



A tridentate *in situ* generated ligand that directs the self-assembly of a transition metal complex: Synthesis and structural characterization of *cis*-dichloro[1-(2-aminoethyl)biguanide]copper(II) monohydrate

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This work is dedicated to the retired Professor Satyaranjan Saha of the Department of Chemistry, Jadavpur University.

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ABSTRACT

One mononuclear penta-coordinated Cu(II) complex, $[\text{CuLCl}_2] \cdot \text{H}_2\text{O}$ (**1**), where L is a tridentate ligand $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}=\text{C}(\text{NH}_2)-\text{NH}-\text{C}(\text{NH}_2)=\text{NH}$ [=1-(2-aminoethyl)biguanide], has been synthesized and characterized crystallographically. In an attempt to prepare bis(ethylenediamine)bis(biguanide)Cu(II), it resulted in a different product, $[\text{CuLCl}_2] \cdot \text{H}_2\text{O}$ (**1**), where Cu(II) was found to occupy the base of a square pyramid formed by N_3Cl_2 coordination. The ligand L is believed to be generated *in situ* in presence of Cu(II), since neither L can be prepared independently nor it can be removed from complex **1**. Similar attempts with Ni(II) Co(II), Zn(II), Fe(II) or Fe(III) salts failed, and we conclude that Cu(II) acted as a template for the formation of **1**. The solid-state structure of **1** is interesting because one monomeric unit, i.e. $[\text{CuLCl}_2]$ self-recognizes other monomeric unit centrosymmetrically to form a supramolecular dimer through N–H...Cl hydrogen bonding. The single lattice water molecule played an important role in the formation of 2D supramolecular sheets involving these dimers and become an integral part of such self-assembled structure. The EPR spectrum of complex **1** in the frozen state is consistent with a typical monomeric tetragonal Cu(II) environment. Electrochemical study of **1** in aqueous medium showed an irreversible reductive response at -0.65 V versus SCE, which can be assigned to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox couple.

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1. Introduction

Self-assembly is a fundamental process that generates structural organizations on all scales from molecules to galaxies in which preexisting parts or disordered components form ordered structures or patterns. Molecular self-assembly is at the heart of crystalline molecular materials which includes molecular recognition of complementary units through various weak forces, the prominent among which remains the hydrogen bonding. During last decades self-assembly process has been extensively used to synthesize and engineer novel organic as well as organic–inorganic hybrid materials [1] where, metals, especially the transition metals are of wide use and these cationic units due to their special stereo-

chemical requirement, influence the self-assembly of organic components in a decisive way. The influence of the metal cations is sometimes catalytic and in their presence the organic components in many cases merge or dissociate to produce novel molecules *in situ*, which in turn propagate the self-assembled superstructure. During recent times the strategy of *in situ* ligand synthesis [2] has become a main stream in the field of crystal engineering.

Cyanamide, NH_2CN , occurs in interstellar space [3] and readily dimerizes to dicyandiamide, $\text{NH}_2\text{C}(=\text{NH})\text{NHCN}$, which is believed to have a role in chemical evolution [4,5]. The conversion of cyanamide to the biosynthetic coupling agent dicyandiamide in water may have contributed to chemical evolution since prebiotic times. Despite this background, literature is not rich [6] in the coordination chemistry of the fundamental molecule, cyanamide.

Reacting cyanamide, ethylenediamine dihydrochloride and Cu(II) chloride in water in 4:2:1 molar ratio resulted a five-coordinated blue Cu(II) complex, $[\text{CuLCl}_2] \cdot \text{H}_2\text{O}$ where $\text{L} = \text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}=\text{C}(\text{NH}_2)-\text{NH}-\text{C}(\text{NH}_2)=\text{NH}$ [=1-(2-aminoethyl)biguanide],

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a tridentate ligand **L** generated *in situ*, and two chlorides directly bonded to Cu(II). The formation of the tridentate ligand is unexpected as the starting materials in the stated molar proportions are used as a synthetic protocols for the preparation of biguanides [7]. Here we report role of the *in situ* generated tridentate ligand on the self-assembly of the superstructure of the molecular complex **1**.

2. Experimental

2.1. Materials and measurements

All reactions were carried out in aerobic condition and in water solvent. Cyanamide (Lancaster), dicyandiamide (Aldrich) and ethylenediamine dihydrochloride (Fluka) were used as received. All other chemicals were of reagent grade and used without further purification. The elemental analyses were done using a Perkin–Elmer 2400 Series-II elemental analyzer. The IR spectra were recorded from KBr pellets at a range of 500–4000 cm^{-1} on a Perkin–Elmer RXI FT-IR spectrophotometer with a spectral resolution of 4 cm^{-1} . UV–Vis spectral data were obtained from Shimadzu UVPC 1601 spectrophotometer. EPR spectral data were recorded using Varian E-109C spectrometer fitted with a liquid nitrogen quartz dewar, 9.1 GHz microwave frequency, 100 kHz modulation, 30 dB power, 3200 G sweep center, 4000 G sweep width, 240 s sweep time. Diphenylpicrylhydrazyl (dpph, $g = 2.0037$) was used to calibrate the spectra. Electrochemical measurements were done in nitrogen atmosphere with a three-electrode setup, consisting of a glassy carbon working, a saturated calomel reference and a Pt wire auxiliary electrodes using a EG&G PARC electrochemical analysis system, model 250/5/0. An ECDA–Pt02 platinum disk electrode obtained from Con-Serv Enterprises, India, and a planar EG&G PARC G0229 glassy carbon milli electrode were used as the working electrodes in cyclic voltammetry. The measurements (1.0 mM Cu(II) complex) were done in aqueous solution in presence of 0.1 M KCl as supporting electrolyte at 25 °C and the data are uncorrected for junction potentials. Room temperature Magnetic moment was measured by using a PAR-155 vibrating sample magnetometer. Solution conductivity was measured by a Systronics (India) direct reading conductivity meter (model 304).

2.2. Synthesis of the complex $[\text{CuCl}_2] \cdot \text{H}_2\text{O}$ (**1**) [**L** = 1-(2-aminoethyl)biguanide] (**1**)

To an aqueous solution of 0.10 mol cyanamide (NH_2CN) added 0.05 mol ethylenediamine dihydrochloride (in 25 mL water). 0.025 mol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (in 25 mL water) was added into this solution. The solution mixture was then either kept for ~2 months at room temperature (25–30 °C) when deep blue crystals suitable for X-ray analysis were separated or refluxed at ~80 °C for 10 h when the same blue crystals were formed on cooling to room temperature. The crystals were separated by filtration, washed with ethanol and dried in air. Alternatively, using dicyandiamide (0.05 mol, half of the cyanamide) instead of cyanamide and following the same procedures as described above resulted in the formation of **1** as confirmed by X-ray crystallography. The compound **1** can be prepared in high yield (80%, based on Cu) in either way. Anal. Calc. for $\text{C}_4\text{H}_{12}\text{Cl}_2\text{N}_6\text{Cu} \cdot \text{H}_2\text{O}$: C, 16.18; H, 4.72; N, 28.32. Found: C, 16.24; H, 4.79; N, 28.18%. Selected IR peaks ($\text{KBr}/\text{cm}^{-1}$): $\nu(\text{C–N})$ 1308 (w) and 1267 (m), $\nu(\text{N–H})$ 3300 (s) and 3231 (s), $\nu(\text{C–H})$ 2940 (m) and $\nu(\text{O–H})$ 3435 (sh).

2.3. X-ray crystallographic study

Suitable single crystals of complex **1** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-mono-

chromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. Absorption corrections were performed using the SADABS program after the diffracting frames were reduced [8]. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL-97 [9]. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms of C and N atoms were located at geometrically calculated positions and treated by a mixture of independent and constrained refinement. H atoms of the water molecule were located from difference Fourier maps.

3. Results and discussion

3.1. Synthetic observations

The tridentate ligand, **L**, $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}=\text{C}(\text{NH}_2)-\text{NH}-\text{C}(\text{NH}_2)=\text{NH}$, is formed *in situ* in the reaction media in presence of Cu^{2+} resulting in complex **1**. In an attempt to remove Cu^{2+} from **1** to isolate the ligand by passing H_2S gas through the aqueous solution of **1** resulted in decomposition of the ligand though Cu(II) can be quantitatively removed as CuS. We have also verified that the tridentate ligand **L** cannot be synthesized separately in absence of Cu^{2+} . We thus conclude that the Cu^{2+} acts as a template in the synthesis of **1**. Though we are unable to uncover the exact role of Cu^{2+} for the formation of this tridentate ligand but we have verified that similar synthetic procedure failed when Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{2+} or Fe^{3+} salts were used instead of Cu^{2+} . A possible route for the formation of the ligand **L** might be proposed as the one-ended attack of one amine group of ethylenediamine to the cyanamide and in turn another cyanamide, Scheme 1 (or one dicyandiamide instead of two molecules of cyanamide, Scheme 2) and simultaneous rearrangements of protons is presented in Schemes 1 and 2. It might also be possible (but could not be resolved at present) that two cyanamide molecules at first dimerises to form dicyandiamide which then reacts with ethylenediamine (Scheme 2).

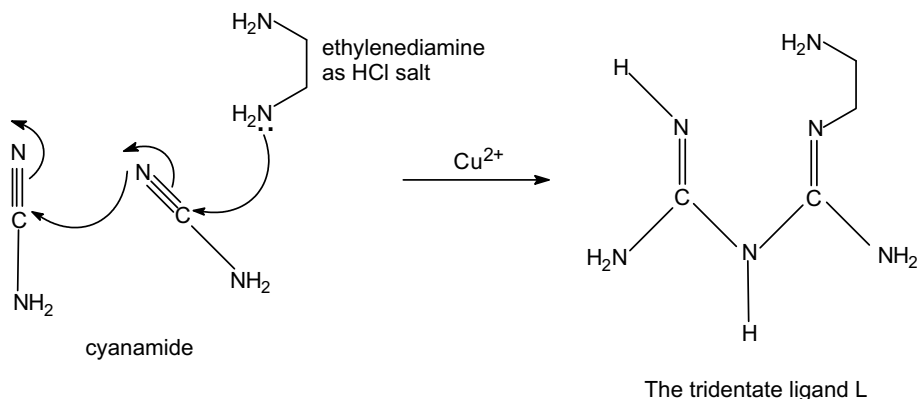
3.2. Physico-chemical observations

The complex **1** shows magnetic moment ($\mu_{\text{eff}} = 1.65 \text{ BM}$ at 25.0 °C) corresponding to a single unpaired electron. Complex **1** is highly soluble in water and conductivity measurements ($438 \Omega^{-1} \text{ cm}^2 \text{ M}^{-1}$) established its 1:2 electrolytic nature in aqueous media [10] indicating that the two chlorides become free from Cu(II) in aqueous media. An aqueous solution of **1** shows spectral peaks at 650 nm ($\epsilon = 48 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 960 nm ($\epsilon = 11 \text{ M}^{-1} \text{ cm}^{-1}$).

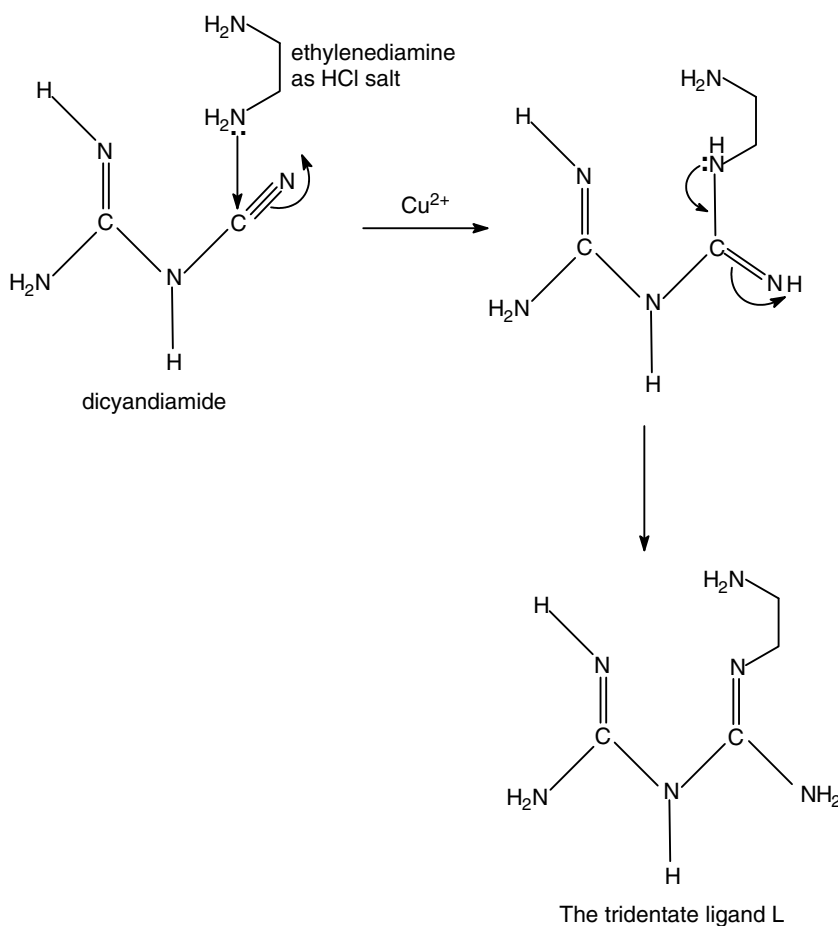
3.3. X-ray crystallographic study

3.3.1. Description of the crystal structure of $[\text{CuCl}_2] \cdot \text{H}_2\text{O}$ (**L** = $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}=\text{C}(\text{NH}_2)-\text{NH}-\text{C}(\text{NH}_2)=\text{NH}$, a tridentate ligand formed *in situ* in the reaction media)

Fig. 1 presents the structure of **1**, $[\text{CuCl}_2] \cdot \text{H}_2\text{O}$ [**L** = 1-(2-aminoethyl) biguanide], showing N_3Cl_2 coordination that results in square pyramid geometry where three N and Cl1 occupy the base of the square pyramidal coordination environment while Cl2 occupies the apical position. The Cu–N bonds in **1** range from 1.917(4) to 1.975(4) Å, similar to those in complexes of $[\text{CuL}(\text{NCS})] \cdot \text{SCN}$ and $[\text{CuL}(\text{cyanoguanidine})] \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$ [11,12], in which four N atoms coordinated to Cu(II) cation in a square plane. The Cu–Cl bonds have two models, their bond distances being 2.327(2) and 2.906(2) Å, respectively. Compared to other coordinated forms of CuN_2Cl_2 and CuN_3Cl [13,14], the Cu–Cl bond lengths are much longer in **1**. The Cu–Cl2 long bond is expected for a d^9 system due to Jahn–Teller effect. The Cu1–Cl2 apical bond (2.906(2) Å)



Scheme 1.



Scheme 2.

length is quite high indicating predominantly ionic nature of this bond compared to $\text{Cu1}-\text{Cl1}$ equatorial bond. The tridentate ligand, L, formed *in situ*, binds to the Cu(II) in a meridional fashion with the $\text{Cu}-\text{N}$ bond distances ranging from 1.918(4)–1.978(4) Å. The five-membered chelate ring is puckered while the adjacent six-membered ring is planar, the planarity being attributed to the π -cloud delocalisation. This is evident from the $\text{N}-\text{C}$ bond lengths, which are considerably shorter in the six-membered ring. Even in the six-membered ring, $\text{N(1)}-\text{C(4)}$ [1.296(6) Å] and $\text{N(2)}-\text{C(3)}$ [1.299(6) Å] are shorter than the other $\text{N}-\text{C}$ bonds [1.350(6)–1.389(6) Å] that suggests the π -electron density is somewhat more

localized over the two terminal $\text{N}-\text{C}$ bonds in the six-membered ring.

The overall 3D supramolecular built-up of the complex is the result of the self-assembly of a primary supramolecular dimeric unit (Fig. 2) through multi directional self-recognition. This multiway self-recognition has been facilitated by the active participation of a solvent water molecule. Monomeric units give rise to centrosymmetric supramolecular dimers through strong hydrogen bonds $\text{N4}\cdots\text{H4}\cdots\text{Cl2}^{\text{iv}}$ and $\text{N5}\cdots\text{H5B}\cdots\text{Cl2}^{\text{iv}}$ ($\text{iv} = 1 - x, -y, 2 - z$). These dimeric units self-recognize each other through $\text{N6}\cdots\text{H6A}\cdots\text{Cl1}^{\text{v}}$ ($\text{v} = x, -1 + y, z$) hydrogen bond and assemble along the b axis. This self-assem-

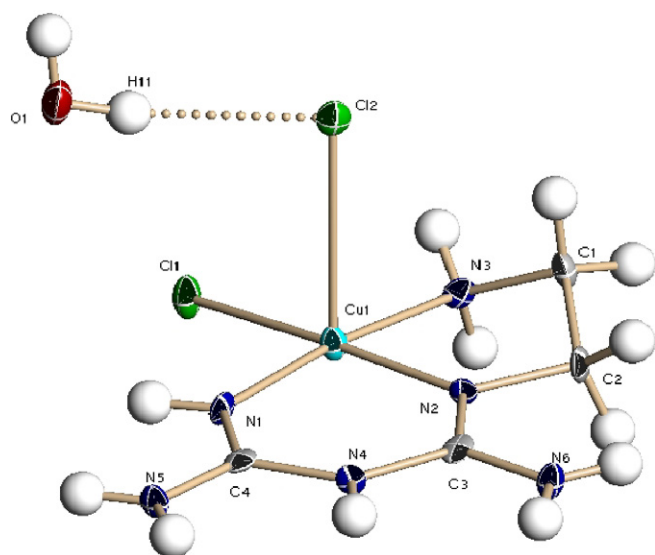


Fig. 1. ORTEP and atom-numbering scheme for $[\text{CuLCl}_2] \cdot \text{H}_2\text{O}$ (**1**), dotted line is for hydrogen bond.

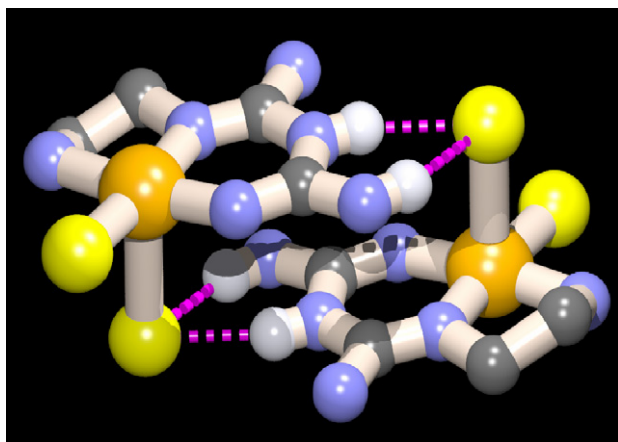


Fig. 2. N–H...Cl hydrogen bond assisted supramolecular dimer. Color code: N, dark turquoise; Cl, bright gold; C, gray; H, silver; Cu, bronze. (For interpretation of the references to colour in figure legends, the reader is referred to the web version of this article.)

bly is reinforced with the participation of a water molecule (O1) that act as acceptor for $\text{N6-H6B} \cdots \text{O1}^{\text{iv}}$, $\text{N1-H1} \cdots \text{O1}^{\text{i}}$, $\text{N5-H5A} \cdots \text{O1}^{\text{i}}$ ($\text{i} = 1 - x, 1 - y, 2 - z$; $\text{iv} = 1 - x, -y, 2 - z$) hydrogen bonds and donor for $\text{O1-H11} \cdots \text{Cl2}$ hydrogen bonds (Fig. 3). The water molecules also cross-link adjacent dimeric units along a axis through $\text{O1-H12} \cdots \text{Cl1}^{\text{vi}}$ ($\text{vi} = 1 + x, y, z$) hydrogen bond and lead the 2D-layered assembly of the dimeric units (Fig. 4). Water in this supramolecular assembly has acted as a T type connector establishing contact among three adjacent dimeric units. It is to be noted that a single water molecule in this 2D assembly has taken part in five hydrogen bonding contacts and thus stabilized the supramolecular assembly in a crucial way.

Self-recognition of dimeric units along the crystallographic c axis through complementary $\text{N3-H3A} \cdots \text{Cl2}^{\text{iii}}$ and $\text{N3-H3A} \cdots \text{Cl1}^{\text{ii}}$ ($\text{ii} = -x, 1 - y, 1 - z$; $\text{iii} = -1 + x, y, z$) hydrogen bonds help the 3D supramolecular assembly of the 2D layers (Fig. 5). Crystallographic data and structural refinements are summarized in Table 1 while the selected bond parameters are shown in Table 2. Hydrogen bond distances and angles are presented in Table 3.

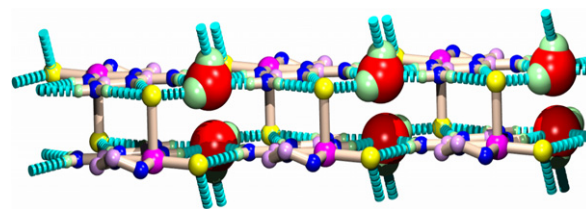


Fig. 3. Assembly of dimers along b -axis through self-recognition via $\text{N6-H6A} \cdots \text{Cl1}^{\text{v}}$ ($\text{v} = x, -1 + y, z$) hydrogen bond that is reinforced by water molecules. Color code: O, red; Cu, pink; N, blue; H, aquamarine; Cl, bright gold.

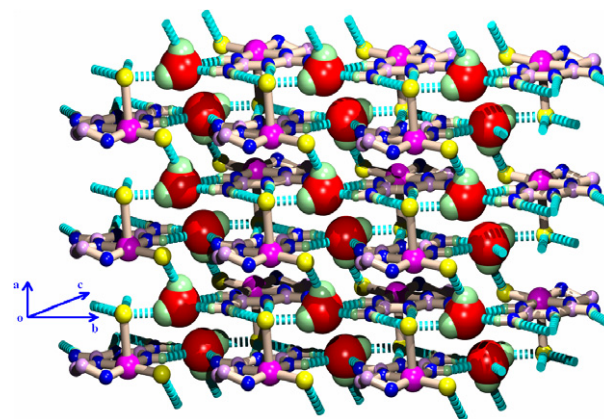


Fig. 4. The water assisted 2D supramolecular assembly of the dimeric units in the ab plane. Color code: O, red; Cu, pink; N, blue; H, aquamarine; Cl, bright gold.

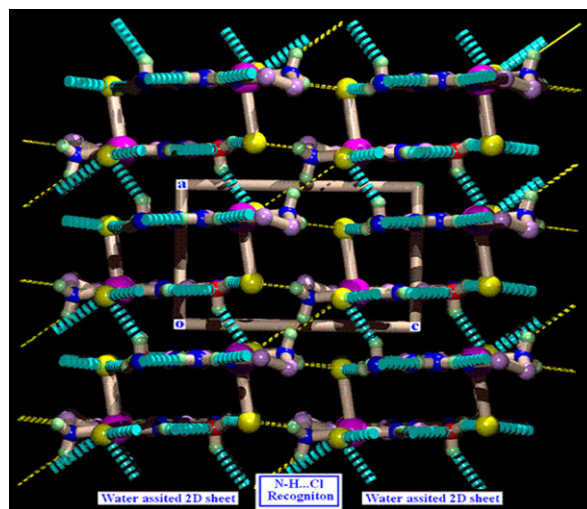


Fig. 5. Packing of 2D layers through self-recognition. Color code: O, red; Cu, pink; N, blue; H, aquamarine; Cl, bright gold.

3.4. Electrochemical studies

Cyclic voltammetric study of **1** in aqueous medium displayed an irreversible reductive response at -0.65 V versus SCE (Fig. 6) which is assignable to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox couple. The anodic counterparts are at -0.13 V and 0.05 V. The peak at -0.13 V in the reverse scan is associated with a narrow width of anodic response with a large peak current and is possibly due to surface adsorbed Cu metal [15]. However, the peak at 0.05 V is not observable on scanning between 700 and -500 mV that possibly indicates the peak at 0.05 V

Table 1
Crystallographic data for **1**

Formula	C ₄ H ₁₂ Cl ₂ CuN ₆ · H ₂ O
<i>M</i>	296.65
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	6.281(1)
<i>b</i> (Å)	8.603(1)
<i>c</i> (Å)	10.633(1)
α (°)	68.386(2)
β (°)	88.607(2)
γ (°)	87.018(2)
<i>V</i> (Å ³)	533.44(9)
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ³)	1.847
μ (mm ^{−1})	2.53
<i>T</i> (K)	298(2)
<i>F</i> (000)	302
Crystal size	0.46 × 0.34 × 0.08
Data/restraint/parameters	1864/0/127
Reflections collected	2871
Unique reflections	1864
Goodness-of-fit	0.902
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.034
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.076
<i>R</i> ₁ (all data)	0.055
<i>wR</i> ₂ (all data)	0.076
(Δ/σ) _{max}	0.001
Residuals (e Å ^{−3})	0.54, −0.50

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Cu1–N1	1.917(4)	Cu1–Cl1	2.327(2)
Cu1–N2	1.964(4)	Cu1–Cl2	2.906(2)
Cu1–N3	1.975(4)		
N1–Cu1–N2	90.9(2)	N3–Cu1–Cl1	93.0(1)
N1–Cu1–N3	173.1(2)	N1–Cu1–Cl2	96.6(1)
N2–Cu1–N3	84.1(2)	N2–Cu1–Cl2	91.8(1)
N1–Cu1–Cl1	91.7(1)	N3–Cu1–Cl2	88.4(1)
N2–Cu1–Cl1	174.6(1)	Cl1–Cu1–Cl2	92.6(1)

Table 3
Hydrogen-bond parameters (Å, °) for **1**

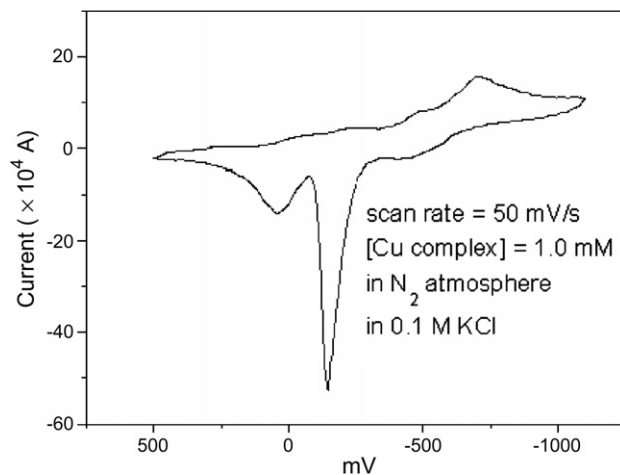
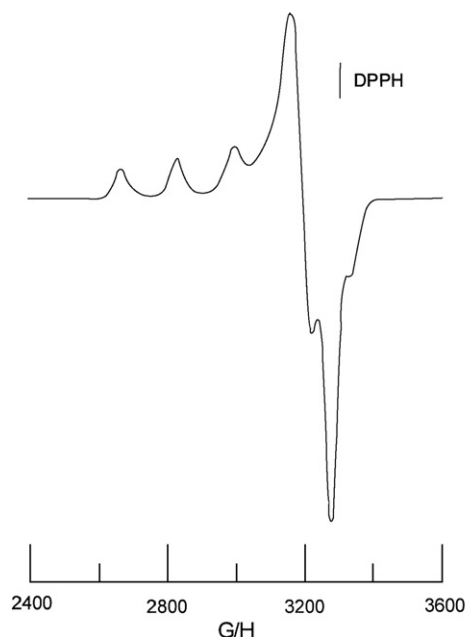
Cg(I) ^a → Cg(J)	D–H	H...A	D...A	D–H...A
N1–H1...O1 ⁱ	0.86	2.60	3.325(6)	143.3
N3–H3A...Cl1 ⁱⁱ	0.90	2.74	3.481(4)	140.9
N3–H3A...Cl2 ⁱⁱⁱ	0.90	2.84	3.491(5)	130.4
N4–H4...Cl2 ^{iv}	0.86	2.33	3.159(4)	162.7
N5–H5A...O1 ⁱ	0.86	2.11	2.928(6)	158.4
N5–H5B...Cl2 ^{iv}	0.86	2.44	3.230(4)	153.8
N6–H6A...Cl1 ^v	0.86	2.44	3.273(4)	163.3
N6–H6B...O1 ^{iv}	0.86	2.30	3.119(5)	159.8
O1–H11...Cl2	0.88	2.37	3.167(4)	150.9
O1–H12...Cl1 ^{vi}	0.87	2.47	3.233(4)	147.2

ⁱ 1 – *x*, 1 – *y*, 2 – *z*; ⁱⁱ *x*, 1 – *y*, 1 – *z*; ⁱⁱⁱ 1 + *x*, *y*, *z*; ^{iv} 1 – *x*, –*y*, 2 – *z*; ^v *x*, –1 + *y*, *z*; ^{vi} 1 + *x*, *y*, *z*.

is not associated with any oxidation of Cu(II) leading to Cu(III), rather may be assigned to reoxidation of deposited Cu on electrode.

3.5. EPR studies

The EPR spectroscopy is particularly informative for understanding the electronic structure of Cu(II) complexes [16,17]. The nearly axial features of the well-resolved X-band spectrum (Fig. 7) of the mononuclear **1** in the frozen state (water:ethylene glycol = 1:1 v/v, 77 K) with *g*_{||} (2.276) > *g*_⊥ (2.035) > 2.00 and *A*_{||} (170 × 10^{−4} cm^{−1}) > *A*_⊥ (60 × 10^{−4} cm^{−1}), are consistent with a typical monomeric tetragonal Cu(II) environment and a ¹B₁ d_{x²−y²} ground state [18]. The *g* tensor and *A* tensor values are quite sim-

**Fig. 6.** Cyclic voltammogram of **1**. Experimental conditions are shown within the figure.**Fig. 7.** EPR spectrum of **1** at 77 K.

ilar for Cu(II) in an analogous pseudoplanar N₂O₂ equatorial environment [19]. Conductivity measurements of **1** in solution indicated loss of two chloride ions and thus in mixed water–ethylene glycol solvent an overall N₂O₂ coordination seems feasible. The apparent similarity in the hyperfine coupling and *g*-values is clearly indicative of the orbital containing unpaired electron (SOMO) involves a predominant metal contribution. Consequently, an alternative hypothetical ground electronic state with an unpaired electron localized mainly on the ligand (Cu^{III}L^{2−}) is clearly ruled out. This fact, that is the localization of larger spin density on the Cu nucleus as is expected for lower electronegativity of the ligand (lower pi-acidity) is further supported by the considerably high *A*_{||} value [20].

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Appendix A. Supplementary data

CCDC 298150 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] [a] C. Janiak, *Dalton Trans.* (2003) 2781;
[b] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629;
[c] J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* 99 (2002) 4763.
- [2] [a] R.-G. Xiong, J. Zhang, Z.-F. Chen, X.-Z. You, C.-M. Che, H.-K. Fun, *Dalton Trans.* (2001) 780;
[b] A. Rodríguez-Diéguez, J. Cano, R. Kivekäs, A. Debdoubi, E. Colacio, *Inorg. Chem.* 46 (2007) 2503;
[c] X.-M. Chen, M.-L. Tong, *Acc. Chem. Res.* 40 (2007) 162.
- [3] [a] B.E. Turner, A.G. Kislyakov, H.S. Liszt, N. Kaifu, *Astrophys. J.* 201 (1975) L149;
[b] A.P.C. Mann, D.A. Williams, *Nature* 283 (1980) 721.
- [4] G. Steinman, R.M. Lemmon, M. Calvin, *Proc. Natl. Acad. Sci. USA* 2 (1964) 27.
- [5] A. Schimpl, R.M. Lemmon, M. Calvin, *Science* 147 (1965) 149.
- [6] [a] B. Bann, S.A. Miller, *Chem. Rev.* 58 (1958) 131;
[b] A.J.L. Pombeiro, *Inorg. Chim. Acta* 198–200 (1992) 179.
- [7] P. Ray, *Chem. Rev.* 61 (1961) 313. Structurally, cyanamide is half of dicyandiamide that is used for the preparation of biguanides.
- [8] G.M. Sheldrick, *SADABS*, University of Göttingen, Germany, 2000.
- [9] G.M. Sheldrick, *SHELXS97* and *SHELXL97*, University of Göttingen, Germany, 1997.
- [10] J. Lewis, T.D. O'Donoghue, P.R. Raithby, *J. Chem. Soc., Dalton Trans.* (1979) 1383.
- [11] G.D. Andreotti, L. Coghi, M. Nardelli, P.S. Sgarabotto, *J. Cryst. Mol. Struct.* 1 (1971) 147.
- [12] L. Coghi, A. Mangia, M. Nardelli, G. Pelizzi, L. Sozzi, *Chem. Commun.* (1968) 1475.
- [13] D.A. Harvey, C.J.L. Lock, *Acta Crystallogr., Sect. C* 42 (1986) 799.
- [14] S. Das, P. Banerjee, S.-M. Peng, G.-H. Lee, J. Kim, S. Goswami, *Inorg. Chem.* 45 (2006) 562.
- [15] B.K. Santra, P.A.N. Reddy, M. Nethaji, A.R. Chakravarty, *Inorg. Chem.* 41 (2002) 1328.
- [16] B.J. Hathaway, D.E. Billing, *Coord. Chem. Rev.* 5 (1970) 143.
- [17] B.J. Hathaway, *Struct. Bond. (Berlin)* 57 (1984) 55.
- [18] [a] E.I. Solomon, M.J. Baldwin, M.D. Lowery, *Chem. Rev.* 92 (1992) 521;
[b] B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, vol. 5, Pergamon Press, Oxford, UK, 1987, p. 663.
- [19] [a] R. Miyamoto, Y. Ohba, M. Iwaizumi, *Inorg. Chem.* 31 (1992) 3138;
[b] M.L. Colon, S.Y. Qian, D. Vanderveer, X.R. Bu, *Inorg. Chim. Acta* 357 (2004) 83.
- [20] M.F. Ottaviani, F. Mantali, N.J. Turro, D.A. Tomalia, *J. Phys. Chem. B* 101 (1997) 158.