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Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Madhusudan Nandy, Shyamapada Shit, Piu Dhal, Corrado Rizzoli, Carlos J. Gómez–García & Samiran Mitra (2015) Ferromagnetic copper(II)–copper(II) interaction in a single chlorido and dicyanamido bridged mixed–valence copper(I/II) 2-D polymer generated by in situ partial reduction of copper(II), Journal of Coordination Chemistry, 68:5, 916-927, DOI: 10.1080/00958972.2014.1003814

To link to this article: http://dx.doi.org/10.1080/00958972.2014.1003814

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Accepted author version posted online: 08 Jan 2015.
Published online: 03 Feb 2015.

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Journal of Coordination Chemistry, 2015
Vol. 68, No. 5, 916–927, http://dx.doi.org/10.1080/00958972.2014.1003814

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Ferromagnetic copper(II)–copper(II) interaction in a single chlorido and dicyanamido bridged mixed–valence copper(I/II) 2-D polymer generated by *in situ* partial reduction of copper(II)

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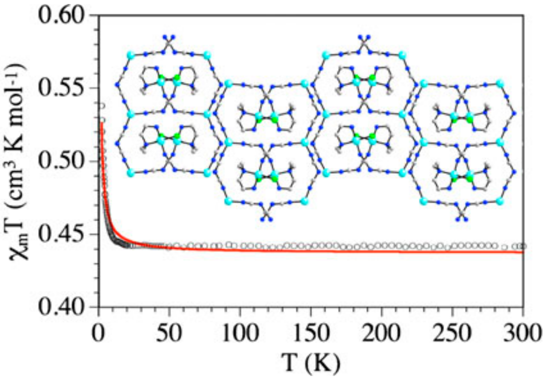
(*Received 15 July 2014; accepted 12 December 2014*)



A mixed-valence 2-D Cu(I/II) complex, $[\{Cu(II)(dmen)(\mu\text{-}Cl)(\mu_{1,5}\text{-}dca)\}\{Cu(I)(\mu_{1,5}\text{-}dca)\}]_n$ (**1**) (dmen = N,N-dimethylethylenediamine, dca = dicyanamide = $[N(CN)_2]^-$), has been synthesized by *in situ* partial reduction of Cu(II) to Cu(I) using benzoin (2-hydroxy-1,2-di(phenyl)ethanone) as reductant. Complex **1** was characterized by spectroscopic techniques, single crystal X-ray diffraction, and low temperature magnetic measurements. Structural investigation reveals that **1** represents a mixed-valence 2-D coordination polymer formed by parallel 1-D $[Cu(II)(dmen)(Cl)Cu(I)(\mu_{1,5}\text{-}dca)_2]_n$ chains running along the *b* axis, where chloride bridges Cu(II) ions of adjacent polymers through long connections (2.8401(1) Å) to form a 2-D network. The metal centers have two different geometrical environments (distorted square pyramidal and distorted trigonal planar geometries for Cu(II) and Cu(I), respectively). The Cu(II) ions in $[Cu(II)(dmen)(\mu\text{-}Cl)(dca)]_n$ are interconnected through single chloride bridges while within the $[Cu(I)(\mu_{1,5}\text{-}dca)]_n$ units, the dca connects adjacent Cu(I) ions through $\mu_{1,5}$-dca bridges. Magnetic susceptibility measurements reveal weak ferromagnetic interactions ($J = +0.3$ cm^{-1}) within the chlorido-bridged Cu(II) regular chain present in **1**. Simultaneous presence of $\mu_{1,5}$-dca and single chlorido bridges with ferromagnetic coupling is believed to be unique in mixed-valence Cu(I)/Cu(II) complexes.

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Keywords: Mixed-valence copper complexes; Coordination polymer; Dicyanamido bridge; Single chlorido bridge; Ferromagnetic interaction

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1. Introduction

Mixed-valence Cu(I/II) complexes have gained attention for their potential applications in enzymology [1], biomimetic chemistry [2], catalysis [3], photoillumination [4], semiconductors [5], magnetic materials [6], etc. These complexes are very interesting from the structural point of view [7] and perform different roles based on the coordination geometries [8] of the metal ions and their diversified nature such as (i) complexes containing Cu(II) cations and Cu(I) anions or vice versa [9, 10], (ii) complexes containing Cu(II) and Cu(I) centers bridged by polydentate ligands [11], (iii) complexes containing Cu(II) and Cu(I) centers bridged by N_3^-, CN^-, NCO^-, SCN^-, $SeCN^-$ pseudohalides [12–17], and (iv) complexes with Cu(II) and Cu(I) centers within a cluster [18]. In order to prepare these mixed-valence Cu(I/II) complexes, two main strategies have been used: (i) partial reduction of Cu(II) centers under solvothermal, basic conditions [19–21] and (ii) the use of specially designed ligands able to accommodate copper ions in both redox states [22]. In the first approach cyanate [17], iodide [23, 24], cyanide [25], and thiocyanate [4, 23, 26, 27] salts have been used as effective reductants under simple reflux or stirring at room temperature. Azo-based ligands [28], hydrazine and its derivatives [29, 30], and several radical anions [31–33] were also found effective for this purpose. Recently, Jana et al. [34] have explored benzoin as a reductant, resulting in complete reduction of Cu(II) to Cu(I). However, unlike the first approach, the second strategy has not been well explored.

Coordination polymers (CPs) constructed with metal ions and bridging ligands is attractive in the field of material science because of their wide structural diversities and rich electronic, magnetic, catalytic, absorption properties, etc. [35–40]. Various pseudo-halides such as CN^-, NCO^-, SCN^-, and $SeCN^-$ along with dicyanamide $[N(CN)_2]^-$ as bridging ligands have been employed in the construction of such homo-/hetero-metallic CPs with metal ions in the same or different oxidation states. However, mixed-valence homo-metallic CPs are still rare and limited to Cu(I/II).

Dicyanamide (dca) as a bridging ligand has different coordination modes shown in scheme 1 [41]. Here, we report the synthesis and characterization of a 2-D mixed-valence Cu(I/II) complex, $[\{Cu(II)(dmen)(\mu\text{-}Cl)(\mu_{1,5}\text{-}dca)\}\{Cu(I)(\mu_{1,5}\text{-}dca)\}]_n$ (**1**) (where dmen = N,N-dimethylethylenediamine), prepared by optimizing the reaction conditions which appear as a key factor for this *in situ* partial reduction of Cu(II) to Cu(I). Complex **1** has been characterized by micro-analytical, FTIR, UV–vis, cyclic voltammetry, and single crystal X-ray crystallographic methods. Structural characterization shows the presence of distorted trigonal planar Cu(I) and distorted square pyramidal (SP) Cu(II) centers. The $\mu_{1,5}$-dca bridges connect both types of Cu ions generating the 2-D mixed-valence complex composed of two types of chains, $[Cu(I)(\mu_{1,5}\text{-}dca)]_n$ and $[Cu(II)(dmen)(\mu\text{-}Cl)(dca)]_n$, running almost perpendicular to each other. Low temperature magnetic susceptibility measurements reveal weak ferromagnetic coupling between Cu(II) ions that can be well fitted with a simple $S = {}^1/_2$ ferromagnetic regular chain model.

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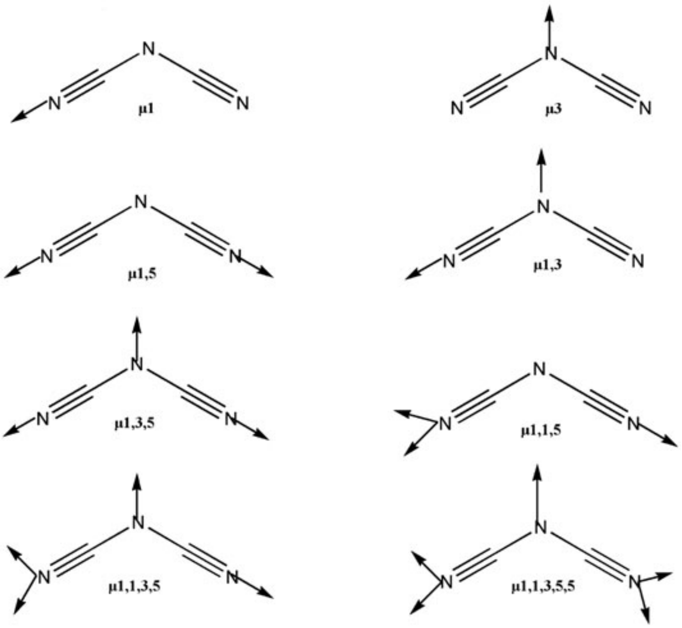

Scheme 1. Different bridging modes of dca.

2. Experimental

2.1. *Materials*

Benzoin (2-hydroxy-1,2-di(phenyl)ethanone), N,N-dimethylethylenediamine, and sodium dicyanamide were purchased from Sigma–Aldrich Co. Copper(II) chloride dihydrate was purchased from E. Merck, India. All chemicals and solvents were of AR grade and used without purification.

2.2. *Synthesis of 1*

To a stirred hot methanolic mixture (10 mL) of benzoin (1 mM, 0.216 g) and N,N-dimethylethylenediamine (1 mM, 0.088 g), a methanolic solution (10 mL) of copper(II) chloride dihydrate (2 mM, 0.340 g) was added dropwise. The resulting solution was heated at 60 °C and stirred for 10 min. An aqueous solution (2 mL) of sodium dicyanamide (1.5 mM, 1.335 g) was slowly added to the reaction mixture with constant stirring. The reaction mixture was heated for another half hour. The resulting solution was filtered and the filtrate kept undisturbed at room temperature for slow evaporation of the solvent. X-ray diffraction quality dark blue prism-shaped single crystals of **1** were obtained after fifteen days. The crystals were filtered, washed with diethyl ether, and dried in air. Yield: 0.153 g (40%). Anal. Calcd for $C_8H_{12}ClCu_2N_8$ (FW: 382.81) (%): C, 25.10; H, 3.16; N, 29.27; Cu, 33.20. Found: C. 25.07; H, 3.13; N, 29.25; Cu, 33.15. ESI-MS (*m*/*z*): $[\{Cu_2Cl(dmen)(dca)_3\}+K]^+$ = 500.1230 [Supporting Information, figure S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.1003814)].

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2.3. *Physical measurements*

Elemental analyses (C, H, and N) were carried out using a Perkin Elmer 2400 II elemental analyzer. Copper content of **1** was estimated quantitatively by standard iodometric procedure. Fourier transform infrared (FT-IR) spectrum of **1** was recorded on a Perkin Elmer RX I FT-IR system with a KBr disk from 4000 to 400 cm^{-1}. The electronic spectrum was recorded on a Perkin Elmer Lambda 40 UV/Vis spectrometer using Nujol performed with a 1-cm quartz cells in the range 200–800 nm. Electrochemical measurements were performed using a PAR VersaStat-potentiostat/Galvanostat II electrochemical analysis system under a dry argon atmosphere using conventional three electrode configurations in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. Platinized platinum Milli-electrode and saturated calomel electrode (SCE) were used as working and reference electrodes, respectively, along with platinum counter electrode in cyclic voltammetry performed at a scan rate of 50 mV·s^{-1}. Magnetic susceptibility measurements were carried out from 2 to 300 K with an applied magnetic field of 0.1 T on a polycrystalline sample of **1** (with a mass of 26.69 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced using Pascal's constant tables ($\chi_{\text{dia}} = -169.82 \times 10^{-6}$ emu·M^{-1}) [42].

2.4. *X-ray crystallography*

A blue prism-shaped single crystal of **1** was mounted on a Bruker APEX-II CCD area detector diffractometer. Intensity data were collected using graphite monochromated molybdenum radiation ($\lambda_{\text{Mo-K}\alpha} = 0.71073$ Å). Crystal data for **1** were collected using Bruker APEX2 [43] software at 294(2) K using ω scan. Multiscan absorption corrections were applied to the intensity values ($T_{\max} = 0.772$, $T_{\min} = 0.488$) empirically using SADABS [44]. The structure of **1** was solved by direct methods using SHELXS-97 [45] and refined with full-matrix least-squares based on F^2 using SHELXL-97 [45]. All non-hydrogen atoms were refined anisotropically. The molecular graphics and crystallographic illustrations for **1** were prepared using ORTEP 3 [46]. Relevant crystallographic data and structure refinement parameters of **1** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

Stoichiometric (1 : 1) reaction of benzoin and Cu(II) salts under reflux oxidizes benzoin to benzil (1,2-diphenylethane-1,2-dione) with concomitant reduction of Cu(II) to Cu(I) with 100% selectivity. Herein, we have employed the same reaction with a Cu(II) : benzoin equal to 2 : 1 to obtain *in situ* partial reduction of Cu(II) to Cu(I). Besides this Cu(II) excess, the optimized conditions for the synthesis of **1** imply a copper(II) chloride dihydrate, benzoin, N,N-dimethylethylenediamine, and dicyanamide ratio of 2 : 1 : 1 : 1.5 under constant stirring and heating at 60 °C.

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Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_8H_{12}ClCu_2N_8$
Formula weight	382.81
Crystal dimension (mm^3)	0.08 × 0.17 × 0.27
Crystal system	Orthorhombic
Space group	$Pca2_1$
a (Å)	26.157(3)
b (Å)	7.8539(10)
c (Å)	6.4201(9)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1318.9(3)
Z	4
T (K)	294(2)
$\lambda_{\text{Mo-K}\alpha}$ (Å)	0.71073
D_c (g cm^{-3})	1.928
μ (mm^{-1})	3.425
F(000)	764
θ range (°)	1.56–25.23
Total data	13,928
Unique data	2387
Observed data [$I > 2\sigma(I)$]	2269
N_{ref};N_{par}	2387, 185
R^a	0.0237
$R_w{}^b$	0.0574
R_{int}	0.036
Goodness-of-fit, S	1.01
$\Delta\rho_{\max}$ (e Å^{-3})	0.31
$\Delta\rho_{\min}$ (e Å^{-3})	−0.23

$^aR = \Sigma(|F_o - F_c|)/\Sigma|F_o|$.
$^bR_w = \{\Sigma[w(|F_o - F_c|)^2]/\Sigma[w|F_o|^2]\}^{½}$.

3.2. *Crystal structure of 1*

Single crystal X-ray diffraction reveals that **1** crystallizes in the orthorhombic crystal system in space group $Pca2_1$. A perspective view of the asymmetric unit of **1** with the atom numbering scheme is shown in figure 1 and selected bond lengths and angles are summarized in table 2. The asymmetric unit of **1** consists of two different copper ions (one is divalent while the other is monovalent), one chloride, two dicyanamide, and a neutral bis-chelating ligand, dmen. Within the asymmetric unit copper ions are in different coordination environments. The divalent Cu1 is five-coordinate by two nitrogens (N1 and N2) of dmen, two bridging chlorides (Cl1 and Cl1^i symmetry code $^i = 1/2 - x, y, 1/2 + z$), and N3 of a dca, which connects Cu1 to the monovalent Cu2. The coordination polyhedron around Cu1 is best described as distorted SP with the best basal plane defined by N3, Cl1, N1, and N2 leaving Cl1^i at the apex. All donors in the mean basal plane are coplanar within ± 0.134 Å while the Cu1 is displaced by 0.1893(4) Å toward apical Cl1^i. The deviation around Cu1 is also evident by the bonding parameters and relative deviations of the bond angles (table 2) from their ideal values. The distortion around Cu1 can also be expressed in terms of τ, an index of the degree of trigonality, which has a value of 0 and 1 for an ideal SP and ideal trigonal bipyramidal (TBP) geometry, respectively [47]. The value of 0.222 for Cu1 is in agreement of its distorted SP geometry. The Cu–N and Cu−Cl distances vary from 1.939(3) to 2.046(2) and 2.2965(8) to 2.840(2) Å, and the chelating bite angle of 90.23° is

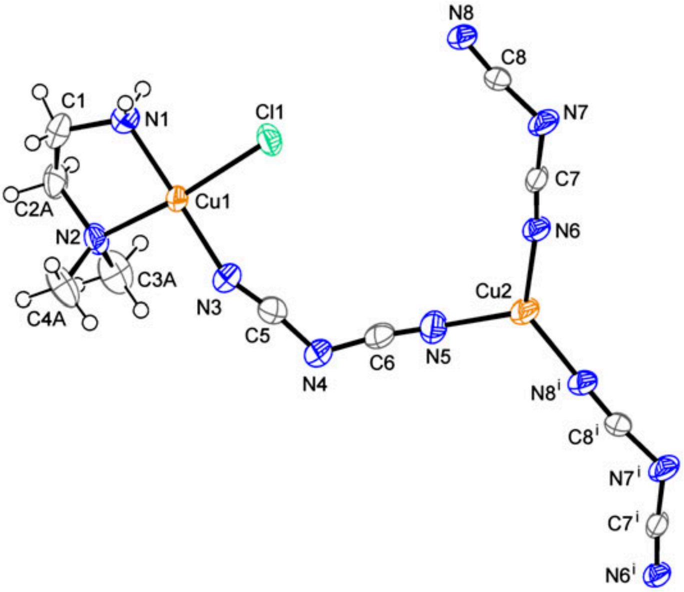

Figure 1. Structure of **1** with atom labels. Only the major component of the disordered C2 carbon is shown. Symmetry code: ^{i} = x, $-1+y$, z.

comparable to other previously reported compounds [48, 49]. The three-coordinate geometry of the monovalent Cu2 is satisfied by three nitrogens (N8^{ii}; ^{ii} = x, $-1+y$, z) from three dca ligands out of which two connect Cu2 ions through $\mu_{1,5}$-bridges while the other is connected to Cu1 through similar bridging mode. The $\mu_{1,5}$-bridged dca connects Cu2 ions in a wavy fashion while the other coordinated dca acts as a tail, ultimately leaving it in Y-shaped distorted trigonal planar geometry. Dissimilar Cu2–N distances and deviations of N–Cu2–N angles (table 2) from an ideal value of 120° support distorted geometry in spite of co-planarity of all donors including Cu2.

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

Bond distances			
Cu1−Cl1	2.2964(9)	Cu1−Cl1^{i}	2.8401(11)
Cu1−N1	1.966(2)	Cu2−N5	1.982(3)
Cu1−N2	2.045(2)	Cu2−N6	1.914(2)
Cu1−N3	1.939(3)	Cu2−N8^{ii}	1.909(2)
Bond angles			
Cl1−Cu1−N1	90.25(8)	N2−Cu1−N3	93.37(11)
Cl1−Cu1−N2	164.19(9)	Cl1^{i}−Cu1−N2	97.58(9)
Cl1−Cu1−N3	91.01(9)	Cl1^{i}−Cu1−N3	94.72(12)
Cl1−Cu1−Cl1^{i}	97.20(3)	N5−Cu2−N6	113.02(11)
N1−Cu1−N2	84.88(10)	N5−Cu2−N8^{ii}	116.33(12)
N1−Cu1−N3	177.59(14)	N6−Cu2−N8^{ii}	129.99(11)
Cl1^{i}−Cu1−N1	87.13(11)	Cu1−Cl1−Cu1^{iii}	97.60(3)

Note: Symmetry code:
^{i}1/2 $-x$, y, 1/2 + z.
^{ii}x, $-1+y$, z.
^{iii}1/2 $-x$, y, $-1/2+z$.

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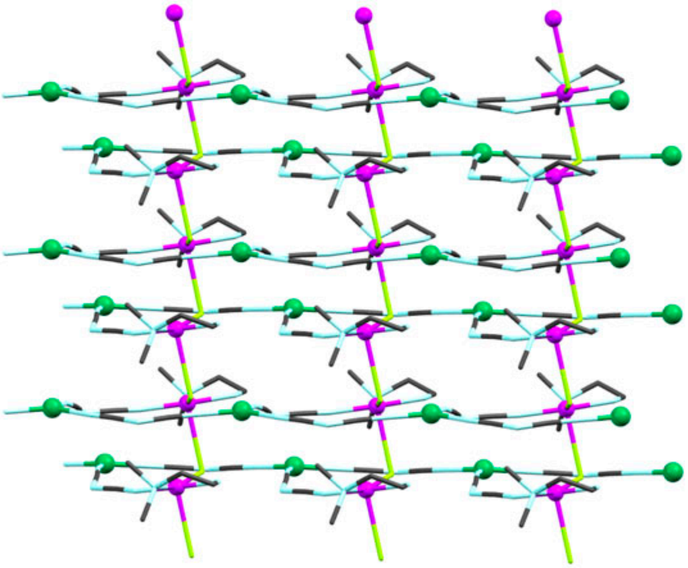

Figure 2. Two-dimensional array of **1** propagating through the crystallographic *bc* plane (magenta = Cu(II), green = Cu(I), gray = carbon, yellow = chlorine, sea green = nitrogen) (see http://dx.doi.org/10.1080/00958972.2014.1003814 for color version).

The 2-D network structure of **1** may be considered as an interlink between parallel neutral mixed-valence 1-D chains of $[Cu(II)(dmen)(Cl)Cu(I)(\mu_{1,5}\text{-dca})_2]_n$. The terminal chlorides of $[Cu(II)(dmen)(Cl)Cu(I)(\mu_{1,5}\text{-dca})_2]_n$ interlink copper of another unit through μ-Cl, thereby propagating the 2-D network along the *bc* plane (figure 2).

Theoretically, the oxidation number of each copper center in a complex may be calculated using Bond Valence Summation (BVS) analysis, where the oxidation state is determined as follows:

$$S_{ij} = \exp[(R_0 - R_{ij})/b] \tag{1}$$

where S_{ij} is the bond valence between two atoms i and j, R_{ij} is the observed bond length between i and j, and R_0 and b are the bond valence parameters [50]. The oxidation number, N_i, of atom i is the algebraic sum of the S_{ij} values of all the bonds around atom i:

$$N_i = \sum S_{ij} \tag{2}$$

The BVS calculations performed for **1** show oxidation states of 1.999 for Cu1 and 1.129 for Cu2, confirming the di- and monovalent oxidation states assumed for Cu1 and Cu2, respectively.

In spite of the different coordination environments, the structural aspects of this complex can be compared with some mixed-valence copper CPs reported earlier [23–25, 27]. Reported complexes were derived from different ethylenediamine like donor sets and different halides and pseudohalides similar to the complexes reported herein. During syntheses of mixed-valence copper complexes using iodide [23, 24], cyanide [25] or thiocyanate [27] salts, the counter anions are incorporated within the products. In the present work, benzoin also is necessary but was not found in the crystal structure of the product. All the

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complexes reported earlier possess only one kind of bridging species but both chlorido and dicyanamido bridging ligands interlinked the copper centers in the complex herein.

3.3. *Electronic spectrum*

UV–vis spectrum of **1** at 300 K in Nujol (Supporting Information, figure S2) shows two distinct strong charge transfer bands at 220 and 258 nm, assigned to interligand charge transfer transitions [51]. Another weak CT band at 309 nm can be attributed to ligand-to-metal charge transfer transitions. Cu(II) with square pyramidal geometry generally shows a broad visible band at 550–660 nm corresponding to a d–d transition, whereas in TBP geometry, this band usually appears at $\lambda > 800$ nm [52]. A weak broad d–d transition band of **1** at 650 nm supports the distorted square pyramidal geometry for the Cu(II) centers.

3.4. *FT-IR spectrum*

The FT-IR spectrum of **1**, from 4000 to 400 cm^{-1}, is consistent with its structure. Thus, the IR spectrum of **1** (Supporting Information, figure S3) shows a broad double band at 3448–3266 cm^{-1} and a sharp band at 998 cm^{-1} assignable to $\nu_{N–H}$ and $\nu_{C–N}$ stretches of coordinated dmen ligand, respectively [53]. A well-defined band for $\nu_{C–H}$ bending vibration is observed at 1458 cm^{-1}. Sharp absorption bands at 2191–2295 cm^{-1} also indicate the presence of coordinated dicyanamide. The dicyanamide anion in $NaN(CN)_2$ shows three sharp and strong bands at 2286, 2232, and 2179 cm^{-1}, attributed to $\nu_{as+}\nu_s$, ν_{as} and $\nu_{s(C\equiv N)}$, respectively. Upon complexation, these bands split and shift to higher frequencies. Thus, in **1,** the $\nu_{as+}\nu_s$ band is at 2295 cm^{-1}, the ν_{as} at 2252 cm^{-1}, and ν_s split at 2191 and 2189 cm^{-1}. This splitting and the displacement of the bands to higher frequencies are indicative of bridging dca in **1** [37]. The coordination of the ligands to metals is also substantiated by the appearance of a weak band at 498 cm^{-1} corresponding to a $\nu_{Cu–N}$ vibration [54].

3.5. *Cyclic voltammetry*

The cyclic voltammogram (figure 3) of **1** was recorded from −1.5 to +1.5 V using tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mV s^{-1}. The cathodic scan shows two reduction peaks at −0.65 and +0.47 V (versus SCE) corresponding to Cu(II)/Cu(I) and Cu(I)/Cu(0) reductions, respectively. The corresponding oxidation processes are observed in the anodic scan at −0.78 and +0.62 V (versus SCE), respectively. The peak-to-peak separations of 130 and 150 mV indicate that these redox processes are irreversible. On changing the scan rate, the redox responses slightly shifted to more anodic values while I_{pc} remains always greater than I_{pa} and the peak-to-peak separations always remain greater than 50 mV, confirming the irreversible nature of the redox processes. The anodic scan shows an additional peak at 1.45 V which may be attributed to an irreversible Cu(II) to Cu(III) oxidation [55]. ESI-Mass spectrum of **1** (Supporting Information, figure S1) shows a peak at *m*/*z*: 500.1230 corresponding to $[\{Cu_2Cl(dmen)(dca)_3\}+K]^+$, indicating that **1** undergoes decomposition to small oligomeric units in solution, which are responsible for the electroactive nature of the complex.

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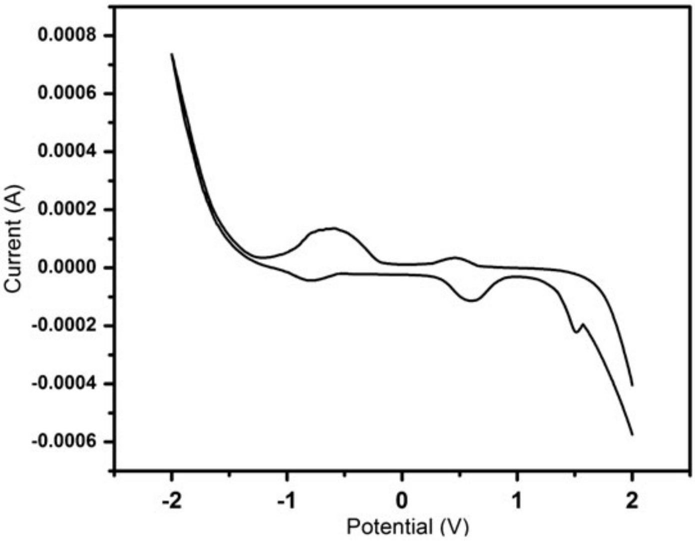

Figure 3. The cyclic voltammogram of **1** in acetonitrile (scan rate 50 mV s^{-1}).

3.6. *Magnetic properties*

The thermal variation of the molar magnetic susceptibility per formula unit (two Cu ions) times the temperature ($\chi_m T$) for **1** shows a room temperature value of *ca.* 0.44 emu·K·mol^{-1}, which is the expected value for a Cu(II) ion with $g \approx 2.17$. When the temperature is decreased, $\chi_m T$ remains constant down to *ca.* 10 K and then increases to reach a value of *ca.* 0.54 emu·K·mol^{-1} at 2 K (figure 4). This behavior indicates that only one of the two copper ions contributes to the magnetic moment (confirming the assumption that we have a Cu(II) and Cu(I) per formula unit) and, on the other hand, that the Cu(II) ion presents a weak ferromagnetic coupling. Since the structure of **1** shows that the Cu(II) ions form a chain with a single μ-chloride that connects a basal position of one Cu(II) with the axial

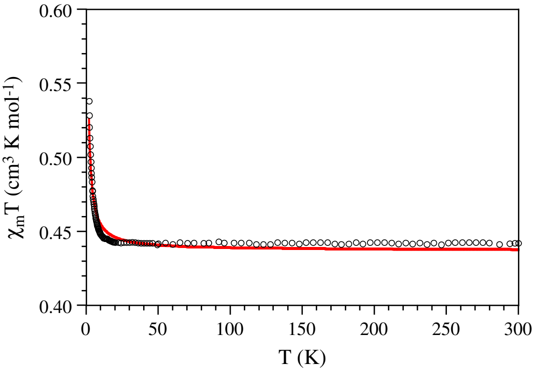

Figure 4. Thermal variation of χ_mT product per Cu(II) dimer for **1**. Solid line represents the best fit to the $S = 1/2$ regular chain model.

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position of the neighboring one, we have fit the magnetic properties of **1** with a simple $S = {}^1/_2$ ferromagnetic regular chain model [56] (Supporting Information). This model reproduces quite satisfactorily the magnetic properties of **1** in the whole temperature range with $g = 2.160$ and $J = +0.3$ cm^{-1}.

The very weak ferromagnetic coupling found in **1** lies within the normal range found for other Cu(II) chain compounds containing single chloride bridges with alternating short and long distances connecting axial and basal positions, where weak ferro- or antiferromagnetic couplings have been found [57–62].

Previous magneto-structural correlations and theoretical calculations have shown that the two most important parameters determining the nature of the weak magnetic coupling are the δ and φ angles, with δ = largest basal angle and φ = Cu–Cl–Cu angle. The ferromagnetic coupling in this kind of bridge is favored when δ and φ are close to 180° and 90°, respectively [59]. In this situation, the overlap of the magnetic orbitals and hence the antiferromangetic coupling is reduced since the magnetic orbital is mainly the d_{x2-y2} when the geometry around the Cu(II) ion is close to the square pyramid (and hence, δ = 180°). In **1**, the geometry of Cu1 is close to a square pyramid as shown by its Addison parameter (τ = 0.22) [47] and the δ (164.28°) and φ (97.59°) angles are close to 180 and 90°, respectively, giving weak ferromagnetic coupling. In fact, **1** has very similar structural parameters to $[Cu(paphy)Cl]_n(PF_6)_n \cdot nH_2O$ (paphy = pyridine-2-carboxaldehyde-2-pyridylhydrazone), where a ferromagnetic coupling of +1.3 cm^{-1} was found [61].

4. Conclusion

The partial *in situ* reduction of Cu(II) with benzoin in the presence of the bridging ligand $N(CN)_2^-$ (dca) and chelating N,N-dimethylethylenediamine (dmen) affords a mixed-valence 2-D CP, $[\{Cu(II)(dmen)(\mu\text{-}Cl)(\mu_{1,5}\text{-}dca)\}\{Cu(I)(\mu_{1,5}\text{-}dca)\}]_n$ (**1**). Bridging dca along with single chloride bridge generates this mixed-valence Cu(I/II) complex, which is believed to be first in this class of complexes. Compound **1** contains SP Cu(II) and trigonal planar Cu (I) ions forming mixed-valence 1-D helical chains $[Cu(II)(dmen)(Cl)Cu(I)(\mu_{1,5}\text{-}dca)_2]_n$, which are further interconnected through μ-Cl bridges to form a 2-D structure in the *bc* plane. The magnetic properties confirm the presence of one Cu(II) and one Cu(I) per formula unit and show the presence of weak Cu(II)–Cu(II) ferromagnetic interactions mediated through the single chloride bridges. This weak ferromagnetic interaction has been rationalized from previous magneto-structural correlations in this kind of bridge. It is interesting to note that though dca played an important structure determining role, it has no role on the resulting magnetic properties of the complex.

Supplementary material

CCDC 949195 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

M. Nandy gratefully acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, Government of India, for awarding Senior Research Fellowship (SRF) to him [CSIR sanction No. 09/096(0598)/2009-EMR-I]. Thanks are also extended to University Grants Commission, New Delhi, for financial assistance to S. Mitra as emeritus fellow to carry out this work. We also thank the Spanish MINECO [grant number project CTQ2011-26507] and the Generalitat Valencia [grant number project Prometeo II/2014/076 and ISIC] for financial support.

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