(II) complexes of strong π -acidic or π -neutral ligands show a small d-d band splitting. The large splitting of the d-d bands in the present complexes indicates the strong π -basic character of ligands, and hence can stabilize the higher oxidation state of the metal ion.

The room temperature magnetic moments of the copper(II) complexes are very close to the spin-only value for one unpaired electron and decrease slightly with the variation of temperature down to 4.2 K, indicating the presence of a weak intramolecular antiferromagnetic interaction through the bridging phenoxide oxygen. The magnetic susceptibility data are detailed in Table 3 and the χ_m versus T and μ_{eff} versus T plots for $\text{Cu}_2(\text{PBH})_2\text{Cl}_2$ complex are illustrated in Fig. 1. The susceptibility for these complexes passes through a maximum and then decreases. Such a behavior is characteristic of antiferromagnetically coupled dicopper(II,II) containing a small amount of paramagnetic impurities. Thus, the values were fitted to the modified Bleaney-Bowers expression (1), which gives the molar paramagnetic susceptibility, χ_m , for a $S_1=S_2=1/2$, experiencing an isotropic exchange interaction (spin Hamiltonian $\mathcal{H} = -2JS_1S_2$) [40]. In this equation the J is

$$\chi_m = N\beta^2 g^2 / 3kT [1 + 1/3 \exp(-2J/kT)]^{-1} (1 - \rho) + [N\beta^2 g^2 / 4kT] \rho + N_a \quad (1)$$

the energy separation between $S=0$ and $S=1$ states of the binuclear complex and the other terms have their usual meanings. The temperature-independent paramagnetism for a binuclear complex, N_a , was taken as 120×10^{-6} cgsu/mol. Fitting the data to the equation gives the solid lines in Fig. 1, which are characterized by the J and g values listed in Table 3.

In DMSO at 77 K the complexes showed axial ESR spectra and each g_{\parallel} component had shown a well resolved seven-line hyperfine structure. A typical spectrum is illustrated in Fig. 2. Since the two copper centers are in the +2 oxidation state, the presence of seven equally spaced lines implies that the unpaired electrons are interacting equally with two copper nuclei. For a Cu-Cu dimer a seven-line pattern (1:2:3:4:3:2:1) is

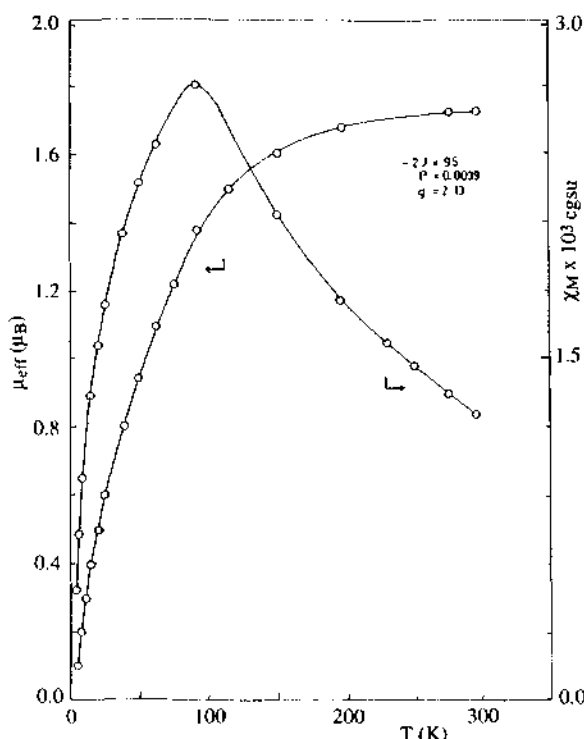


Fig. 1. Temperature variations of the magnetic susceptibility and magnetic moment of $\text{Cu}_2(\text{PBH})_2\text{Cl}_2$. The solid line was calculated from eqn. (1) with $g=2.13$, $-2J=97 \text{ cm}^{-1}$, $N_a=120 \times 10^{-6}$ cgsu and $\rho=0.0039$.

expected. The observed intensities are qualitatively consistent with the predicted ratio, the central line being most intense. It is assumed that the center of the pattern is at $g=2.31$ with a coupling of 75 G. In addition, a weak 'half-field line', which is characteristic of the Cu(II)-Cu(II) dimer, is observed at about 1600 G. The observation of this band strongly suggests that the hyperfine structure arises from a spin-triplet species. At room temperature, the ESR spectral features resemble those of monomeric copper(II) complexes with $g_{\text{iso}} \approx 2.13$ and $A_{\text{iso}} \approx 75$ G. The three-line superhyperfine structure ($A^N \approx 12$ G) on the high field line (Fig. 2, spectrum D) is consistent with the tridentate $\text{O}^*-\text{N}^*-\text{O}^*$ ligation.

The redox behavior of the complexes has been examined by recording cyclic voltammograms in acetonitrile. In general, two irreversible oxidation waves were observed in each complex at positive potentials but no wave at negative potential down to -2.0 V. When the CV was recorded only for the first oxidation, the voltammograms showed much improved reversibility. Coulometric experiments at 0.4 V indicate an electric current equivalent to the transfer of an electron. For the second wave, however, we were not able to determine the number of transferred electrons because of partial decomposition upon electrolysis at 1.0 V. Since the free ligands do not show any electrochemical waves up

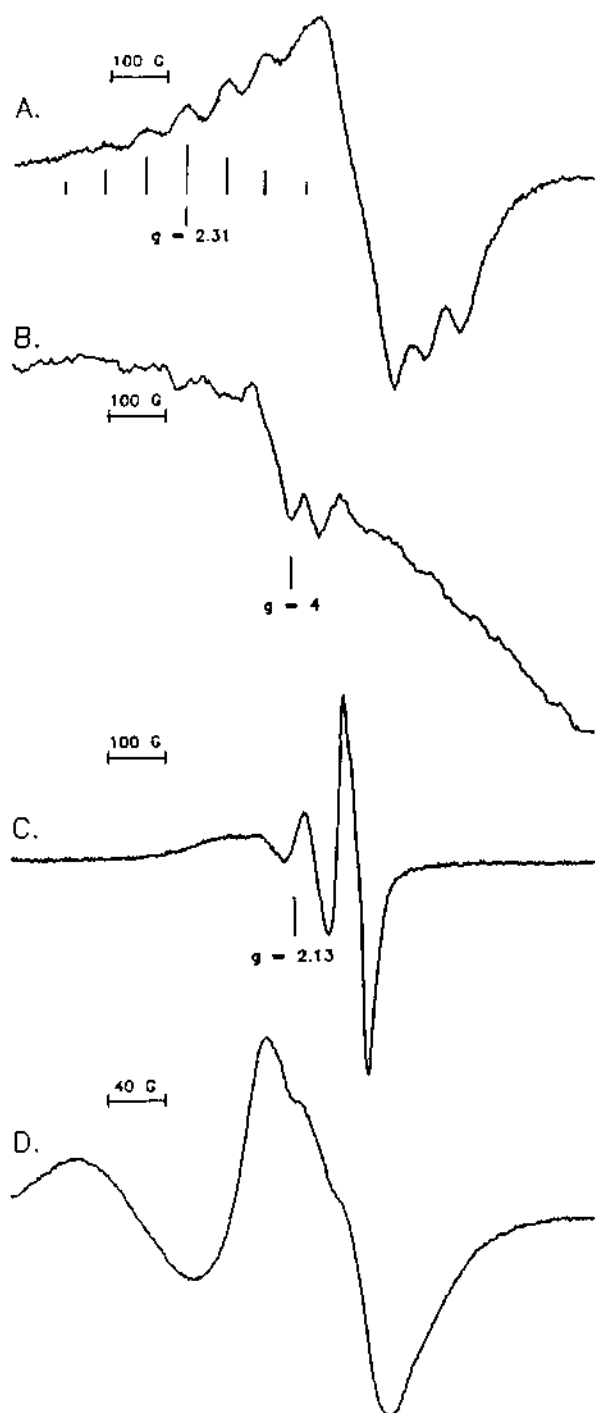


Fig. 2. X-band EPR spectrum of $\text{Cu}_2(\text{PBH})_2\text{Cl}_2$ complex in DMSO (1 mM) at 77 K (A and B) and room temperature (C and D).

to +1.2 V, we assigned tentatively the two waves to the oxidation processes $\text{Cu}_2^{\text{II,II}} \rightarrow \text{Cu}_2^{\text{II,III}}$ and $\text{Cu}_2^{\text{II,III}} \rightarrow \text{Cu}_2^{\text{III,III}}$, respectively. It should, however, be noted that both oxidation potentials are extremely low. The facile oxidation to the dicopper(II,III) and -(III,III) species can be ascribed to the strong donating ability of the ligands, and this is in accordance with the

TABLE 4. Electrochemical data (in V vs. SCE)^a for the complexes

Complex	Wave (1)			Wave (2)	ΔE
	E_{Pa}	E_{Pc}	$E_{1/2}$		
$\text{Cu}_2(\text{PBH})_2\text{Cl}_2$	0.45	0.36	0.41	1.09	0.68
$\text{Cu}_2(\text{PHBH})_2\text{Cl}_2$	0.40	0.33	0.37	1.06	0.69
$\text{Cu}_2(\text{PPH})_2\text{Cl}_2$	0.38	0.30	0.34	1.05	0.71
$\text{Cu}_2(\text{PNH})_2\text{Cl}_2$	0.42	0.31	0.36	1.07	0.71
$\text{Cu}_2(\text{PINH})_2\text{Cl}_2$	0.42	0.34	0.38	1.06	0.68

^aScan rate 0.1 V s^{-1} .

electronic spectral data described above. The results are detailed in Table 4.

Conclusions

We have reported the preparation, characterization and electrochemistry of the phenoxide bridged binuclear copper(II) complexes of hydrazones. These complexes represent the examples of binuclear copper(II) systems that involve two successive one-electron oxidation steps to produce $\text{Cu}(\text{II})\text{-Cu}(\text{III})$ and $\text{Cu}(\text{III})\text{-Cu}(\text{III})$ species at significantly low potentials.

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