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Metal Complexes Derived from Hydrazoneoxime Ligands: I. Synthesis, Characterization and Magnetochemical Studies of (Acyldiazazoneoxime) Copper(II) Complexes

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METAL COMPLEXES DERIVED FROM HYDRAZONEOXIME LIGANDS: I. SYNTHESIS, CHARACTERIZATION AND MAGNETOCHEMICAL STUDIES OF (ACYLHYDRAZONEOXIME) COPPER(II) COMPLEXES

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Reactions of 2-hydroxyimino-1-methylpropylidene (acetyl-) and (benzoylhydrazine) with copper(II) chloride, nitrate and acetate were studied. Three types of copper(II) complexes of general formula $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$, $[\{\text{Cu}(\text{HL})\}_2] \cdot 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ and $[\{\text{Cu}(\text{L})\}_2]$, where H_2L , HL , and L refer, respectively, to the neutral, monoanionic and dianionic ONN tridentate acylhydrazoneoxime ligands, were isolated and characterized. Variable-temperature magnetic susceptibility measurements for $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$ suggest Curie–Weiss behavior. Both $[\{\text{Cu}(\text{HL})\}_2] \cdot 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ and $[\{\text{Cu}(\text{L})\}_2]$ show strong antiferromagnetic exchange coupling with $-2J$ values of 898–934 and 718–757 cm^{-1} , respectively, indication dimeric structures with oximate bridges.

Keywords: 2-Hydroxyimino-1-methylpropylidene(acetylhydrazine); 2-Hydroxyimino-1-methyl-propylidene (benzoylhydrazine); Copper(II) complexes; Magnetic studies; Oximate bridges

INTRODUCTION

Acylhydrazone-oximes, Fig. 1 (1), react with copper(II) salts giving either mono- or binuclear copper(II) complexes [1–4]. The acylhydrazone residue may react in the ketoamide or deprotonated enolimine form [5,6]. The oxime group, on the other hand, is a very weak acid and can only be deprotonated by strong bases [7]. N-Coordination of the oxime group to a metal ion leads to a dramatic increase in its acidic character and formation of an oximate ligand is favoured [7]. Similar to other tridentate Schiff-base monoxime dicopper(II) complexes [8–12], the deprotonated oximate group can function as a bridging group giving binuclear copper(II) complexes

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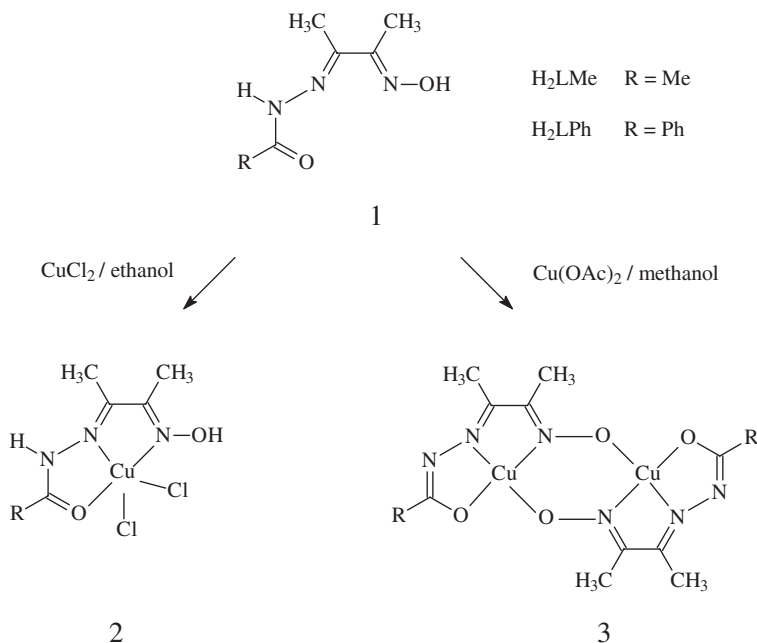


FIGURE 1 Proposed structures of the acylhydrazoneoximes (**1**) and their corresponding monomeric dichloro- (**2**) and dimeric neutral (**3**) copper(II) complexes.

with a $\text{Cu}_2\text{N}_2\text{O}_2$ framework. Magnetic properties of dicopper(II) complexes with different types of NNO tridentate Schiff-base monoximes have been studied [8–12]. Antiferromagnetic interactions via N–O bridges was found to be directly related to the distortion from planarity of the $\text{Cu}_2\text{N}_2\text{O}_2$ ring [12]. To the best of our knowledge, no such attention has been paid to detailed magnetic studies on dicopper(II) complexes derived from acylhydrazoneoximes.

As part of a systematic study of the structural and magnetic properties of mono-, bi- and polynuclear metal(II) complexes with acylhydrazoneoximes, we describe the synthesis and characterization of some copper(II) complexes derived from 2-hydroxyimino-1-methylpropylidene(acetylhydrazine) [H_2LMe], Fig. 1 (**1**, $\text{R} = \text{Me}$), and the corresponding benzoylhydrazine derivative [H_2LPh] (**1**, $\text{R} = \text{Ph}$).

EXPERIMENTAL

Materials

Acetyl- and benzoylhydrazines were prepared by the hydrazinolyses of the corresponding methyl esters as previously described [13]. Diacetylmonoxime was obtained from Sigma and used without further purification.

Preparation of Acylhydrazoneoximes, H_2LMe and H_2LPh

A hot solution of diacetylmonoxime (0.01 mol) in absolute ethanol (50 mL) was treated with a solution of acetylhydrazine or benzoylhydrazine (0.01 mol) in absolute ethanol

(50 mL). The reaction mixture was boiled under reflux for 2 h, then evaporated to half its volume. On cooling, the precipitate formed was filtered, then crystallized from ethanol and dried under vacuum.

H₂LMe (**1**, R = Me): yield: 72%; m.p. 241°C [4]; Anal. Calcd. for C₆H₁₁N₃O₂(%): C, 45.85; H, 7.05; N, 26.74. Found: C, 45.59; H, 7.01; N, 26.77. Electronic spectrum (EtOH, λ_{max}/nm (log ε): 250 (4.16), 267 (4.13); 0.1 M KOH (EtOH), 285 (4.37); ¹H NMR (DMSO-*d*₆, TMS, ppm): 11.51, 11.46 (1H, oxime OH), 10.46, 10.32 (1H, CONH), 2.17 (3H, s, CH₃C=NN), 2.02 (3H, s, CH₃C=NO), 1.97 (3H, s, CH₃CO). EI MS (*m/z* (RA%), 157 (31), 140 (7), 114 (83), 87 (7), 69 (41), 57 (80), 43 (100); FD MS (methanol), *m/z* = 156 (100%).

H₂LPh (**1**, R = Ph): yield: 80%; m.p. 190°C. Anal. Calcd. for C₁₁H₁₃N₃O₂(%): C, 60.26; H, 5.95; N, 19.2. Found: C, 59.97; H, 5.72; N, 19.17. Electronic spectrum (EtOH, λ_{max}/nm (log ε): 230 (4.19), 270 (4.25), 285 (4.22); 0.1 M KOH (EtOH), 290 (4.20); ¹H NMR (DMSO-*d*₆, TMS, ppm): 11.62, (1H, oxime OH), 10.75 (1H, CONH), 7.54 (3H, m, aromatic), 7.86 (2H, m, aromatic), 2.17 (3H, s, CH₃C=NN), 2.02 (3H, s, CH₃C=NO). EI MS (*m/z* (RA%), 219 (12.6), 202 (13.0), 161 (10.4), 114 (29.6), 105 (100), 77 (81.5), 68 (4.4), 51 (18.5); FD MS, *m/z* = 219 (100%).

Preparation of [Cu(H₂LMe)Cl₂] and [Cu(H₂LPh)Cl₂]

A solution of acylhydrazone monooxime (**1**, R = CH₃ or C₆H₅) (1.0 mmol) in absolute ethanol (40 mL) was added to a solution of copper(II) chloride dihydrate (1.0 mmol) in absolute ethanol (30 mL). The reaction mixture was stirred at room temperature for about 2 h. The isolated dichloro complex was filtered off, washed with absolute ethanol then dried under vacuum. Cu(H₂LMe)Cl₂: Yield 65%. Anal. Calcd. for C₆H₁₁N₃O₂CuCl₂(%): C, 24.71; H, 3.80; N, 14.41; Cu, 21.79. Found: C, 24.47; H, 3.65; N, 14.15; Cu, 21.60. Cu(H₂LPh)Cl₂: Yield, 70%. Anal. Calcd. for C₁₁H₁₃N₃O₂CuCl₂(%): C, 37.35; H, 3.70; N, 11.88; Cu, 17.97. Found: C, 37.07; H, 3.52; N, 11.72; Cu, 17.85.

Preparation of [Cu(LMe)₂]·H₂O and [Cu(LPh)₂]·H₂O

To a solution of acylhydrazone oxime (**1**, R = Me or Ph) (1.0 mmol) in methanol (30 mL), a solution of copper(II) acetate monohydrate (1.0 mmol) was added. The resulting mixture was treated with a solution of KOH (2.0 mmol) in methanol (20 mL). The reaction mixture was then boiled under reflux with constant stirring for 3 h. The isolated complex was filtered off while hot, washed with boiling methanol then dried under vacuum. [Cu(LMe)₂]·H₂O: Yield, 75%. Anal. Calcd. for C₁₂H₂₀N₆O₅Cu₂(%): C, 31.65; H, 4.43; N, 18.45; Cu, 27.91. Found: C, 31.71; H, 4.13; N, 18.49; Cu, 27.73. [Cu(LPh)₂]·H₂O: Yield 78%. Anal. Calcd. for C₂₂H₂₄N₆O₅Cu₂(%): C, 45.59; H, 4.17; N, 14.50; Cu, 21.93. Found: C, 45.44; H, 4.31; N, 14.53; Cu, 21.68.

Preparation of [Cu(HLMe)₂]·(NO₃)₂·H₂O and [Cu(HLPh)₂](NO₃)₂

A solution of copper(II) nitrate trihydrate (1.0 mmol) in methanol (20 mL) was added dropwise with constant stirring to a solution of acylhydrazone oxime (**1**, R = Me or Ph)

(0.01 mol) in methanol (30 mL). The reaction mixture was stirred at room temperature for 3 h and the complex formed was filtered, washed with methanol then dried under vacuum. $[\{\text{Cu}(\text{HLMe})_2\}] \cdot 2\text{NO}_3 \cdot \text{H}_2\text{O}$: Yield, 55%. Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_8\text{O}_{11}\text{Cu}_2$ (%): C, 24.79; H, 3.81; N, 19.27; Cu, 21.9. Found: C, 24.55; H, 3.7; N, 19.09; Cu, 21.65. $[\{\text{Cu}(\text{HLPh})\}_2] \cdot 2\text{NO}_3$: Yield, 58%. Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_8\text{O}_{10}\text{Cu}_2$ (%): C, 38.43; H, 3.52; N, 16.30; Cu, 18.48. Found: C, 38.28; H, 3.35; N, 16.22; Cu, 18.35.

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 1430 data system or a Perkin-Elmer (FTIR) Paragon 1000 PC spectrophotometer. Calibrations of frequency were made with polystyrene film. Solid samples were examined as KBr discs. Ultraviolet and visible absorption spectra were recorded on double beam, ratio recording Perkin-Elmer Lambda 4B or Cary 17 spectrophotometers. Magnetic susceptibilities of dried powdered samples were recorded on a Faraday magnetometer using a sensitive computer-controlled D-200 Cahn RG microbalance in the temperature range 4.2–298 K. The magnetic field applied was ~ 1.5 T. Details concerning the apparatus have been described elsewhere [14,15]. Experimental susceptibility data were corrected for diamagnetism using Pascal's constants [16].

RESULTS AND DISCUSSION

Synthesis

Condensation of diacetylmonoxime with acetyl- or benzoylhydrazine in ethanol afforded the corresponding acylhydrazoneoxime H_2LMe and H_2LPh . Reaction of H_2LMe and H_2LPh with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol afforded the corresponding dichloro complexes $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$, Fig. 1, (**2**, R = Me, and Ph) where H_2L refers to the neutral acylhydrazoneoxime ligand. The reaction of copper(II) acetate, on the other hand, proceeded with the deprotonation of both the oxime (=NOH) and enolimine hydrazone ($\text{NN}=\text{C}(\text{OH})\text{R}$) protons and eventually gave neutral dimeric complexes $[\{\text{Cu}(\text{L})\}_2]$. Figure 1 (**3**, R = Me, Ph). FD mass spectra of these neutral complexes show molecular ions at $m/z = 436$ and 560 , corresponding, respectively, to the dimeric species $[\{\text{Cu}(\text{LMe})\}_2]^+$ and $[\{\text{Cu}(\text{LPh})\}_2]^+$.

Reaction of H_2LPh with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was previously reported by Ghosh and Bandyopadhyay [4] to give the monomeric nitrate complex $[\text{Cu}(\text{H}_2\text{LPh})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}]$, where the benzoylhydrazoneoxime ligand acts as neutral ligand. However, attempts to prepare this type of monomeric nitrate complex by reaction of copper(II) nitrate with H_2LMe or H_2LPh using a 1:1 mole ratio were unsuccessful and complexes of composition $\text{Cu}(\text{HL})(\text{NO}_3) \cdot x\text{H}_2\text{O}$ were isolated. FD mass spectra of the isolated nitrate complexes show molecular ion peaks at $m/z = 436$ and 560 , corresponding to the dimeric species $[\{\text{Cu}(\text{HLMe})\}_2]^+$ and $[\{\text{Cu}(\text{HLPh})\}_2]^+$, respectively.

Infrared Spectra

Relevant IR bands of H_2LMe and H_2LPh , and the copper(II) complexes are listed in Table I. Spectra of the dichloro complexes $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$ (**2**, R = Me, Ph), display

TABLE I Significant bands in the IR spectra of the ligands and their copper(II) complexes

Compound	$\nu(\text{OH})$	$\nu(\text{N-H})$	Amide I $\nu(\text{C=O})$	$\nu(\text{C=N})_{\text{h}}$	Amide II	$\nu(\text{C=N})_{\text{ox}}$	Amide III	$\nu(\text{N-O})$
H ₂ LMe	3300 sh	3241 s	1655 s	1600 sh	1525 w	1553 m	1320 m	1120 m
[Cu(H ₂ LMe)Cl ₂]	3285 m	3195 m	1615 s	1590 s	1530 m	1532 m	1345 m	1080 s
[{Cu(HLMe)} ₂]·2NO ₃ ·H ₂ O	3380 b	—	—	1590 s	—	1525 w	1340 m	1087 sh
[{Cu(LMe)} ₂]·H ₂ O	—	—	—	1620 m	—	1530 sh	1330 m	1080 m
H ₂ LPh	3328 m	3270 m	1640 s	1615 m	1530	1580 m	1290 s	1140 m
[Cu(H ₂ LPh)Cl ₂]	3285 m	3195 m	1610 sh	1575 m	1520s	1560 m	1300 s	1105 m
[{Cu(HLPh)} ₂]·2NO ₃	3370 b	—	—	1615 s	—	1495 m	1305 s	1130 m
[{Cu(LPh)} ₂]·H ₂ O	—	—	—	1560 s	—	1550 w	1300 s	1130 m
[{Cu(LPh)} ₂]·H ₂ O	—	—	—	1618 m	—	1550 w	1300 s	1130 m

(C=N)_h = acylhydrazone C=N, (C=N)_{ox} = oxime C=N; s = strong, m = medium, w = weak, b = broad and sh = shoulder.

a series of bands due to $\nu(\text{N-H})$ amide I [$\nu(\text{C=O})$], $\nu(\text{C=N})_{\text{h}}$, amide II [$\delta(\text{N-H})$] and amide III [$\nu(\text{C-N})$] of the acylhydrazone residue besides $\nu(\text{O-H})$, $\nu(\text{C=N})_{\text{ox}}$ and $\nu(\text{N-O})$ of the hydroxyimino group. The amide I [$\nu(\text{C=O})$], $\nu(\text{C=N})_{\text{h}}$, $\nu(\text{C=N})_{\text{ox}}$ and $\nu(\text{N-O})$ bonds are shifted to lower frequencies while $\nu(\text{C-N})$ absorptions are shifted to higher frequencies, relative to those of the free ligands. Based on both IR data and the stoichiometry of the dichloro complexes, the acylhydrazoneoxime in these complexes acts as a neutral NNO tridentate ligand as shown in Fig. 1 (**2**, R = Me, Ph). Spectra of the neutral complexes [{Cu(L)}₂], Fig. 1 (**3**, R = Me, Ph), on the other hand, suggest the deprotonation of both acylhydrazone and oxime residues. The spectra lack absorption due to $\nu(\text{O-H})$, $\nu(\text{N-H})$, amide I [$\nu(\text{C=O})$] and amide II [$\delta(\text{N-H})$], but show absorptions due to $\nu(\text{C=N-N=C})$ and $\nu(\text{C=N})_{\text{ox}}$, respectively, at *ca.* 1620 ± 10 and $1570 \pm 20 \text{ cm}^{-1}$.

Spectra of the nitrate complexes lack absorptions due to $\nu(\text{N-H})$, amide I [$\nu(\text{C=O})$] and amide II [$\delta(\text{N-H})$], but show an intense absorption at *ca.* $1610 \pm 10 \text{ cm}^{-1}$ due to $\nu(\text{C=N-N=C})$, indicating the deprotonation of the enolimine form of the acylhydrazone residue. According to these results the oxime group remains protonated, but this cannot account for the dimeric nature of this type of complex, as dimerization usually occurs via the deprotonated oximate group. Dimerization, however, may occur via deprotonated enolimine oxygen, while the oxime group remains protonated as shown in Fig. 2 (**4**). In this case the bands at *ca.* 3385 cm^{-1} in the IR spectra of [{Cu(HL)}₂](NO₃)₂ complexes can be attributed to hydrogen-bonded $\nu(\text{OH})$ of the oxime group. Dimerization of copper(II) complexes with deprotonated acylhydrazone copper via enolimine oxygen, although not common, was reported by Lukov *et al.* [17]. Alternatively, it can be assumed that reaction of acylhydrazoneoximes with copper(II) nitrate may proceed with the initial formation of an intermediate, Fig. 2 (**5**), in which the acylhydrazone residue is deprotonated while the bridging oxime group remains protonated. Coordination of copper(II) to the oxime nitrogen in this intermediate will increase the oxime proton acidity and enhance proton transfer to the acylhydrazone enolimine oxygen, thus giving the dinuclear copper(II) Complex **6** (Fig. 2). The two copper(II) atoms in **6** are bridged by the deprotonated oximate group. IR data, however, cannot provide concrete evidence concerning the structure of these dimeric nitrate complexes. The actual structure must remain in doubt until a complete X-ray molecular structure is available.

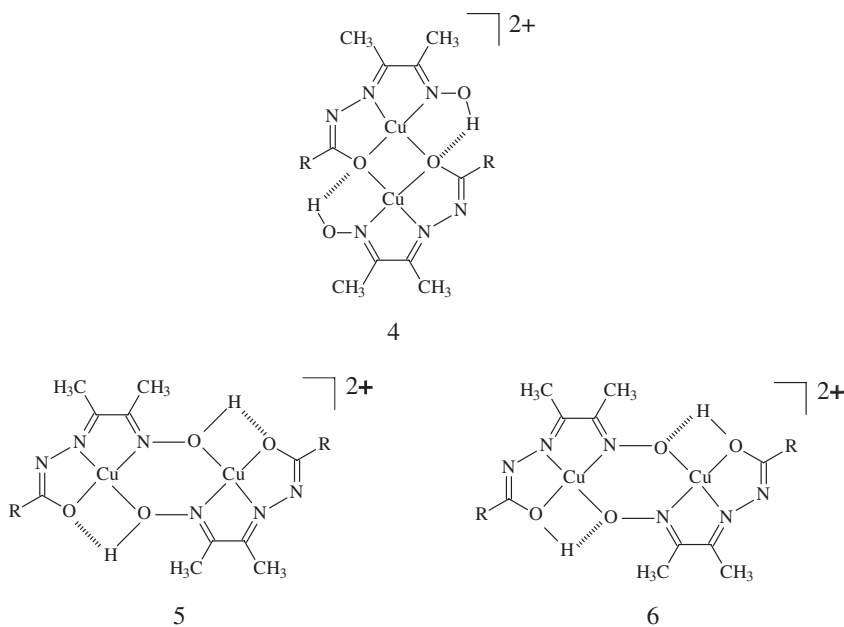
FIGURE 2 Possible structures for the dimeric $[\{Cu(HL)\}_2]^{2+}$ cation.

TABLE II Electronic absorption data for the Cu(II) complexes (nm)

Complex		Solvent	<i>L-L</i>	<i>LMCT</i>	<i>d-d</i>
<i>R</i>	<i>n</i>				
$[Cu(H_2L)Cl_2] \cdot nH_2O$					
Me	0	THF	285	365	750
Ph	0	THF	285	380 sh, 390	750
$[\{Cu(HL)\}_2] \cdot 2NO_3 \cdot nH_2O$					
Me	1	EtOH	260 (4.6), 280 sh	370 (4.3)	650 (2.65)
Ph	0	EtOH	255 sh	340 (4.3), 420 sh	650 (2.65)
$[\{Cu(L)\}_2] \cdot nH_2O$					
Me	1	DMSO	280 sh	370 (4.6), 410 sh	600 (2.9)
Ph	1	DMSO	260 sh, 315 sh	385 (4.6)	600 (2.9)

Electronic Spectra

The spectrum of H_2LMe in methanol shows two absorptions at 250 and 265 nm due to $\pi-\pi^*$ transitions of the neutral ligand. On replacing the acylhydrazone methyl group of H_2LMe by a phenyl group in H_2LPh these two bands show an appreciable red shift and appear at 270 and 285 nm, implying extended conjugation. In 0.1 M KOH the absorption bands are shifted to lower energy owing to the deprotonation of the acylhydrazone residue, and the acylhydrazoneoxime exists as a mononegative anion.

Spectra of copper(II) complexes, Table II, show absorption bands due to $L-L^*$, $LMCT$ and $d-d$ transitions [18]. The $d-d$ bands recorded for $[\{Cu(L)\}_2] \cdot nH_2O$ are within the range reported for square planar complexes [18]; the $d-d$ spectra of $[\{Cu(HL)\}_2] \cdot 2NO_3 \cdot nH_2O$ complexes suggest the formation of a solvated species $[\{Cu(HL)\}_2 \cdot (MeOH)_2]^{2+}$ in which the copper(II) ion lies in a distorted trigonal

bipyramidal environment [18]. The d–d transitions of $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_2]$ complexes in DMSO appear at lower energies, implying the formation of distorted octahedral species $[\text{Cu}(\text{H}_2\text{L})(\text{DMSO})_3]^{2+}$ in equilibrium with $[\text{Cu}(\text{H}_2\text{L})\text{Cl}_n(\text{DMSO})_{(3-n)}]^{(2-n)+}$ [18].

Magnetochemical Studies

Room temperature magnetic moments of the dichloro complexes are within the range reported for magnetically dilute systems [18]. Plots of $1/\chi_M$ vs. T for both $[\text{Cu}(\text{H}_2\text{LMe})\text{Cl}_2]$ and $[\text{Cu}(\text{H}_2\text{LPh})\text{Cl}_2]$ suggest Curie–Weiss behaviour. Recorded θ values, Table III, imply weak antiferromagnetic interactions, which most probably arise from intramolecular interactions in the crystal lattice.

The neutral dicopper(II) complexes show low-lying room temperature magnetic moments of 0.74 and 0.76 μ_B , indicating strong antiferromagnetic exchange interactions. The variation of χ_M and μ_{eff} as a function of temperature (4.5–300 K) recorded for $[\{\text{Cu}(\text{LPh})\}_2] \cdot \text{H}_2\text{O}$ is shown in Fig. 3. Similar behaviour was observed for $[\{\text{Cu}(\text{LMe})\}_2] \cdot \text{H}_2\text{O}$. Experimental data for both $[\{\text{Cu}(\text{LPh})\}_2] \cdot \text{H}_2\text{O}$ and

TABLE III The best-fit magnetic parameters for the Cu(II) complexes

Complex	μ_{eff} (298 K)	$-2J$ (cm^{-1})	g	θ	ρ
$[\text{Cu}(\text{H}_2\text{LMe})\text{Cl}_2]$	1.88		2.21	−1.4	
$[\text{Cu}(\text{H}_2\text{LPh})\text{Cl}_2]$	1.90		2.18	−1.2	
$[\{\text{Cu}(\text{LMe})\}_2] \cdot \text{H}_2\text{O}$	0.74	718	2.08	−3.2	0.70
$[\{\text{Cu}(\text{LPh})\}_2] \cdot \text{H}_2\text{O}$	0.76	757	2.08	−4.0	3.22
$[\{\text{Cu}(\text{HLMe})\}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	0.59	898	2.20	−3.2	0.76
$[\{\text{Cu}(\text{HLPh})\}_2](\text{NO}_3)_2$	0.61	934	2.05	−4.0	2.04

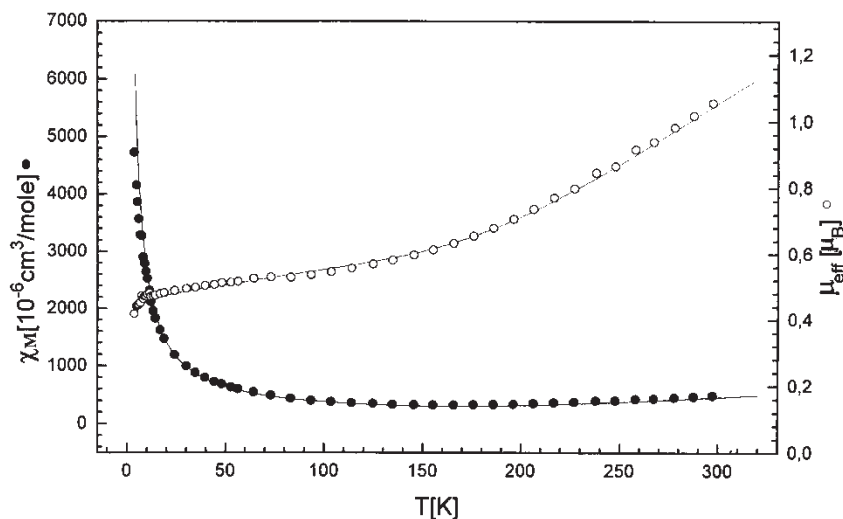


FIGURE 3 Magnetic susceptibilities χ_M (●) and magnetic moments μ_{eff} (○) vs. temperature for $[\{\text{Cu}(\text{LPh})\}_2] \cdot \text{H}_2\text{O}$. Solid lines represent the best least-squares fit to the Bleaney–Bowers equation with $J = -378 \text{ cm}^{-1}$, $g = 2.08$ and $\rho = 3.22$.

$[\{\text{Cu}(\text{LMe})\}_2] \cdot \text{H}_2\text{O}$ were fitted to a revised Bleaney–Bowers equation [16], using the isotropic exchange Hamiltonian ($H = -2JS_1S_2$) for two interacting $S = \frac{1}{2}$ centres,

$$\chi_M = (1 - \rho) \frac{2N_L \mu_B^2 g^2 \exp(2J/kT)}{k(T - \theta)(1 + 3 \exp(2J/kT))} + \rho \frac{2N_L \mu_B^2 g}{4kT} + 2N_\alpha,$$

where χ_M is the magnetic susceptibility per two copper atoms, N_α is the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per copper(II)], ρ is the mole fraction of uncoupled copper(II) ions and θ is the corrective term to account for interdimer interactions [19,20]. A non-linear regression analysis was carried out with J , ρ and θ as floating parameters. The obtained best-fit magnetic parameters and listed in Table III. The $-2J$ values recorded for (**3**, R = Me, Ph) are within the range reported for other oximate-bridged dicopper(II) complexes [8–12].

Room temperature magnetic moments of the nitrate complexes (**6**) were much lower than expected for spin-only values. The variation of the experimental χ_M values as a function of temperature, Figs. 4 and 5, indicates strong antiferromagnetic interaction between the two copper(II) centres in the dimers. The best-fit magnetic parameters ($2J$, g and ρ) derived from the Bleaney–Bowers equation are also included in Table III. The $-2J$ values of the dimeric nitrate complexes are much higher than to account for dimerization via enolimine oxygen, (**4**) [13], but are comparable to those reported for dimeric Schiff-base oximate copper(II) complexes [12], suggesting dimerization via oximate bridges and in favour of structure **6**.

Magnetic interactions mediated by two N–O bridges in dicopper(II) oximate complexes have been extensively studied [8–12, 21, 22]. The extent of spin–spin exchange coupling between the two copper(II) centres depends on the configuration of the $\text{Cu}_2\text{N}_2\text{O}_2$ core. Planar configurations show a very strong antiferromagnetic

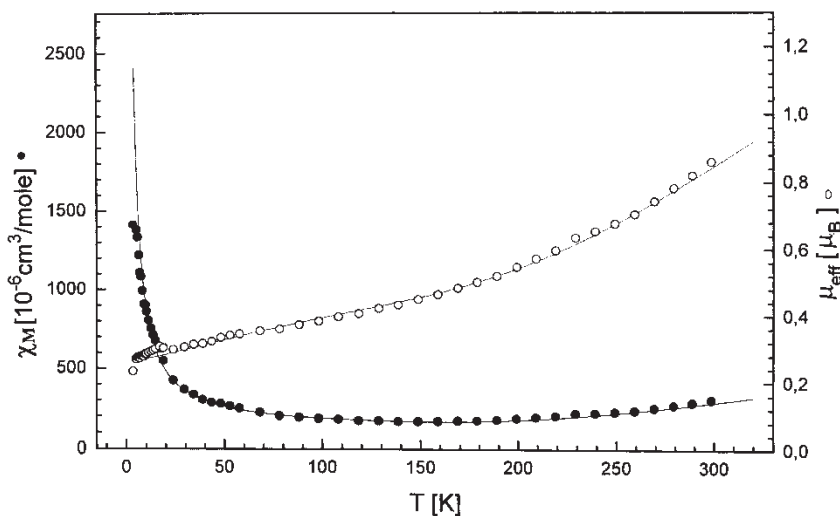


FIGURE 4 Magnetic susceptibilities χ_M (●) and magnetic moments μ_{eff} (○) vs. temperature for $[\{\text{Cu}(\text{HLMe})\}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. Solid lines represent the best least-squares fit to the Bleaney–Bowers equation with $J = -449 \text{ cm}^{-1}$, $g = 2.20$ and $\rho = 0.76$.

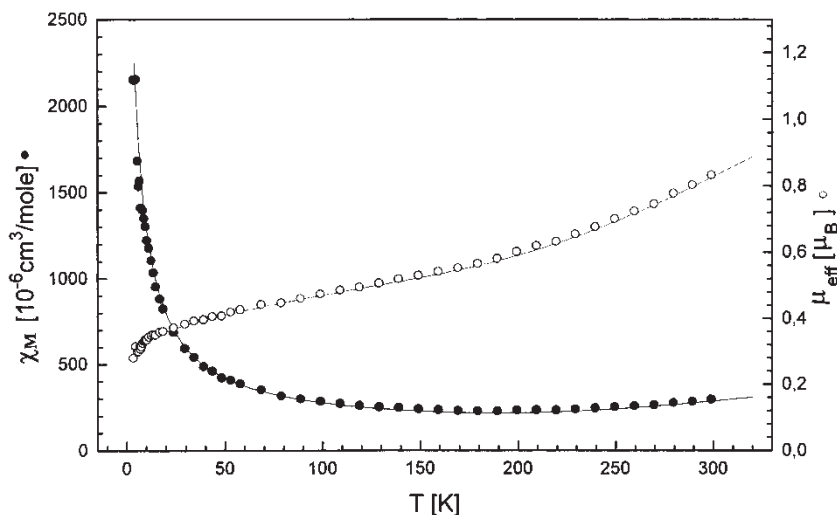


FIGURE 5 Magnetic susceptibilities χ_M (\bullet) and magnetic moments μ_{eff} (\circ) vs. temperature for $[\{\text{Cu}(\text{HLPh})\}_2](\text{NO}_3)_2$. Solid lines represent the best least-squares fit to the Bleaney–Bowers equation with $J = -467 \text{ cm}^{-1}$, $g = 2.05$ and $\rho = 2.04$.

interaction ($-2J \sim 1000 \text{ cm}^{-1}$) or are almost diamagnetic, even at room temperature [8, 21, 22]. The large overlap between the $d_{x^2-y^2}$ copper(II) orbitals through the diatomic oximate bridge accounts for such strong magnetic coupling. Deviation from planarity due to the coordination of solvent or counter ion as well as steric requirements of the ligand eventually gives rise to either twisted boat or twisted chair configurations [12]. The magnetic coupling is antiferromagnetic ($-2J \sim 600\text{--}800 \text{ cm}^{-1}$) in the former, but relatively reduced antiferro- ($-2J \sim 500\text{--}100 \text{ cm}^{-1}$) or ferromagnetic ($2J = 1\text{--}10 \text{ cm}^{-1}$) in the latter [12, 21, 22]. The nitrate complexes, although containing nitrate counter ions, show stronger antiferromagnetic interactions ($-2J = 898\text{--}934 \text{ cm}^{-1}$) as compared to the corresponding neutral complexes, ($-2J = 718\text{--}756 \text{ cm}^{-1}$). This suggests a more or less planar $\text{Cu}_2\text{N}_2\text{O}_2$ ring in the nitrate complexes, most probably due to intramolecular hydrogen bonds between the oximate oxygens and the protonated enolimine oxygens as shown in Fig. 2 (6). Such a planar configuration allows effective overlap between the oximate N–O orbitals and the copper(II) $d_{x^2-y^2}$ orbital. Neutral complexes which lack such hydrogen bonds may adopt a twisted boat configuration, as evident from the lower $-2J$ values.

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