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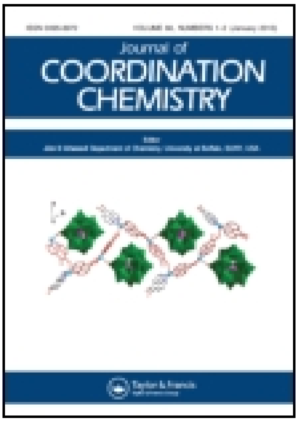

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Binuclear copper(II) complexes of 1-amidino-O-alkylurea (alkyl = *n*-propyl, *n*-butyl, or *i*-butyl) and vanadate: an EPR study

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Five new complexes of bis(1-amidino-O-alkylurea)Cu(II)vanadate where alkyl = methyl, ethyl, *n*-propyl, *n*-butyl or *i*-butyl have been synthesized by reaction of ammonium metavanadate with bis(1-amidino-O-alkylurea)Cu(II)perchlorate complexes. Electron paramagnetic resonance (EPR) spectra of bis(1-amidino-O-*n*-propylurea)Cu(II)vanadate (**1**), bis(1-amidino-O-*n*-butylurea)Cu(II)vanadate (**2**) and bis(1-amidino-O-*i*-butylurea)Cu(II)vanadate (**3**) gave half-field signal ($\Delta M_s = \pm 2$) *ca* 1623G, in addition to fine structure due to zero field splitting (ZFS) characteristics of the $S = 1$ system. From the observed ZFS the average Cu–Cu distance was estimated. The isotropic exchange constant J was evaluated by recording EPR spectra at different temperatures. The photoacoustic signal of the complexes indicated square-planar geometry around Cu^{2+}. X-ray powder diffraction studies on **2** suggested orthorhombic structure with unit cell dimensions $a = 21.11$ Å, $b = 24.11$ Å, $c = 27.11$ Å, $\alpha = \beta = \gamma = 90°$. The crystal structure of bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate is also reported.

Keywords: Binuclear; Ferromagnetic; EPR; Vanadate ion; Photoacoustic signal

1. Introduction

The magnetic parameters measured in the electron paramagnetic resonance (EPR) study of complexes are related to the structure of the paramagnetic species, the number of ligands, bonding, and spatial arrangements of the ligands around the central metal ion. The reaction of Cu(II) salts with dicyandiamide in different alcohols and detailed spectroscopic investigations including EPR were first reported by Wasson and Trapp [1]. They reported the mononuclear nature ($S = 1/2$) for square-planar structures of the complexes. The unusual pink color arises from the strong ligand field of $[CuN_4]^{2-}$ chromophore. There are many papers published on creation of supramolecular architectures based on $[CuL_2]^{2+}$ in which copper(II) is coordinated by tetradentate bis(amidino-O-alkylurea) ligands, which have extensive hydrogen-bonding potential

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(eight N–H donor centers and two oxygen acceptor centers). In such cases, the hydrogen bonds are used to link cationic transition coordination complexes through non-coordinated anions to 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 bonds involving anions and solvent [2]. Blake *et al.* [3] reported the extraordinary results obtained when using Cu(II) sulfate as the template for the alcoholysis reaction and the anion recognition properties of the various hydrogen-bonding sites of the $[CuL]^{2+}$ cations where L = amidino-O-alkylurea.

In continuation of our efforts to synthesize ferromagnetically coupled copper(II) complexes containing ligands with hydrogen-bonding capabilities [4–7] and formation of binuclear complexes in frozen solution [8], we report here spectroscopic investigations on new Cu(II) vanadate complexes prepared by treatment of bis(1-amidino-O-alkylurea)Cu(II) perchlorate complexes (alkyl = methyl, ethyl, *n*-propyl, *n*-, or *iso*-butyl) with ammonium metavanadate in order to study the role of vanadate in the newly synthesized compounds. While preparing bis(1-amidino-O-alkylurea)Cu(II)perchlorate complexes, we obtained a single crystal of bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate and report the structure of this compound.

Bis(1-amidino-O-alkylurea)Cu(II)vanadate complexes are insoluble in organic solvents and are light pink. We have confirmed spectroscopically the formation of binuclear Cu(II) complexes, namely bis(1-amidino-O-*n*-propylurea)Cu(II)vandate (**1**), bis(1-amidino-O-*n*-butylurea)Cu(II)vanadate (**2**), and bis(1-amidino-O-*i*-butylurea) Cu(II)vanadate (**3**). In order to further investigate the structure of insoluble binuclear copper(II) complexes, we have recorded X-ray powder diffraction pattern of **2** at room temperature. In our earlier report on EPR studies at high temperature on some binuclear copper(II) complexes [4, 5] the triplet state disappears completely converting into mononuclear species. Our present studies at high temperatures on insoluble binuclear complexes indicated the formation of VO^{2+} species at high temperature. Synthesis, characterization, and spectroscopic studies on the new Cu(II) complexes are reported in this article.

2. Experimental

2.1. *Methods and materials*

All reagents and chemicals used were of reagent grade. Purity of dicyandiamide was checked by m.p. (210°C) and IR spectra. Copper perchlorate was synthesized in the laboratory.

Caution: Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

2.2. *Preparation of complexes*

(1) Bis(1-amidino-O-alkylurea)Cu(II)perchlorate complexes (where alkyl = CH_3, C_2H_5, $C_3^nH_7$, $C_4^nH_9$, or $C_4^iH_9$) were prepared by refluxing copper(II) perchlorate (0.1 mmol) and dicyandiamide (0.2 mmol) on a steam bath for 1–2 h in the appropriate alcohols.

Table 1. Analytical, yield, magnetic susceptibilities, and molar absorptivity of the complexes.

Compound	Yield (%)	Found (Calcd) (%)				Electronic spectra λ_{max}, nm (ε, (mol $L^{-1})^{-1}$ cm^{-1})	μ_{eff} (B.M.)
		C	H	N	Cu		
$[CuL_1](ClO_4)_2H_2O$	70	14.05 (14.02)	3.51 (3.45)	21.85 (21.55)	12.40 (12.38)	553 (51)	1.73
$[CuL_2](ClO_4)_2$	65	18.37 (18.25)	3.83 (3.75)	21.43 (21.21)	12.16 (12.81)	553 (50)	1.83
$[CuL_3](ClO_4)_2$	75	21.80 (21.63)	4.36 (4.27)	20.34 (20.12)	11.54 (11.02)	553 (40)	1.89
$[CuL_4](ClO_4)_2$	70	24.89 (24.82)	4.84 (4.79)	19.36 (19.36)	10.98 (10.75)	553 (38)	1.88
$[CuL_5](ClO_4)_2$	75	24.89 (24.85)	4.84 (4.81)	19.36 (19.26)	10.98 (10.48)	553 (36)	1.86

L_1 = 1-amidino-O-methylurea; L_2 = 1-amidino-O-ethylurea; L_3 = 1-amidino-O-*n*-propylurea; L_4 = 1–amidino-O-*n*-butylurea; L_5 = 1-amidino-O-*i*-butylurea.

The intense pink complexes so obtained were filtered off, washed several times with alcohol, and dried in air. (2) Bis(1-amidino-O-alkylurea)Cu(II)vanadate complexes (where alkyl = CH_3, C_2H_5, $C_3^nH_7$, $C_4^{n,i}H_9$) were prepared by dissolving bis(1-amidino-O-alkylurea)Cu(II) perchlorate complexes in water and by treating with ammonium metavanadate dissolved in water in 1 : 1 ratio. The precipitated light pink complexes were filtered off without delay and washed repeatedly with water and then with acetone, and dried in air. The analytical, magnetic susceptibilities, and yield (%) of the different Cu(II) complexes are presented in tables 1 and 2.

2.3. *Physical measurements*

Infrared (IR) spectra of KBr disc were recorded on a Shimadzu FT-IR-8400S. EPR experiments were conducted using a BRUKER ESP-300 spectrometer operated at X-band frequency (9–10 GHz) with 100 kHz field modulation. DPPH was used as field marker. Temperature was varied in the range 100–300 K using the variable temperature accessory Eurotherm BVT 2000 with liquid nitrogen as coolant in a flow system. The EPR parameters for copper complexes have been precisely determined from the calculated spectra, which were obtained with a Bruker SIMFONIA program based on perturbation theory (Weber, R.T., WIN-EPR SIMFONIA manual, 1995). The theoretical EPR signals for binuclear complexes ($S = 1$) were calculated using the spin Hamiltonian

$$H = \beta gHS + D[S_z^2 - 1/3(S(S+1)] + E\left(S_x^2 - S_y^2\right)$$

where H is the applied field, β is the Bohr magneton, S_x, S_y, S_z are the components of spin along three mutually perpendicular crystalline axes x, y, and z, D and E are second-order crystal field terms with axial and rhombic structure parameters, S is the total spin of the electron, and g is the spectroscopic factor. In polycrystalline sample, EPR signals have been simulated by generating 9000 random orientations of the magnetic field and by summing the corresponding 9000 absorption signals. The final signal was obtained

Table 2. Analytical, yield, and magnetic susceptibilities of the copper vanadate complexes.

		Found (Calcd) (%)					
Compound	Yield (%)	C	H	N	Cu	V	μ_{eff} (B.M.)
$[CuL_1]V_2O_6$	70	14.59 (14.32)	3.24 (3.11)	22.69 (22.90)	12.87 (11.99)	20.66 (19.89)	1.73
$[CuL_2]V_2O_6$	70	18.40 (17.45)	3.83 (3.67)	21.47 (20.56)	12.18 (12.15)	19.55 (18.23)	1.85
$[CuL_3]_2(V_2O_6)_2$	60	21.84 (21.45)	4.37 (4.32)	20.38 (20.05)	11.56 (11.05)	18.56 (18.52)	2.14
$[CuL_4]_2(V_2O_6)_2$	65	24.89 (24.82)	4.85 (4.72)	19.39 (19.12)	11.00 (10.90)	17.66 (17.68)	2.44
$[CuL_5]_2(V_2O_6)_2$	65	24.89 (24.93)	4.85 (4.67)	19.39 (19.05)	11.00 (10.50)	17.66 (17.26)	2.24

L_1 = 1-amidino-O-methylurea; L_2 = 1-amidino-O-ethylurea; L_3 = 1-amidino-O-*n*-propylurea; L_4 = 1-amidino-O-*n*-butylurea; L_5 = 1-amidino-O-*i*-butylurea.

by performing a convolution (Gaussian or Lorentzian line shape) of each transition line, adding all contributions and calculating the first derivative signal; the line width of each component has been optimized in order to obtain the best fit with the observed experimental values.

EPR signals for mononuclear complexes ($S = 1/2$) in the axial field were calculated using the spin Hamiltonian

$$H = g_{||}\beta H_z S_z + g_{\perp}\beta\left(H_x S_x + H_y S_y\right) + A_{||}^{Cu} I_z S_z + A_{\perp}^{\mathrm{Cu}}\left(I_x S_x + I_y S_y\right).$$

The errors in calculation of the spin Hamiltonian parameters g, A (hyperfine coupling constant), and D (zero field splitting, ZFS) are ±0.0005, ±2.0 G, and ±5.0 G, respectively. The rhombic distortion term, E term, is zero in the present case. There is close resemblance between the experimental and theoretical spectra (simulated spectra) suggesting overall goodness of fit. In fact simulations allow obtaining the spin Hamiltonian parameters. The photoacoustic spectrum (PAS) experiments were performed using an indigenously designed spectrometer consisting of a 250 W tungsten-halogen lamp used as an excitation source, the radiation of which was modulated by a variable speed chopper (33 Hz). A monochromator, in combination with appropriate absorption filters, was used for wavelength selection and to eliminate higher order effects. The beam leaving the monochromator was directed into a PA cell. The signal was pre-amplified and fed to a lock-in amplifier connected to a computer. The PA signal was normalized by taking the ratio of the signal due to sample to that of carbon black to eliminate the spectral variation of the illumination source [9]. The electronic spectra of the complexes in solution were recorded on a Perkin Elmer UV-Vis Lamda 35 spectrometer. The fluorescence spectra were recorded by a Perkin Elmer LS55 spectrophotometer. The room temperature magnetic moments (μ_{eff}) were measured using the Sherwood magnetic susceptibility balance. Thermal studies of the compounds were carried out in an air atmosphere with a Perkin Elmer STA 6000. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 2400 analytical instrument. Cu and V were estimated by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a JY-50 P model Panorama ICP spectrometer.

Table 3. Crystal data and structure refinement of bis(1-amidino-O-*n*-butylurea)Cu(II) perchlorate.

Empirical formula	$C_{12}H_{28}Cl_2CuN_8O_{10}$
Formula weight	578.86
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	*P2(1)/c*
Wavelength (Å)	0.71073
Unit cell dimensions (Å, °)	
a	15.6527(8)
b	5.3499(3)
c	14.3469(7)
α	90.00
β	104.479 (2)
γ	90.00
Volume (Å^3), Z	1163.26(10), 2
Calculated density ($Mg\,m^{-3}$)	1.653
$F(000)$	598
θ range for data collection (°)	2.2–28.1
Crystal size (mm^3)	0.38 × 0.20 × 0.18
Index ranges	$-20 \leq h \leq 20$; $-7 \leq k \leq 6$; $-19 \leq l \leq 18$
Independent reflections	2797 [$R(\text{int}) = 0.089$]
Reflections collected	9302
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.12
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0566$, $wR_2 = 0.1646$
Largest difference peak and hole (e Å^{-3})	1.34 and −1.58

2.4. *Crystallographic studies*

Diffraction data of bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate was collected with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) on a Bruker-SMART CCD area detector at 296 K. Data reductions and absorption corrections were performed with the SAINT software packages [10]. Structures were solved by direct methods using the SHELXL-97 software package [11]. Non-H atoms were anisotropically refined using the full-matrix least-squares method on F^2. All hydrogen atoms were placed at calculated positions and refined riding on the parent atoms. The crystallographic details about the data collection and structure refinement are summarized in table 3.

As single crystals of Cu(II) vanadate complexes could not be obtained, we have carried out powder XRD studies on **2** using a set program called Powder X program [12] so as to give a typical idea about the single phase nature of the complex. The complex crystallizes in orthorhombic structure with unit cell dimensions $a = 21.11$ Å, $b = 24.11$ Å, $c = 27.11$ Å, $\alpha = \beta = \gamma = 90°$. The typical fit parameters of this complex are given in Supplementary material.

3. Results and discussion

3.1. *Electronic spectral studies*

Electronic spectra of bis(1-amidino-O-alkylurea)Cu(II)perchlorate complexes exhibit a broad absorption at *ca* 537 nm corresponding to $^2E_g \rightarrow {}^2T_{2g}$ transition.

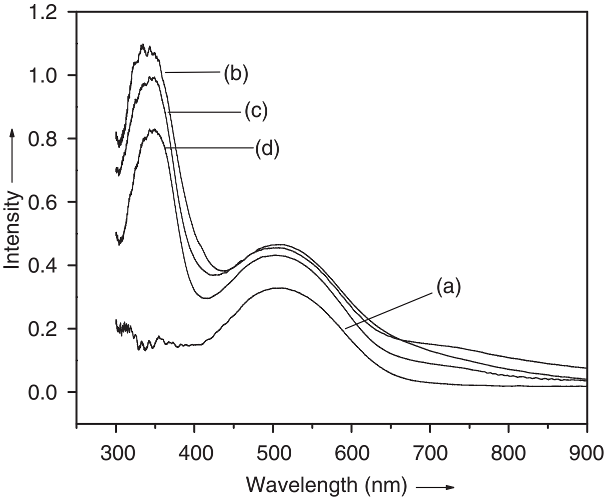

Figure 1. PAS of (a) [Cu(II)(1-phenylamidino-O-*i*-butylurea)en]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$, (b) **1**, (c) **2**, (d) **3**.

The $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, and $^2B_{1g} \rightarrow {}^2E_g$ transitions were not resolved, suggesting the presence of square-planar geometry in the solid state [13]. Absorption spectra of the perchlorate complexes recorded in DMSO showed a typical broad absorption at *ca* 553 nm which may be due to axial ligation of the solvent. The molar absorptivity values of the complexes (table 1) are found to be comparable with that of the reported Cu(II) square-planar complexes [13]. The PAS was recorded for the binuclear, square-planar complex [Cu(II)(1-phenylamidino-O-*i*-butylurea)en]$_2$(H$_2$O)$_2$(Cl$_2$)$_2$ [4] used as reference sample and for **1**, **2**, and **3**. The PAS spectra for **1**, **2**, and **3** (figure 1) consisted of two broad bands at *ca* 350 nm and 525 nm. The band at *ca* 525 nm is attributable to d–d electronic transitions. This absorption band is similar to that observed in square-planar copper(II) complexes [14], copper(II)-O-alkyl-1-amidinourea complexes [1], and closely related biguanide compounds [15]. The band at *ca* 350 nm in PAS spectrum is attributed to charge transfer from O^{2-}(2p) → V^{5+} (3d) bands (CTBs) localized within the tetrahedrally coordinated $(VO_4)^{3-}$ group [16, 17].

3.2. *IR spectral studies*

The IR spectral data of the complexes that are diagnostic of the coordinating groups are identical to our reported data [4, 5]. IR spectra of bis(1-amidino-O-alkylurea) Cu(II)perchlorate exhibit bands *ca* 1168 cm^{-1} (ν_3) and 935 cm^{-1} (ν_4) from ionic ClO_4^- [18]. The IR spectrum of ammonium metavanadate shows bands *ca* 2951 cm^{-1} (ν_1) and 3211 cm^{-1} (ν_3) which may be assigned as the N–H stretching vibrations. The sharp band *ca* 1417 cm^{-1} is assigned for H–N–H(ν_4) bands of $NH_3(NH_4^+)$. IR spectra of bis(1-amidino-O-alkylurea)Cu(II)vanadate complexes exhibit a complex pattern of broad bands at 740–842 cm^{-1}. Two stretching frequencies of the vanadate tetrahedron are expected in this region. The appearance of band *ca* 784 cm^{-1} can be assigned for $\nu_{a(V\text{–}O)}$ and bands *ca* 837 cm^{-1} and 918 cm^{-1} for $\nu_{s(V\text{–}O)}$ [19]. The absence of bands *ca*

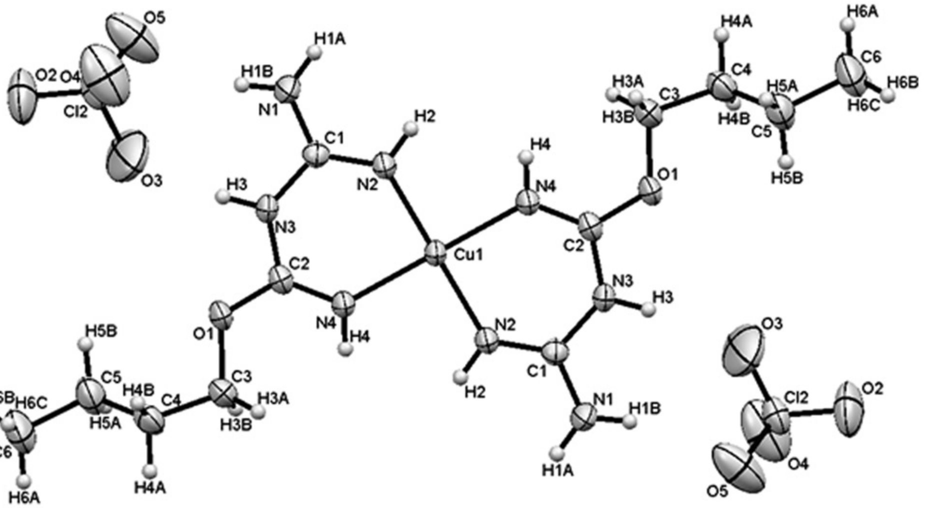

Figure 2. ORTEP structure of bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate and numbering scheme showing 50% thermal ellipsoids.

1417 $\mathrm{cm^{-1}}$ in IR spectra of bis(1-amidino-O-alkylurea)Cu(II) vanadate complexes at 300 K and heated at 490 K suggests the absence of NH_4^+ in the complexes (figure S1).

3.3. *Description of the crystal structure*

Bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate crystallizes in the monoclinic space group *P2(1)/c* with copper(II) located on an inversion centre coordinated by two N,N-bidentate ligands (figure 2) in a *trans*-configuration to give square planar $[CuL_2]^{2+}$ (L = 1-amidino-O-*n*-butylurea). The complex maintains a distorted square-planar geometry N(2)–Cu(1)–N(2)#1, 180.00(13), N(4)#1–Cu(1)–N(4) 180.00(17); however, N(2)#1–Cu(1)–N(4)#1, 88.68(10) and N(2)–Cu(1)–N(4)#1, 91.32(10) of the six-membered chelate ring is slightly distorted due to the presence of butyl. Selected bond lengths and angles are given in table 4. The complex shows weak interaction between complexes *via* perchlorate ion in a 2-D zig-zag array nearly perpendicular to each other.

3.4. *EPR spectral studies*

3.4.1. EPR spectra of bis(1-amidino-O-alkylurea)Cu(II) perchlorate complexes. Room temperature EPR spectra of polycrystalline complexes of bis(1-amidino-O-alkylurea) Cu(II) perchlorate complexes (alkyl = methyl, ethyl, *n*-propyl, *n*- or *iso*-butyl), which were used as starting compounds for preparation of (1-amidino-O-alkylurea) Cu(II) vanadate complexes (alkyl = methyl, ethyl, *n*-propyl, *n*- or *iso*-butyl), consist of a weak shoulder with $g_{||} = 2.254$ and an intense signal corresponding to $g_{\perp} = 2.0522$, having a typical derivative line shape (not shown in figure). These are well-established features in

Table 4. Selected bond lengths (Å) and angles (°) of bis(1-amidino-O-*n*-butylurea)Cu(II)perchlorate.

Cu(1)–N(2)#1	1.941(2)	Cu(1)–N(2)	1.941(2)
Cu(1)–N(4)	1.973(2)	Cu(1)–N(4)#1	1.973(2)
N(2)–Cu(1)–N(2)#1	180.00(13)	N(2)–Cu(1)–N(4)#1	91.32(10)
N(2)#1–Cu(1)–N(4)#1	88.68(10)	N(2)–Cu(1)–N(4)	88.68(10)
N(2)#1–Cu(1)–N(4)	91.32(10)	N(4)#1–Cu(1)–N(4)	180.00(17)
N(3)–C(1)–N(2)–Cu(1)	4.4(4)	N(2)–Cu(1)–N(2)–C(1)	25(87)
N(4)–Cu(1)–N(2)–C(1)	176.6(3)	N(4)–Cu(1)–N(2)–C(1)	−3.4(3)
O(1)–C(2)–N(4)–Cu(1)	−172.9(2)	N(3)–C(2)–N(4)–Cu(1)	8.0(4)
N(2)–Cu(1)–N(4)–C(2)	−2.8(3)	N(2)–Cu(1)–N(4)–C(2)	177.2(3)
N(4)–Cu(1)–N(4)–C(2)	−159(63)		

Symmetry operation used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

EPR spectra of mainly mononuclear complexes in polycrystalline samples with random orientation of microcrystallites. The hyperfine structure due to ^{63,65}Cu (natural abundance 69 and 31%, respectively, each having a nuclear spin $I = 3/2$) was not observed, apparently due to strong spin–spin interaction, characteristic of concentrated paramagnetic salts. In order to reduce the broadening due to spin–spin interaction in solids and to resolve the hyperfine interaction and super-hyperfine interactions, EPR spectra of the (1-amidino-O-*n*-butylurea)Cu(II) perchlorate complex in DMSO were recorded at 100 K (figure 3). The EPR spectra of magnetically diluted sample showed a quartet hyperfine structure with m_I dependent line widths (figure 3a). The intense perpendicular component of the spectrum showed a well-resolved nine component super-hyperfine structure (SHFS) with super-hyperfine coupling constant on the order of 15 G typical of nitrogen coordination (^{14}N, $I = 1$, 100% abundance) (figure 3e). This suggests square-planar coordination of four equivalent nitrogen donors around copper as confirmed from the crystal structure. In addition to this, EPR spectra consisted of a weak doublet (*g ca* 2.07) due to fine-structure transitions ($\Delta M_s = \pm 1$) with ZFS of 0.04 cm^{-1} and a half-field signal ($\Delta M_s = \pm 2$) at *ca* 1600 G corresponding to forbidden transition were also obtained suggesting the formation of binuclear copper ($S = 1$). The presence of seven line hyperfine structure on the forbidden transition ($\Delta M_s = \pm 2$) with hyperfine coupling nearly half ($A = 100$ G) compared to that observed on parallel component for the corresponding mononuclear complex ($A = 202$ G) suggested formation of the binuclear complex (figure 3d). The simulated spectrum was obtained by adjusting the relative concentrations of the binuclear and mononuclear complexes. The best fit of the simulated experimental spectrum was obtained by using a binuclear to mononuclear complex weight ratio of 0.2 : 0.8. The spin Hamiltonian parameters used for the simulation of binuclear and mononuclear complexes are given in table 5. The observed *g* values for the copper(II) complexes were close to those reported for complexes having square-planar geometry. The trend in *g* value ($g_{||} > g_{\perp} > 2.00$) suggested that the unpaired electron in copper(II) ion is in the $d_{x^2-y^2}$ orbital.

3.4.2. EPR spectra of bis(1-amidino-O-alkylurea)Cu(II)vanadate complexes. EPR spectra of bis(1-amidino-O-alkylurea)Cu(II)vanadate (alkyl = methyl, ethyl) consisted of a symmetrical signal at *g ca* 2.07. EPR spectra of bis(1-amidino-O-*n*-propylurea)Cu(II)vanadate (**1**) (figure 4b), bis(1-amidino-O-*n*-butylurea)Cu(II)vanadate (**2**) and bis(1-amidino-O-*i*-butylurea)Cu(II)vanadate (**3**) (figure 4c) consisted of an

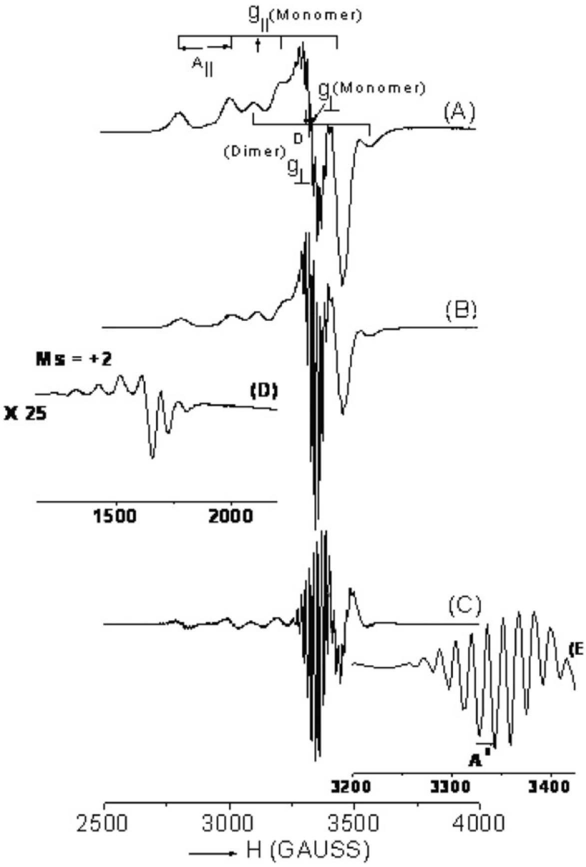

Figure 3. EPR spectra of (1-amidino-O-*n*-butylurea)Cu(II) perchlorate in DMSO at liquid nitrogen temperature (a) Experimental spectrum in first derivative mode, (b) Simulated spectrum (EPR parameters used for simulation are given in table 5) using binuclear to mononuclear complex weight ratio of 0.2 : 0.8, (c) Experimental spectrum recorded in second derivative mode to improve resolution, (d) inset showing forbidden $\Delta M_S = \pm 1$ transition and (e) inset showing nine component SHFS on the perpendicular component of the Cu(II) mononuclear complex having square-planar geometry with four equivalent nitrogen nuclei.

intense doublet (*g ca* 2.05) due to fine-structure transitions ($\Delta M_s = \pm 1$) with ZFS of $0.041\,\mathrm{cm}^{-1}$ and a half-field signal ($\Delta M_s = \pm 2$) at *ca* 1600 G corresponding to forbidden transition were also obtained. These features suggest formation of binuclear copper(II) complex ($S = 1$). These complexes are insoluble in most organic solvents. Since the samples are not magnetically dilute the hyperfine and super-hyperfine interactions are unresolved due to spin–spin broadening yielding a broad doublet. The magnetic moment values obtained for **1**, **2**, and **3** which are more than two (~2.12) further supported our finding that the complexes are binuclear. The most accurate values of $g_{||}$, $g_{\perp}$, and D for binuclear complexes were deduced by computer simulation assuming axial symmetry (table 5).

We recorded EPR spectra of vanadate complexes from 100 to 300 K. The population of the triplet state is governed by the Boltzmann distribution and the Curie law following the equation $3/T\exp(-J/\kappa T)$ where κ is the Boltzmann constant and J is the

Table 5. Spin Hamiltonian parameters of Cu(II) mononuclear (M) and binuclear (B) complexes with different ligands.

Complex name	$g_{\|\|}$	$g_\perp$	g_{iso}	$A_{\|\|}$ (G)	$A_\perp$ (G)	D (cm^{-1})	J (cm^{-1})	r (Å)
[Cu(II)(1-amidino-O-alkylurea)$_2$]Cl$_2$ [1]	2.2400	2.0600		218	25			
[Cu(II)(1-amidino-O-methoxyethylurea)$_2$]$_2$(H$_2$O)$_2$(SO$_4$) [5]	2.1650	2.0425		100		0.0515	+59	3.83
[Cu(II)(1-amidino-O-ethoxyethylurea)$_2$]$_2$(H$_2$O)$_2$(SO$_4$) [5]	2.1645	2.0422		100		0.0510	+50	3.84
[Cu(II)(1-PhAB^{i}UH)en(H$_2$O)]$_2$(Cl$_2$)$_2$(B) [4]	2.1640	2.0525		100		0.0493	+55	3.99
[Cu(II)(1-amidino-O-methylurea)$_2$](ClO$_4$)$_2$ (M)	2.2540	2.0522	2.1195					
[Cu(II)(1-amidino-O-propylurea)$_2$](ClO$_4$)$_2$	2.1992	2.0562	2.1039	205				
[Cu(II)(1-amidino-O-*n*-butylurea)$_2$](ClO$_4$)$_2$	2.1990	2.0560	2.1037	202				
[Cu(II)(1-amidino-O-methylurea)$_2$](V$_2$O$_6$) (M)			2.07					
[Cu(II)(1-amidino-O-ethylurea)$_2$](V$_2$O$_6$) (M)			2.07					
[Cu(II)(1-amidino-O-*n*-propylurea)$_2$]$_2$V$_2$O$_6$)$_2$ (B)	2.1801	2.0512	2.0941			0.0408	+28	4.15
[Cu(II)(1-amidino-O-*n*-butylurea)$_2$]$_2$(V$_2$O$_6$)$_2$ (B)	2.1801	2.0512	2.0941			0.0410	+30	4.14
[Cu(II)(1-amidino-O-*i*-butylurea)$_2$]$_2$(V$_2$O$_6$)$_2$ (B)	2.1801	2.0512	2.0941			0.0408	+32	4.15

Error in g is ±0.0005, in A is ±2.0 G and D (ZFS) is ±5.0 G.
[Cu(II)(1-amidino-O-methylurea)$_2$](ClO$_4$)$_2$: EPR spectra were recorded at room temperature for polycrystalline sample [Cu(II)(1-amidino-O-propylurea)$_2$](ClO$_4$)$_2$ and [Cu(II)(1-amidino-O-*n*-butylurea)$_2$](ClO$_4$)$_2$: EPR spectra were recoded for frozen solutions in DMSO. The observed ZFS (D term) for weak binuclear complex in [Cu(II)(1-amidino-O-*n*-butylurea)$_2$](ClO$_4$)$_2$ is 395 G. This D value is used for EPR simulations in figure 3.

exchange parameter. From this equation, the isotropic exchange interaction constant J (splitting between the singlet and triplet state) was calculated by following temperature dependence of the peak to peak intensity (I) of the allowed EPR transitions, $\Delta M_s = \pm 1$ for **1**, **2**, and **3**. The plot of $\ln IT/3$ *versus* $1/T$ was used for evaluation of isotropic exchange interaction constant J. Plots of $1/I$ [EPR signal intensity (a.u.)] *versus* T (K) are given as supplementary figures (figure S2). The plot of $1/I$ *versus* T is a straight line with a positive intercept on the temperature axis, thereby indicating a ferromagnetic interaction between two neighboring Cu^{2+} ions. The average distance r between the two unpaired electrons was calculated using $D = 3g^2\beta^2/2r^3 = 1.39 \times 10^4\ (g/r^3)$ where D is in gauss and r in Angstroms (table 5). We have evaluated the angle ξ (21.5°) for **2** using the equation $g_z^2 = g_{||}^2\cos^2(\xi) + g_\perp \sin^2(\xi)$ [20], where g(2.1990) and $g_\perp$(2.056) represent g values for the mononuclear complex, ξ is the angle between the Cu–Cu direction and the parallel direction and g is replaced by g_z^2(2.1801) as g and Cu–Cu direction for binuclear complex do not coincide.

On heating **1**, **2**, and **3** above 490 K, the triplet-state EPR signal completely disappeared while weak signal having unresolved hyperfine structure on broad perpendicular component was observed. The signal was found to be axially symmetric with spin Hamiltonian parameters $g_\perp = 1.998$, $g_{||} = 1.9561$, $A_{||} = 170$ G, and $A_\perp = 60$ G which are typical of VO^{2+} species (figure S3). At temperatures greater than 475 K these complexes were completely destroyed indicating thermal decomposition as confirmed from thermal gravimetry. The possible mechanism for the formation of VO^{2+} species from the thermal decomposition of ammonium metavanadate had been reported [19]. The VO^{2+} ion (3d^1 electron configuration) is formed when a V^{4+} is bound to an oxygen ion by a strong, double covalent bond. The nature of this bond has been described in terms of molecular orbitals of the vanadyl pentahydrate complex (VO$^{2+}\cdot$5H$_2$O) by Ballhausen and Gray [21].

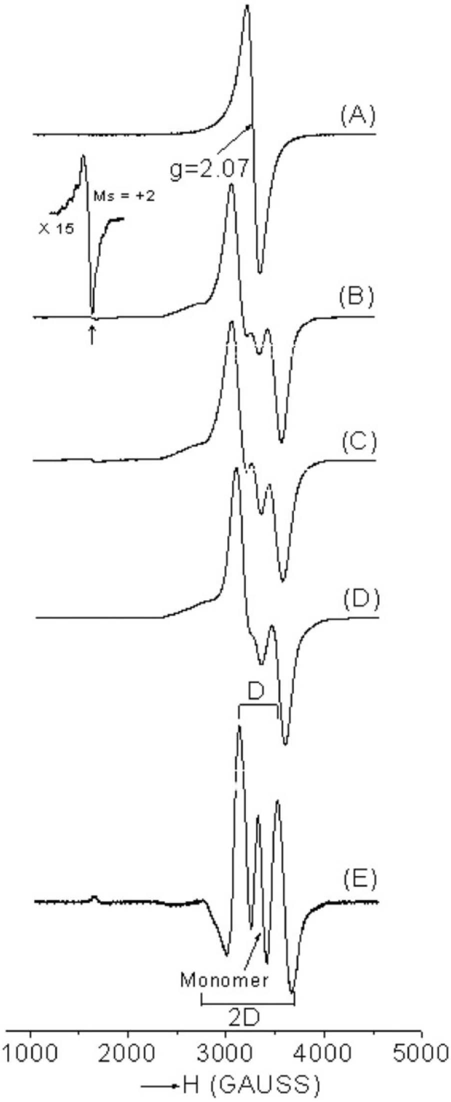

Figure 4. EPR spectra of different Cu(II) complexes at 300 K: (a) bis(1-amidino-O-methylurea) Cu(II) vanadate complex, (b) **1**, (c) **3**, (d) simulated spectrum using mononuclear to binuclear complex weight ratio of 0.1 : 0.9 (EPR parameters used for simulation are given in table 5), and (e) second derivative of **3**.

Elemental analyses of bis(1-amidino-O-alkylurea)Cu(II)vanadate, where alkyl = methyl or ethyl suggest the presence of $V_2O_6^{2-}$. The existence of $V_2O_6^{2-}$ has been reported in [Cu(bpy)$_2$V$_2$O$_6$] [22], [Cu(prn)$_2$V$_2$O$_6$] [23], [Cu(dien)V$_2$O$_6$], and α-[Cu(terpy)V$_2$O$_6$] [24, 25] where 1-D chains made by corner-sharing of tetrahedral [VO$_4$] are the main structural motif. The 2-D network in [Cu(dpa)VO$_3$] is constructed by two distinct chains of corner-sharing [VO$_4$] tetrahedra, which are linked by $\{Cu(dpa)\}_n^{n+}$ chains [26]. A 2-D network is also observed in [Cu(en)V$_2$O$_6$], but in this case the chains are linked by $\{Cu(en)\}^{2+}$ units [22]. Another way for construction of a

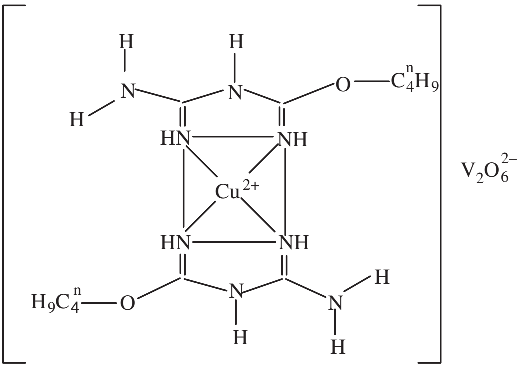

Figure 5. Proposed structure of [bis(1-amidino-O-*n*-butylurea)Cu(II)](V_2O_6).

2-D structure is realized in [Cu(terpy)V_2O_6] where chains of corner-sharing [VO_4] tetrahedral are linked by binuclear copper sites [27].

The possibility of vanadium present as $(VO_3)^-$ anion in these complexes is ruled out, as ammonium metavanadate has a tendency to get oxidized to $(VO_4)^{3-}$ in the presence of strong oxidizing agents like nitric acid and perchloric acid. Ningthoujam *et al.* [28] show that during the preparation of YVO_4 from NH_4VO_3, nitric acid used as an oxidizing agent converts $(VO_3)^-$ to $(VO_4)^{3-}$ anion. The presence of $(VO_4)^{3-}$ in the bimetallic complexes is supported by fluorescence spectra of these complexes at room temperature on excitation with ultra violet irradiation which showed weak photo emission peak at *ca* 426 nm which may arise from the transition of excited state to the ground state of charge transfer or molecular transfer band of V–O [28]; ammonium metavanadate is colorless and does not exhibit any absorption and fluorescence at room temperature.

The proposed structure of [Cu(II)(1-amidino-O-alkylurea)$_2$](ClO_4)$_2$ mononuclear complexes (X-ray crystallography and EPR studies) consists of two discrete Cu(II)(1-amidino-O-*n*-alkylurea) molecules and perchlorate anions (figure 2). The Cu(II)(1-amidino-O-aklylurea)$_2$ molecule, as a whole, is square planar. Copper is located in centro symmetric square-planar coordination of four nearly equivalent nitrogen donors of N=H group of ligand. Discrete molecules of Cu(II)(1-amidino-O-alkylurea)$_2$ form parallel planes. The square-planar coordination of four nitrogen donors around copper(II) was confirmed from EPR studies of perchlorate complex in DMSO which clearly showed a well-resolved nine component SHFS on the perpendicular component with super-hyperfine coupling constant of 15 G typical of nitrogen coordination (^{14}N, $I = 1$, 100% abundance). Since the reaction of (1-amidino-O-alkylurea) Cu(II)perchlorate complexes with ammonium metavanadate in aqueous solutions gives immediate precipitation of insoluble solid complexes, possible replacement of perchlorate by vanadate ion without disturbing the CuN_4 chromophore is suggested. The structures of **1**, **2**, and **3** may consist of two mononuclear units of Cu(II)(1-amidino-O-alkylurea)$_2$ involving interaction with the anions. However, proposing the structure without single-crystal X-ray data will be speculative. On the basis of our experimental evidence, we suggest the most probable structure of monomers in forming binuclear **2** (figure 5). From EPR spectroscopy, we have calculated exchange parameter J, Cu–Cu internuclear distance r, and angle ξ between principal Z-direction of the binuclear complex and Cu–Cu vector which gave some information about the structure of these complexes.

Although there are many reports of forming $V_2O_6^{2-}$ species prepared hydrothermally, our method provides a new method of synthesizing binuclear Cu(II) complexes by using ammonium metavanadate and this is the first report wherein EPR studies conclusively established the formation of binuclear species.

As the crystal chemistry of vanadate is of interest because of the possibility of the existence of a series of framework structure analogous to those of silicates, our report may attract further research to identify the role of vanadate species in forming binuclear complexes.

4. Conclusion

Five Cu(II) complexes of the type bis(1-amidino-O-alkylurea)Cu(II)perchlorate, where alkyl = methyl, ethyl, *n*-propyl, *n*-butyl, or *i*-butyl, were synthesized and structurally characterized.

With the hope of synthesizing binuclear Cu(II) complexes and to study the nature of the complexes at different temperatures, we have synthesized and characterized the complexes by reaction of bis(1-amidino-O-alkylurea)perchlorate with ammonium metavanadate in water (immediate precipitation of insoluble pink complexes). It is the first EPR report of forming binuclear Cu(II) complexes with $V_2O_6^{2-}$ having interactions between ligands and anions. Complex **2** crystallizes in an orthorhombic structure with $a = 21.11$ Å, $b = 24.11$ Å, $c = 27.11$ Å, $\alpha = \beta = \gamma = 90°$. EPR studies on the binuclear complexes at high temperatures indicated the existence of VO^{2+} species.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 743687. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif). DTA/TGA data of **3**; IR spectra of ammonium metavanadate, **3** at RT and heated sample; plot of 1/I *versus* temperature of **1** and **3**; packing structure of bis(1-amidino-O-*n*-butylurea)Cu(II) perchlorate showing zig-zag array with a weak interaction in between the complexes *via* perchlorate ion; powder X-ray diffraction data of **2** has been attached as supplementary information.

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