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Synthesis and Spectroscopic Studies on Copper(II) Binuclear Complexes of 1-Phenylamidino-*O*-alkylurea (alkyl = *n*-propyl, *n*- and *iso*-butyl) with 1,3-Diaminopropane or Ethylenediamine

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Copper(II) binuclear complexes [Cu(II)(1-phenylamidino-*O*-*n*-propylurea)tn]$_2$ (H_2O)$_2$(Cl_2)$_2$ (**1**), [Cu(II)(1-phenylamidino-*O*-*n*-butylurea)tn]$_2$(H_2O)$_2$(Cl_2)$_2$(**2**), [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)tn]$_2$(H_2O)$_2$(Cl_2)$_2$(**3**), and [Cu(II)(1-phenyamidino-*O*-*i*-butylurea)en]$_2$(H_2O)$_2$(Cl_2)$_2$ (**4**) have been reported. The binuclear complexes **3** and **4** crystallize in a monoclinic structure with unit cell dimensions $a = 15.252(17)$ Å, $b = 14.682(10)$ Å, $c = 13.606(13)$ Å, and $\beta = 111.2(1)°$ and $a = 15.278(35)$ Å, $b = 14.665(21)$ Å, $c = 13.603(27)$ Å, and $\beta = 111.1(1)°$, respectively. The EPR spectra of all the solid complexes at room temperature consisted of fine-structure transitions ($\Delta M_s = 1$) with zero-field splitting (ZFS) of 0.0500 cm^{-1} and a half-field signal ($\Delta M_s = 2$) at ca. 1600 G, suggesting the formation of binuclear complexes ($S = 1$). From the observed ZFS, we estimated the average Cu–Cu distance. From the temperature dependence of the EPR signal intensity, we evaluated the isotropic exchange interaction constant J. It appears that the exchange interaction between the two interacting spins of the binuclear complexes is ferromagnetic in nature. The formation of ferromagnetically coupled copper binuclear complexes was further confirmed from the high magnetic-moment values at room temperature. When the EPR spectra were recorded in the temperature range 300–400 K, it was observed that the triplet-state EPR signal completely and irreversibly disappeared at ca. 380 K with the appearance of a new signal attributable to the mononuclear complex ($S = 1/2$). Thermal studies of these complexes in this temperature range suggested the loss of two water molecules, which might be responsible for binding two mononuclear species. EPR, IR, and thermal studies indicate a long-range ferromagnetic exchange mediated through hydrogen bonding between copper(II) ions ($S = 1/2$).

Introduction

Electron paramagnetic resonance (EPR) spectroscopy has been extensively used for the elucidation of the molecular structures of several binuclear complexes, such as copper DL-tartrates,[1] vanadyl tartrates,[2] citrates,[3] copper hydroxylcarboxylate,[4] and peptide[5] complexes. The main goal of such investigations was to understand metal−metal interaction among d-electron systems and also to gain insight into the structural aspects, with a special emphasis on investigating the nature of magnetic coupling in these complexes.

In recent years, many papers have been published on the creation of supramolecular architectures based on $[CuL_2]^{2+}$ cations in which the copper(II) center is coordinated by tetradentate bis(amidino-*O*-alkylurea) ligands, which have extensive hydrogen-bonding potential (eight N−H donor centers and two oxygen acceptor centers). In such cases, the hydrogen-bonded supramolecular architects are used to link cationic transition coordination complexes through non-coordinated anions and generate 1-D chains and 2-D sheet architectures. In $[CuL_2]Cl_2{\cdot}2H_2O$, the chains are linked into sheets through hydrogen-bonding contacts involving anions and solvent molecules. Although hydrogen-bonding interactions have long been considered to be of importance in

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biological systems, it is only recently that the transition-metal complexes containing ligands with versatile hydrogen-bonding capabilities have been used to bind DNA bases and other anions and to construct a network of coordinated complexes connected through intermolecular interactions.[6]

In a continuation of our earlier investigations[7,8] on binuclear complexes and with the aim of obtaining an improved insight into the chemical and structural factors that govern the formation of binuclear complexes, we have extended our investigations to a number of newly synthesized copper(II) complexes of 1-phenylamidino-*O*-alkylurea with 1,3-diaminopropane and 1,2-diaminoethane. We have also confirmed the formation of ferromagnetically coupled binuclear complexes [Cu(II)(1-phenylamidino-*O*-*n*-propylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**1**), [Cu(II)(1-phenylamidino-*O*-*n*-butylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**2**), [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**3**), and [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)en]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**4**). The X-ray powder diffraction studies of [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ and [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)en]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ suggested monoclinic structures for these complexes. Thermal, magnetic, and spectroscopic investigations on these complexes are presented in this paper.

Experimental Section

Methods and Materials. Phenyldicyandiamide (PD) was prepared by following a published procedure.[9]

Preparation of Complexes. (A) Dichloro-mono-(1-phenylamidino-*O*-alkylurea)copper(II) (where alkyl = CH_3, C_2H_5, $C_3{}^nH_7$, $C_4{}^nH_9$) was prepared using our published procedure.[10]

(B) Dichloro-mono-(1-phenylamidino-*O*-*i*-butylurea)copper(II) was prepared by refluxing cupric chloride (0.85 g) and phenyldicyandiamide (0.80 g) in isobutanol on a steam bath for 2 h. The intense blue complex was filtered off immediately, washed several times with acetone ,and dried in air. Yield = 80%; mp = 195 °C; λ_{max}(DMF) = 13 927 cm^{-1}; μ_{eff} = 1.88 μ_B. Anal. Calcd. for $C_{12}H_{18}Cl_2CuN_4O$: C, 39.07; H, 4.88; N, 15.19; Cu, 17.23. Found: C, 38.92; H, 4.81; N, 15.20; Cu, 17.31.

(C) For the complexes [Cu(II)(1-phenylamidino-*O*-alkylurea)tn]Cl$_2$, where alkyl = CH_3, C_2H_5, $C_3{}^nH_7$, $C_4{}^{n,i}H_9$; tn = 1,3-diaminopropane and en = 1,2-diaminoethane, the respective blue dichloromono-(1-phenylamidino-*O*-alkylurea)copper(II) complexes (0.1 mol) were dissolved in hot ethanol. Tn or en (1.0 mol) was added with constant stirring in a beaker on a steam bath for 30−45 min. After being kept overnight in a refrigerator, the complexes were obtained. They were washed repeatedly with ethanol and dried in air.

Analytical, electronic spectra, and magnetic moment data of the complexes are summarized below.

(i) [Cu(II)(1-phenylamidino-*O*-*n*-propylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**1**). Color, violet; yield = 65%; mp = 128 °C; λ_{max}(DMF) = 18 484 cm^{-1}; μ_{eff}: 2.01 μ_B. Anal. Calcd. for $C_{28}H_{56}Cl_4Cu_2N_{12}O_4$: C, 37.62; H, 6.27; N, 18.81; Cu, 14.22. Found: C, 37.80; H, 6.20; N, 19.11; Cu, 14.30.

(ii) [Cu(II)(1-phenylamidino-*O*-*n*-butylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**2**). Color, violet; yield = 75%; mp = 129 °C; λ_{max}(DMF) = 19 323 cm^{-1}; μ_{eff} = 2.2 μ_B. Anal. Calcd. for $C_{30}H_{60}Cl_4Cu_2N_{12}O_4$: C, 39.08; H, 6.51; N, 18.24; Cu, 13.78. Found: C, 40.01; H, 6.60; N, 18.44; Cu, 13.61.

(iii) [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)tn]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**3**). Color, violet; yield = 80%; mp =128 °C; λ_{max}(DMF) = 19 455 cm^{-1}, μ_{eff} = 2.42 μ_B. Anal. Calcd. for $C_{30}H_{60}Cl_4Cu_2N_{12}O_4$: C, 39.08; H, 6.51; N, 18.24; Cu, 13.78. Found: C, 39.21; H, 6.48; N ,18.30; Cu, 13.76.

(iv) [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)en]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ (**4**). Color, violet; yield = 70%; mp = 132 °C; λ_{max}(DMF) = 19 120 cm^{-1}; μ_{eff} = 2.61 μ_B. Anal. Calcd. For $C_{28}H_{56}Cl_4Cu_2N_{12}O_4$: C, 37.62; H, 6.27; N, 18.81; Cu, 14.22. Found: C, 38.10; H, 6.32; N, 19.11; Cu, 14.30.

(v) [Cu(II)(1-phenylamidino-*O*-methylurea)tn]Cl$_2$ (**5**). Color, pale pink; yield = 65%; mp = 132 °C; λ_{max} (DMF) = 19 065 cm^{-1}; μ_{eff} = 1.82 μ_B. Anal. Calcd. for $C_{12}H_{22}Cl\ _2CuN_6O$: C, 35.95; H, 5.49; N, 20.97; Cu, 15.85. Found: C, 35.81; H, 5.60; N, 21.22; Cu, 15.81.

(vi) [Cu(II)(1-phenylamidino-*O*-ethylurea)tn]Cl$_{2.}$ H$_2$O (**6**). Color, pale pink; yield = 60%; mp = 133 °C; λ_{max}(DMF) = 19 055 cm^{-1}; μ_{eff} = 1.88 μ_B. Anal. Calcd. for $C_{13}H_{26}Cl_2CuN_6O_2$: C, 36.06; H, 6.01; N, 19.42; Cu, 14.68. Found: C, 35.91; H, 6.30; N, 19.81; Cu, 14.44.

Physical Measurements. Microanalyses were performed on a carbon, hydrogen, nitrogen analyzer Perkin-Elmer 240C model; IR spectra were recorded on KBr disks on a Shimadzu FT-IR-8400S. The X-ray powder patterns of complexes were obtained on a Philips X-ray diffractometer Model PW 1710 with Ni-filtered Cu Kα radiation in the 2θ range of 10−40°. Photo acoustic spectra (PAS) on solid samples were recorded using a homemade spectrometer in the 350−800 nm range using a Tungsten halogen lamp as the source,[11] whereas solution spectra were recorded on a Beckmann DU-640 spectrophotometer. EPR experiments were conducted using a BRUKER ESP-300 spectrometer operated at X-band frequency (9.5 GHz) with 100 kHz field modulation. DPPH was used as a field marker. Temperature was varied in the range 100−400 K using a Eurotherm BVT 2000 variable temperature accessory with liquid nitrogen as the coolant in a flow system. The room-temperature magnetic moments (μ_{eff}) were measured using a PAR vibrating sample magnetometer (VSM) model 155. Molar conductance in MeOH was measured at room temperature on an Elico conductivity bridge type CM-82T. Thermal studies of the compounds were carried out in an air atmosphere with a Shimadzu thermal analyzer DT-30.

X − Ray Powder Diffraction Studies. Because single crystals of these compounds could not be obtained despite our repeated attempts, the exact crystal structure determination could not be done. To give a typical idea about the single phasic nature of the compounds, we have carried out powder XRD studies on these compounds. The binuclear complexes **3** and **4** crystallize in

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monoclinic structures with unit cell dimensions $a = 15.252(17)$ Å, $b = 14.682(10)$ Å, $c = 13.606(13)$ Å, and $\beta = 111.2(1)°$ and $a = 15.278(35)$ Å, $b = 14.665(21)$, Å, $c = 13.603(27)$ Å, and $\beta = 111.1(1)°$, respectively. Most of the prominent diffraction lines could be satisfactorily indexed on the basis of a monoclinic unit cell using Powder X program.[12] The typical fit parameters of these phases are given in the Supporting Information.

Results and Discussion

Electronic Spectra. The complexes of copper(II) with 1-phenylamidino-*O*-alkylurea (alkyl = CH_3, C_2H_5, C_3H_7, $C_4{}^{n,i}H_9$) with 1,2-diaminoethane (en) or 1,3-diaminopropane (tn) and bis(1-phenylamidino-*O*-methylurea)copper(II) chloride are violet/light pink in color. The unusual pink coloration arises from the strong ligand field in the $[CuN_4]$ chromophore group. The photoacoustic (PA) spectra of the solid complexes showed a broad band at ca. 19 000 cm^{-1} attributable to high energy d−d electronic transitions. This absorption band is almost similar to that observed in square planar copper(II) complexes with succinimidato copper(II) complexes,[13] copper(II)-*O*-alkyl-1-amidinourea complexes,[14] and closely related biguanide compounds.[15] In addition, a weak absorption band at ca. 26 400 cm^{-1} was observed in the spectra of complexes **1**, **2**, **3**, and **4**, which may be attributable to weak metal−metal bonding.[7,16] When the electronic spectra of the binuclear complexes were recorded in DMF solvent, the broad absorption band arising from the d → d transitions was shifted in the range 18 382−19 455 cm^{-1}. The shift may be due to axial ligation of solvent molecules. An intense absorption band at ca. 25 906 cm^{-1} in the solution spectra is due to the charge-transfer band.[14]

Ir Spectra. The Ir spectrum of phenyldicyandiamide shows a $\nu_{C\equiv N}$ band at 2167 cm^{-1} and a $\nu_{C=N}$[7,17] band at 1656 cm^{-1}. In all the complexes, the presence of the $\nu_{C=N}$ band in the range 1571−1596 cm^{-1} indicates coordination through the C=N group of the phenylamidine part. The N=C−O−C fragment of 1-phenylamidino-*O*-alkylurea is more delocalized, and the bond order of the =C−O− group is raised, which gives a new $\nu_{C=N}$ in the range 1680−1690 cm^{-1} after coordination.[8,10,18,19] Bands in the 470−480 cm^{-1} range and at ca. 315 cm^{-1} have been assigned to the ν_{Cu-N} and ν_{Cu-Cl} bands of the dichloro-mono(1-phenylamidino-*O*-*i*-butylurea)-copper(II) complex, respectively. In the IR spectra of complexes **1**, **2**, **3**, and **4**, a broad and strong band in the range 3255−3266 cm^{-1} is assigned to the ν_{N-H} band of the primary amine,[20,21] and the appearance of medium bands in the range 3637−3648 cm^{-1} and at ca. 1630 cm^{-1} may be assigned to ν_{O-H} and ν_{H-O-H}, respectively, for lattice water present in the complexes.[22,23] Two bands at ca. 1062 and ca. 1392 cm^{-1} are due to the ν_{C-C} and ν_{C-N} bands of 1,2-diaminoethane and 1,3-diaminopropane.[24] An interesting observation in the IR spectra of complex **3**, recorded carefully after heating the complex and KBr at 100 °C, is the substantial decrease in the band assigned for ν_{OH}, suggesting the loss of water molecules in this temperature range.

EPR Spectra. The room-temperature EPR spectrum of a powdered sample of dichloromono(1-phenylamidino-*O*-*i*-butyurea)copper(II) complex, which was used as a starting compound for the preparation of binuclear copper complexes, showed an axially symmetric signal with $g_{\|} = 2.2075$ and $g_{\perp}= 2.0450$. EPR spectra were also recorded on polycrystalline samples of a number of copper(II) complexes of 1-phenylamidino-*O*-alkylurea (alkyl = CH_3, C_2H_5, $C_3{}^nH_7$, $C_4{}^nH_9$, $C_4{}^iH_9$) with 1,3-diaminopropane (tn) and 1-phenylamidino-*O*-*i*-butylurea with 1,2-diaminoethane (en). The EPR spectra of solid complexes **5** (Figure 2a) and **6** showed a single broad-band resonance at ca. $g = 2.0550$. However, well-resolved spectra with a quartet hyperfine structure (Cu, $I = 3/2$) on parallel components were obtained when EPR spectra of dilute solutions of these complexes in MeOH or DMF were recorded at 77 K.

Interesting results were obtained in the case of copper complexes **1**, **2**, **3**, and **4**, for which the EPR spectra were recorded in the solid state (shown in Figures 1c, 1d, 2a, and 1b, respectively). The EPR spectra of these complexes consisted of two intense bands, separated by ca. 500 G, with features of perpendicular components (*D*). On either side of these intense perpendicular components, a signal consisting of several narrow lines with nearly double the separation as that of perpendicular separation were observed (2*D*). The seven-line hyperfine structure on the low-field parallel component with the relative intensity ratio 1:2:3:4:3:2:1 is due to interaction of unpaired spins with two equivalent Cu^{2+} nuclei ($I = 3/2$). The hyperfine coupling observed on the parallel components ($A_{\|} = 100$ G) is nearly half of that observed for the corresponding mononuclear complexes in DMF/MeOH. In addition, a weak signal at 1600 G corresponding to the forbidden transition $\Delta M_s = \pm 2$ and exhibiting a seven-line hyperfine structure was observed, confirming the formation of the binuclear complex. Similar spectra have been reported for binuclear complexes of copper DL-tartrate[1] and copper dimers stabilized in a CeO_2 matrix.[25] It may be noted that EPR spectra of binuclear complexes in MeOH and DMF at 77 K mainly consist of mononuclear complexes, indicating dissociation of these complexes to their monomers, which is supported by the conductance value in MeOH ($\Lambda_M = 154-168\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a bi-univalence electrolyte).

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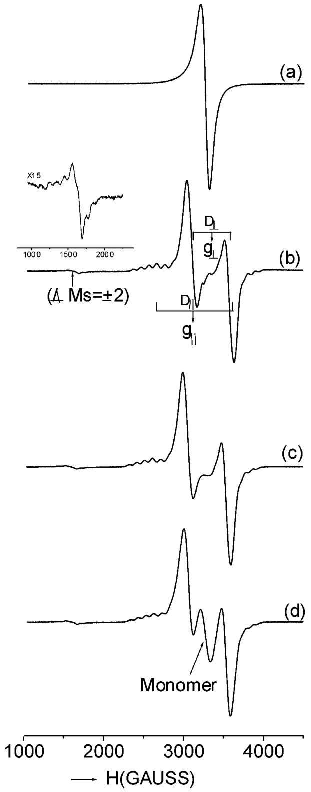

Figure 1. EPR spectra of different Cu(II) dimers and monomers at 300 K (a) complex **5**, (b) complex **4**, (c) complex **1**, and (d) complex **2**.

The most accurate values of $g_{\|}$, $g_{\perp}$, $A_{\|}^{\mathrm{Cu}}$, $A_{\perp}^{\mathrm{Cu}}$, and D for binuclear complexes were deduced by computer simulation assuming axial symmetry and are given in Table 1.

EPR Spectra at Low Temperatures (77−300 K). The isotropic exchange-interaction constant J, or the separation between the singlet and triplet, was calculated from the temperature dependence of the intensity of the half-field signal[7,25] $\Delta M_s = \pm 2$ for complexes **1**, **2**, **3,** and **4**. The increase in the intensity of the EPR signal ($\Delta M_s = \pm 2$) with decreaing temperature is much more than that expected from the Boltzmann population difference within the triplet manifold. It appears that the isotropic exchange interaction between the interacting spins of the binuclear complex is ferromagnetic in nature. In addition to an increase in the intensity of allowed and forbidden transitions, there was also an increase in the zero-field splitting as the temperature was lowered in the range 350−77 K (complex **4**, $D = 0.0493$ cm^{-1} at 300 K and $D = 0.0530$ cm^{-1} at 77 K). The increase in the D value is significant and may occur because of lattice contraction at lower temperatures.[29]

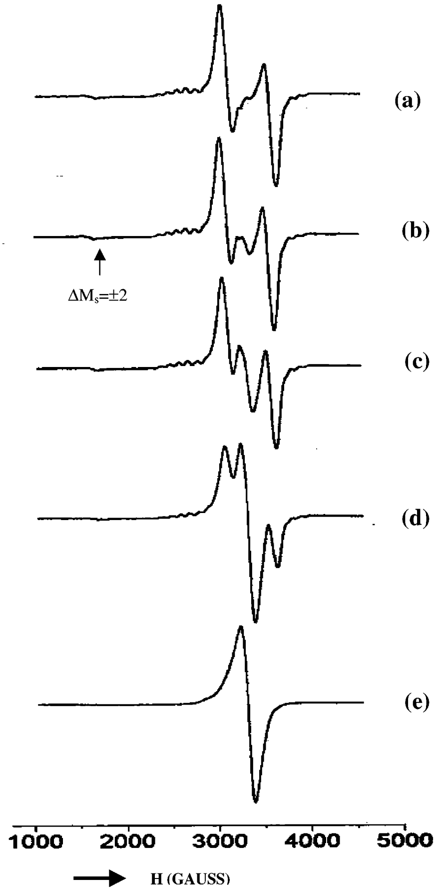

Figure 2. EPR spectra of complex **3** in the solid state at (a) 300, (b) 365, (c) 368, (d) 375, and (e) 390 K.

EPR Spectra at High Temperatures (300−400 K). The temperature dependence of the EPR spectra was studied in the high-temperature range 300−400 K for complex **3** (Figure 2). Above 360 K, the intensity of the triplet-state signal decreases abruptly with the appearance of a new signal at g =2.0555, which was attributed to the formation of mononuclear complex. The triplet-state EPR signal completely disappeared at about 380 K. The changes in the EPR spectra were found to be irreversible and were associated with the loss of water molecules in binuclear complexes. Thermal gravimetric (TG) experiments of complex **3** showed weight loss in the 360−380 K range, which corresponds to the loss of two water molecules. The coordinated water in hydrated complexes is usually lost at higher temperatures (550−600 K). The loss of water molecules at relatively low temperatures suggests that water is weakly bound by hydrogen bonds to the ligands in all binuclear complexes **1**, **2**, **3**, and **4**. Comparison of the IR spectra of the virgin complex **3** with the one recorded after heating the complex at 380 K indicates a substantial decrease in the intensity of band at 3637 cm^{-1} without any noticeable changes in other band positions, which is attributed to the loss of water molecules. Also, the absence of the IR bands at ca. 650, 740, and 950 cm^{-1}, which are characteristic of coordinated water, further confirmed that water is not coordinated to the complex but is instead weakly bound by hydrogen bonds to the ligands.

The values of $g_{\|}$, $g_{\perp}$, $A_{\|}^{\mathrm{Cu}}$, and $A_{\perp}^{\mathrm{Cu}}$ measured for a number of mononuclear **5**, **6**, and binuclear Cu(II) complexes **1**, **2**, **3**, and **4** are typical of those values for Cu(II) atoms coordinated to nitrogen ligands with a square planar coordination around a metal ion. The measured EPR (g and A)

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Table 1. EPR Parameters of Cu(II) Mononuclear (M) and Binuclear (B) Complexes with Different Ligands

matrix	$g_{\|}$	$g_{\perp}$	g_{iso}	$A_{\|}$ (G)	$A_{\perp}$ (G)	A_{iso} (G)	D (cm^{-1})	J (cm^{-1})	r (Å)	ref
[Cu(1-phAB^{i}UH)Cl$_2$] (M)	2.2075	2.0450	2.0992							
complex **5** (M)	2.1774	2.0400	2.0858	210	30	90				
complex **6** (M)	2.1779	2.0405	2.0863	212	32	92				
[Cu(1-AAUH)$_2$]Cl$_2$ (M)	2.24^a	2.06^a	2.1200	218	25	89				14
	2.176^b	2.058^b	2.0973							
[Cu(NH$_3$)$_4$]$^{2+}$ (M)	2.216	2.034	2.0947	160						26
[Cu(NH$_3$)$_4$][PtCl$_4$] (M)	2.217	2.051	2.1063	211	28	89				27
complex **4** (B)	2.1640	2.0525	2.0897	100			0.0493^c	+55	3.99	
	2.1650	2.0425	2.0833				0.0530^b			
complex **1** (B)	2.1599	2.0435	2.0823	100			0.0510 .0520^b		3.84	
complex **2** (B)	2.1595	2.0430	2.0818	100			0.0495		3.88	
complex **3** (B)	2.1730	2.0485	2.0900	100			0.0505 0.0525^b	+50	3.96	
[Cu(1-PhABUH)en(H$_2$O)]Cl$_2$ (B)	2.1200	2.0525	2.0750	90			0.0525	+57	4.00	6
[Cu(1-PhAMUH)SO$_4$]$_2$ (B)	2.2383	2.1773	2.1976				0.0225	+27	4.70	6
(Cu^{2v})$_2$^{i,n}(DL)-(tart)$^{4-}$$_2$ (B)	2.224	2.0860	2.1320	82			0.0057	−18	3.85	1
(Cu^{2+})$_2$ ^{i,n}CeO$_2$ (B)	2.2079	2.0403	2.0962	85	13.5	37.5	0.066	−52	4.50	25
(Cu^{2+})$_2$^{i,n}Y zeolite (B)	2.3450	2.0660	2.1590	81			0.048			28

^{a} At room temperature. ^{b} At 77 K. ^{c} At 300 K.

parameters for mononuclear complexes ([Cu(1-phAB^{i}UH)-Cl$_2$], **5**, and **6**) are close to those values for [Cu(amidino-*O*-alkylurea)$_2$]Cl$_2$,[14] Cu(NH$_3$)$_4$,[26] and [Cu(NH$_3$)$_4$][PtCl$_4$][27] complexes having square planar geometry. We have evaluated the angle x (28°) using the equation $g_2{}^2 = g_{\|}{}^2\cos^2(x) + g_{\perp}{}^2\sin^2(x)$,[30] where $g_{\|}$ (2.1943) and $g_{\perp}$ (2.0530) represent g values for the mononuclear complex, and x is the angle between the Cu−Cu direction and the parallel direction; $g_{\|}$ is replaced by g_2 (2.1640), as $g_{\|}$ and the Cu−Cu direction for binuclear complex **4** do not coincide. The average distance between two unpaired electrons was calculated by using the equation $D = 3g^2\beta^2/(2r^3) = 1.39 \times 10^4\ g\ r^{-3}$.[31] The average distance r between the two unpaired electrons estimated for different binuclear complexes is given in Table 1.

Recently, it has been shown that, in solid state, chromium complexes[32] with the general formula *cis*-[CrA$_4$(OH)$_2$(OH)]$_2$ (where A$_4$ represents four nitrogen ligators from an appropriate number of monodentate and polydentate ligands) have a dimeric structure, in which two molecules are bound together by powerful hydrogen bonds such that it can transmit an antiferromagnetic interaction between the two chromium centers, even though they are separated by a distance of 5 Å. Similarly, in cyano-bridged Cu(II)−Ni(II) heterobimetallic complexes,[33] a weak long-range (9.75 Å) ferromagnetic interaction between two copper ions through hydrogen bonding was observed.

A series of coordination complexes containing a polymethylene-linked bis(*N*-alkylamidino-*O*-alkylurea)copper(II) cation, e.g., [CuL$_2$]$^{2+}$, with nitrate, halides, and tetrafluoroborate anions, has been synthesized because of the polydentate nature of the ligand (eight N−H donor centers and two oxygen acceptor centers). The tetradentate ligand coordinates Cu(II) to give square planar [CuL$_2$]$^{2+}$complex cations, which, because of their versatile hydrogen-bonding capacity, form diverse hydrogen-bonded supramolecular architectures with anions. In [CuL$_2$]Cl$_2$·2H$_2$O, alternating cations and chloride anions are hydrogen bonded to form a one-dimensional chain. These one-dimensional chains are further linked by complex hydrogen-bonding contacts involving anions and water molecules, forming two-dimensional sheets.[34] In our present study, we have synthesized a series of binuclear complexes [Cu(II)(1-phenylamidino-*O*-alkyllurea)en/tn(H$_2$O)]Cl$_2$ (alkyl = C$_3$H$_7$ and C$_4$H$_9$) using the bidentate ligand 1-phenylamidino-*O*-alkyl urea (4 N−H donor sites) and bidentate ligands en (ethylenediamine) or tn (1,3-diaminopropane). There are four N−H donors available in the ligand 1-phenylamidino-O-alkylurea. Two N−H groups from this ligand and two from either 1,2-diaminoethane or 1,3-diaminopropane occupy the equatorial positions around the copper(II), giving a nearly square planar geometry. The loss of water on heating the binuclear complexes at relatively low temperatures (380 K) and dissociation of all binuclear complexes in MeOH and DMF, as evident from EPR and conductivity studies, clearly suggest that two monomers are held together by weak hydrogen bonding to form a ferromagnetic interaction between two copper atoms. In our complexes, there is also room for possible interaction between the chloride and NH group of the ligands in the solid state.[34] The structure of the binuclear complexes will consist of monomers involving interaction of the ligands, anions, and water molecules; however, proposing the structure without single-crystal X-ray data will be highly speculative. Our study will attract further research for structure determination of these binuclear complexes.

On the basis of our experimental evidence, we suggest the most probable structure of the monomer (Figure 3) in forming binuclear complex **3**.

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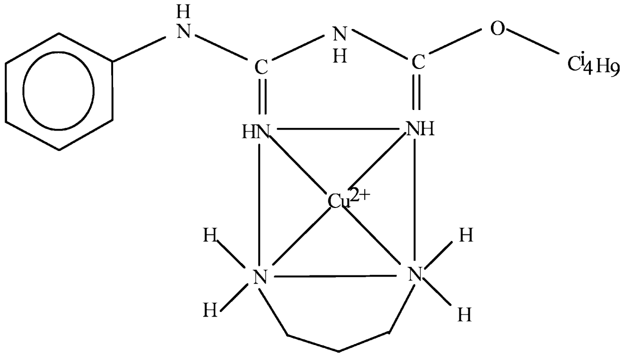

Figure 3. Proposed structure of [Cu(II)(1-phenylamidino-*O*-*i*-butylurea)-tn]$^{2+}$ in forming complex **3**.

Conclusions

EPR studies on newly synthesized copper(II) mixed-ligand complexes of 1,2-diaminoethane or 1,3-diaminopropane with 1-phenylamidino-*O*-alkylurea (alkyl = CH_3, C_2H_5, C_3H_7, and $C_4{}^{n,i}H_9$) have shown that some of them (**1**, **2**, **3**, and **4**) exist as binuclear complexes ($S = 1$). The high magnetic-moment values of these complexes and an increase in EPR intensity with a decrease in the temperature clearly indicate ferromagnetic coupling between two interacting Cu(II) ions. EPR studies on solid complexes in the temperature range 300−400 K suggested irreversible dissociation of the binuclear complex into the mononuclear complex by the loss of weakly bonded water. This was confirmed independently by IR and thermal studies. Our present investigations clearly indicate that hydrogen-bonding interactions involving ligands, water, and anions play an important role in forming ferromagnetic coupling between two Cu atoms.

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Supporting Information Available: The IR spectra of complex **4** and crystallographic data for complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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