

Article

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## Antiferromagnetic mixed-valence Cu(I)-Cu(II) 2D coordination polymers constructed by double oximato bridged Cu(II) dimers and Cu<sup>I</sup>SCN based 1D anionic chains

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#### ABSTRACT

One dinuclear Cu(II) complex  $[Cu_2L_2^2(EtOH)_{0.5}(ClO_4)](ClO_4)$  (1) has been synthesized by reacting an oxime-based tridentate Schiff base ligand, 3-[2-(diethylamino)ethylimino]butan-2-one oxime (HL<sup>2</sup>) with  $Cu^{II}(ClO_4)_2$  whereas the reaction of another similar ligand, 3-[2-(dimethylamino)ethylimino]butan-2-one oxime (HL<sup>1</sup>) and this ligand (HL<sup>2</sup>) with  $Cu^{II}(ClO_4)_2$ in presence of NaSCN vielded two rare mixed-valence Cu(I)-Cu(II) 2D coordination polymers,  ${}^{2}_{\infty}[\{(Cu^{II}_{2}L^{1}_{2})\}\{Cu^{I}_{4}(\mu_{1,3}-SCN)_{2}(\mu_{1,1,3}-SCN)_{4}\}]_{n}$  (2) and  ${}^{2}_{\infty}[\{(Cu^{II}_{2}L^{2}_{2})\}\{Cu^{I}_{2}(\mu_{1,3}-SCN)_{4}\}]_{n}$  $SCN_2(\mu_{1,1,3}-SCN_2)]_n$  (3), respectively. The presence of  $SCN^-$  during synthesis of the complexes induces reduction of a part of the Cu(II) to Cu(I) giving rise to these two novel mixed-valence 2D coordination polymers 2 and 3. All three complexes have been structurally and magnetically characterized. In complex  $\mathbf{1}$ , the square pyramidal Cu(II) atoms are joined by the double oximato bridges. On the other hand, the railroad track-like 2D sheet of 2 and stair-like arrangement of 2D layer of 3 have been constructed by the connection of 1D anionic chains  $([Cu_2^I(SCN)_3]_n^{n-}$  in 2 and  $[Cu_2^I(SCN)_2]_n^{n-}$  in 3) through the cationic oximato bridged dinuclear units ( $[Cu_2^{II}L_2^{1}]^{2+}$  in **2** and  $[Cu_2^{II}L_2^{2}]^{2+}$  in **3**) via sulphur atom of thiocyanato ligand. In both complexes, Cu(I) and thiocyanato ligand form 1D infinite chains, but their different stoichiometry and coordination environment around copper centers result in different structures. Variable-temperature (2–300 K) magnetic susceptibility measurements show that complexes 1-3 exhibit a strong antiferromagnetic interaction between two Cu(II) ions via N,O oximato bridges with J values -549.6, -578.7 and -663.8 cm<sup>-1</sup> respectively.

#### Introduction

The chemistry of mixed-valence Cu(I/II) coordination complexes are gaining popularity due to its great biological importance for their structural relevance with certain metalloenzymes.<sup>1,2</sup> In addition, they show interesting electronic properties<sup>3-6</sup> as well as good electrical conductivity and bistability.<sup>7,8</sup> Copper(I) and copper(II) centers prefer different geometries and stereochemistries and both oxidation states are highly labile and stereochemically flexible,<sup>9-11</sup> which is not usually the case for various other mixed-valence species e.g Fe, Co and Ru complexes. All these characteristics increase the possibility of construction of coordination framework of Cu(I)/Cu(II) with diverse structural features and topologies. However, there are great difficulties in controlling the final product with two different oxidation states and thus the numbers of mixed-valence copper complexes are limited. The mixed-valence copper complexes which are reported till date can largely be grouped into four categories:<sup>12</sup> (i) complexes containing Cu(II) cation and Cu(I) anion, (ii) biand polynuclear complexes in which Cu(II) and Cu(I) centers bridged by polydentate ligands, (iii) complexes containing Cu(II) and Cu(I) centers bridged by CN<sup>-</sup>/SCN<sup>-</sup>/SeCN<sup>-</sup> pseudohalides and (iv) complexes with Cu(I) and Cu(II) ions enclosed in a cluster. The general method for the synthesis of cyano, thiocyanato and selenocyanato Cu(II)-Cu(I) complexes is the partial reduction of Cu(II) salts in the presence of a ligand (CN<sup>-</sup>/SCN<sup>-</sup>/SeCN<sup>-</sup>) which serves both as a ligand and as a reducing agent.<sup>12-16</sup> Such in situ Cu(II) to Cu(I) reduction is a usual phenomenon when Cu(II) salts are subjected to high energy closed vessel solvothermal reactions in presence of the ligand,<sup>17,18</sup> but is a rare case at room temperature open pot synthesis.<sup>19-21</sup> The reduction leads to the formation of Cu<sup>I</sup>X (where  $X^{-} = CN^{-}/SCN^{-}/SeCN^{-}$ ) based species which generates mixed-valence polymeric coordination framework with the help of Cu(II) and other ancillary ligands attached to the Cu(II) ion.

The linear triatomic pseudohalide, thiocyanate (SCN<sup>-</sup>), is an excellent versatile ambidentate ligand with two donor atoms N and S. It can coordinate to metal ions both in terminal and bridging coordination modes. The common bridging coordination modes of thiocyanato ligand are  $\mu_{1,3}$ -NCS,<sup>22,23</sup>  $\mu_{1,1}$ -NCS<sup>24</sup> and  $\mu_{1,1}$ -SCN<sup>25</sup> (Scheme 1, A-C). The rare variety of coordination modes *e.g.*  $\mu_{1,1,3}$ -SCN<sup>26</sup> and  $\mu_{1,1,1,3}$ -SCN<sup>27</sup> (Scheme 1, D-E) have also been reported in some complexes. It bridges Cu(I) and Cu(II) ions to form polymeric complexes with different dimensionalities and topologies.<sup>25-29</sup> The dimension and topology of the final framework depend upon several factors. Firstly, the different binding modes of both

thiocyanato and ancillary ligands furnish different coordination environment around both Cu(I) and Cu(II) ion and this leads to the formation of various frameworks.<sup>28,29</sup> Secondly, the different dimensionalities of Cu<sup>I</sup>SCN based species influence the structure of polymers. As for example, Cu<sup>I</sup>SCN based 1D chains are connected by Cu(II) moieties to construct 2D polymer whereas Cu<sup>I</sup>SCN based 2D layers are associated with Cu(II) moieties to produce 3D polymer.<sup>20,21,30</sup> Finally, the nature, size and structure of the ancillary ligands attached to the Cu(II) ion can also influence the resulting structure.<sup>21</sup>



Scheme 1. Different coordination modes of thiocyanato ligand.

In this paper, we report three new oximato-bridged copper complexes by using two oxime based mono-condensed Schiff base ligands, 3-[2-(dimethylamino)ethylimino]butan-2-one oxime (HL<sup>1</sup>) and 3-[2-(diethylamino)ethylimino]butan-2-one oxime (HL<sup>2</sup>) having different substitution in amine part. The reaction of copper(II) perchlorate with HL<sup>2</sup> leads to the formation of discrete dinuclear complex  $[Cu_2L^2_2(EtOH)_{0.5}(ClO_4)](ClO_4)$  (1). On the other hand, the reaction of copper perchlorate with either HL<sup>1</sup> or HL<sup>2</sup> in presence of SCN<sup>-</sup> at room temperature leads to *in situ* Cu(II) to Cu(I) partial reduction generating two mixed-valence Cu(I/II) 2D coordination polymers  ${}^2_{\alpha}[\{(Cu^{II}_2L^1_2)\}\{Cu^1_4(\mu_{1,3}-SCN)_2(\mu_{1,1,3}-SCN)_4\}]_n$  (2) and  ${}^2_{\alpha}[\{(Cu^{II}_2L^2_2)\}\{Cu^1_2(\mu_{1,3}-SCN)_2(\mu_{1,1,3}-SCN)_2\}]_n$  (3) with different framework. Complex 2, in which the Cu<sup>1</sup>SCN based infinite chain is formed in an unprecedented manner, represents a unique example of "supramolecular isomers" of a previously reported 3D mixed-valence coordination polymer.<sup>21</sup> The structures and variable-temperature magnetic susceptibility measurement of complexes (1–3) is presented here in detail.

#### **Experimental section**

#### **Starting materials**

Diacetylmonoxime, N,N-dimethyl-1,2-ethanediamine, N,N-diethyl-1,2-ethanediamine and sodium thiocyanate were purchased from commercial sources and used as received. Copper(II) perchlorate hexahydrate was prepared by the standard laboratory method; solvents were of reagent grade and used without further purification.

Caution! Perchlorate salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

## Syntheses of Schiff base ligands (HL<sup>1</sup> and HL<sup>2</sup>)

The two mono-condensed Schiff base ligands, 3-[2-(dimethylamino)ethylimino]butan-2-one oxime (HL<sup>1</sup>) and <math>3-[2-(diethylamino)ethylimino]butan-2-one oxime (HL<sup>2</sup>) were prepared by standard methods. 8 mmol of diacetylmonoxime (0.808 g) were mixed with 8 mmol of the required amine (N,N-dimethyl-1,2-ethanediamine (0.878 mL) or N,N-diethyl-1,2-ethanediamine (1.120 mL)) in ethanol (20 mL). The resulting solutions were refluxed for*ca*. 5 h and allowed to cool. The yellow coloured ethanolic solutions were used directly for complex formation.

## Synthesis of complex [Cu<sub>2</sub>L<sup>2</sup><sub>2</sub>(EtOH)<sub>0.5</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) (1)

An ethanolic solution of (20 mL) of  $Cu^{II}(ClO_4)_2 \cdot 6H_2O$  (1.480 g, 4 mmol) was allowed to react with an ethanol solution of  $HL^2$  (4 mmol, 5 mL). The green coloured mixture was stirred for 1 h at room temperature and it was filtered. The filtrate was allowed to stand at open atmosphere. A prismatic shaped green (1) X-ray quality single crystals appeared at the bottom of the vessel after 5 days. The crystal were then washed with diethyl ether and dried in a desiccator containing anhydrous CaCl<sub>2</sub>, then characterized by elemental analysis, spectroscopic methods and X-ray diffraction.

Complex 1: Yield: 1.318 g (88%). Anal. calc. for  $C_{21}H_{42.5}O_{10.5}N_6Cu_2Cl_2$ : C 33.85, H 5.75, N 11.28. Found: C 33.77, H 5.75, N 11.39 %. m. p. = 200°C. IR (KBr pallet, cm<sup>-1</sup>): 3473mb, 2979m, 1658w, 1525m, 1222m, 1101sb and 623m. UV/Vis (in (CH<sub>3</sub>CN):  $\lambda_{max}$  in nm ( $\xi_{max}$  in  $M^{-1}$  cm<sup>-1</sup>) = 577 (1312), 429 (4750) and 282 (16030) nm.

# Syntheses of complexes ${}^{2}_{\infty}[\{(Cu^{II}_{2}L^{1}_{2})\}\{Cu^{I}_{4}(\mu_{1,3}-SCN)_{2}(\mu_{1,1,3}-SCN)_{4}\}]_{n}$ (2) and ${}^{2}_{\infty}[\{(Cu^{II}_{2}L^{2}_{2})\}\{Cu^{I}_{2}(\mu_{1,3}-SCN)_{2}(\mu_{1,1,3}-SCN)_{2}\}]_{n}$ (3)

To an ethanolic solution (20 mL) of copper(II) perchlorate hexahydrate (1.480 g, 4 mmol), the ethanolic solution of  $HL^1$  (4 mmol, 5 mL) was added followed by the addition of an aqueous solution (2 mL) of sodium thiocyanate (0.180 g, 2 mmol) to this solution. The mixture was stirred for 1 h at room temperature and then filtered off. The green filtrate was allowed to stand at open atmosphere resulting in the formation of green crystalline product after 10 days. Needle shaped X-ray quality single crystals suitable for X-ray diffraction of **2** were grown in an ethanolic solution of the green mass by a slow diffusion of ether in a sealed tube. Similarly, green needle shaped single crystals of **3** were obtained by following the same procedure for **2**, but using  $HL^2$  instead of  $HL^1$ .

Complex **2**: Yield: 0.471 g (66%, based on metal). Anal. calc. for  $C_{22}H_{32}Cu_6N_{12}O_2S_6$ : C 24.69, H 3.01, N 15.71 %. Found: C 24.83, H 3.12, N 15.67%. m. p. = does not melt up to 300°C, above this temperature it starts to decompose. IR (KBr pallet, cm<sup>-1</sup>): 2901w, 2126sb, 2093sb, 1651w, 1509m and 1213m. UV/Vis (in CH<sub>3</sub>CN):  $\lambda_{max}$  in nm ( $\xi_{max}$  in M<sup>-1</sup> cm<sup>-1</sup>) = 603 (1362), 420 (7650) and 278 (16290) nm.

Complex **3**: Yield: 0.556 g (63%, based on metal). Anal. calc. for  $C_{24}H_{40}Cu_4N_{10}O_2S_4$ : C 32.64, H 4.57, N 15.86. Found: C 32.61, H 4.52, N 15.77 %. m. p. = 245°C. IR (KBr pallet, cm<sup>-1</sup>): 2978m, 2112sb, 2091sb, 1651w, 1504m and 1217m. UV/Vis (in CH<sub>3</sub>CN):  $\lambda_{max}$  in nm ( $\xi_{max}$  in M<sup>-1</sup> cm<sup>-1</sup>) = 603 (1126), 419 (6210) and 280 (16300) nm.

#### **Physical Measurements**

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm<sup>-1</sup>) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile were recorded in a Hitachi U-3501 spectrophotometer. The magnetic measurements were carried out in the "Servei de Magnetoquimica (Universitat de Barcelona)" on polycrystalline samples with a Quantum Design SQUID MPMSXL magnetometer in an applied field of 7000 and 400 G in the temperature ranges of 2–300 K and 2–30 K, respectively. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables.<sup>31</sup>

#### Crystallographic data collection and refinement

Suitable single crystals of each complex were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The crystals were positioned at 60 mm from the CCD. Frames (360) were measured with a counting time of 5 s. The structures were solved by Patterson method using the SHELXS 97 program. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program.<sup>32</sup> All the calculations were carried out using SHELXS 97,<sup>33</sup> SHELXL 97,<sup>34</sup> PLATON 99,<sup>35</sup> ORTEP-32<sup>36</sup> and WINGX system ver-1.64.<sup>37</sup> Data collection, structure refinement parameters and crystallographic data for the three complexes (1–3) are given in Table 1.

#### **Results and Discussion**

#### Syntheses of the complexes

The Schiff base ligands HL<sup>1</sup> and HL<sup>2</sup> were synthesized using the reported procedures. When the Schiff base ligand HL<sup>2</sup> was allowed to react with copper perchlorate hexahydrate in EtOH medium, it resulted in the dinuclear complex  $[Cu_2L^2_2(EtOH)_{0.5}(ClO_4)](ClO_4)$  (1). It is to be to mentioned that the reaction of HL<sup>1</sup> with copper perchlorate in EtOH medium also produced a dinuclear Cu(II) complex  $[Cu_2L^1_2(H_2O)_2](ClO_4)_2$  which has been reported previously by other groups.<sup>21,38</sup> In both complexes, the oximato oxygen atoms of Schiff base ligand were deprotonated and coordinated to Cu(II). On the other hand, when HL<sup>1</sup> and HL<sup>2</sup> reacted with copper(II) perchlorate hexahydrate and sodium thiocyanate in EtOH medium, mixed-valence Cu(I)-Cu(II) 2D coordination framework,  ${}^2_{\infty}[\{(Cu^{II}_2L^1_2)\}\{Cu^I_4(\mu_{1,3}-SCN)_2(\mu_{1,1,3}-SCN)_4\}]_n$  (2) and  ${}^2_{\infty}[\{(Cu^{II}_2L^2_2)\}\{Cu^I_2(\mu_{1,3}-SCN)_2(\mu_{1,1,3}-SCN)_2\}]_n$  (3) based on double oximato bridged Cu(II) dimers were produced in both cases (Scheme 2). Here, the use of sodium thiocyanate induced the partial reduction of Cu(II) to Cu(I) at room temperature, giving rise to the mixed-valence 2D coordination frameworks. Page 7 of 26

 2D polymer (2)

 $X = H_2O$  or EtOH or ClO<sub>4</sub>

RR

Dinuclear

(1)

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It should be noted that using HL<sup>1</sup> ligand, Mitra et. al. synthesized a mixed-valence Cu(I/II) 3D coordination network by applying similar approach using methanol as solvent instead of ethanol. The molecular building blocks  $[(Cu_2^{II}L_2^1) \{Cu_4^{I}(SCN)_6\}]$  of that 3D polymer have identical chemical compositions to our 2D polymer (2) but their network structures and topologies are completely different. Therefore, complex 2 represents an isomeric form of reported 3D network and thus these two are "supramolecular isomers". The crystal structure and magnetic property of dinuclear complex,  $[Cu_2L_2^1(H_2O)_2](ClO_4)_2)$  have been studied by others<sup>21,38</sup> However, as this complex is related to the other complexes reported in this paper, we just mention it here but do not describe its structure and magnetic property.

#### IR and UV-Vis spectra of the complexes

The infrared spectra of complexes 1-3 show the characteristic bands of the coordinated oxime based Schiff base ligands (Figures S1–S3, in Supporting Information). These display strong and sharp absorption bands in the regions 1658–1651 and 1222–1213 cm<sup>-1</sup> which can be assigned to the v(C=N) and v(N–O) vibrational modes, respectively of the coordinated Schiff base ligands. In addition, a couple of strong and medium-intensity bands at *ca*. 1101 and 623 cm<sup>-1</sup>, readily confirming the presence of ionic perchlorate in complex **1**. On the other hand, complexes **2** and **3** exhibit intense doublets appearing in the regions 2126–2091 cm<sup>-1</sup>, confirm the presence of the bridging thiocyanato groups. In both cases, a strong and broad peak at 2126 and 2112 cm<sup>-1</sup> along with a shoulder at 2093 and 2091 cm<sup>-1</sup> appeared in the spectra of **2** and **3**, respectively. The splitting of the thiocyanato band may be attributed to the presence of two different types of SCN<sup>-</sup> anion in both the complexes.

The electronic spectra of all three complexes are recorded in acetonitrile solution. The complexes exhibit a broad absorption band in the visible region at 577, 603 and 603 nm for **1–3**, respectively (Figure S4, in Supporting Information). These bands are attributed to d–d transitions of Cu(II) ions in the square based environment. In addition, sharp, single absorption bands are found near the respective wavelengths of 429, 420 and 419 nm for **1–3**, which can be attributed to ligand-to-metal charge transfer transitions. Moreover, absorption bands at 282, 278 and 280 nm for **1–3**, respectively, assignable to intra-ligand charge transfer transitions, are observed for all three complexes.

#### **Structure descriptions of the complexes**

The structure of **1** consists of cationic dinuclear unit of formula  $[Cu_2L_2]^{2+1}$  (where  $HL^2$  is 3-[2-(diethylamino)ethylimino]butan-2-one oxime) along with two perclorate anions and a coordinated ethanol molecule with half occupancy. The dinuclear unit is shown in Figure 1, while selected bond lengths and angles are summarized in Table 2. The two copper atoms present different environments: one (Cu1) is a penta-coordinated square pyramid and the other (Cu2) is a four-coordinated distorted square planar. The basal planes around both the copper atoms are constituted by the three nitrogen atoms of one ligand and oxygen of a second ligand from the tridentate Schiff base. However, one of the axial positions of Cu1 is occupied by the oxygen atom (O31) of the ethanol solvent at a distance of 2.396(9) Å. The four donor atoms around Cu1 are approximately planar showing r.m.s. deviations of 0.006 Å while the metal atom (Cu1) is 0.115(1) Å from this plane towards the axially coordinating

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oxygen atom. The Addisons parameter ( $\tau = 0.148$ ) indicates a square pyramidal geometry around Cu1 with a slight distortion. This value is 0 for the ideal square pyramid and 1 for the trigonal bipyramid.<sup>39</sup> On the other hand, in Cu2, there is slight tetrahedral distortion in the square plane with r.m.s deviations of 0.033 Å for the donor atoms. The Cu2 atom deviates 0.075(1) Å from this plane. The Cu–O and Cu–N bond lengths of the two copper atoms in the basal plane vary within a short range from 1.870(4) to 1.881(5) Å and from 1.905(6) to 2.104(7) Å, respectively.



Figure 1. The structure of complex 1 with ellipsoids at 30% probability. Weak interaction is shown by open bond. One non-coordinated  $ClO_4^-$  anion is not shown here. In this structure both the copper atoms (Cu1 and Cu2) are divalent.

The Cu2 atom is weakly coordinated with oxygen atom of a perchlorate anion in its axial position. Thus, the geometry of Cu2 may be viewed as distorted square pyramid by considering the weak Cu2–O2 bond distance of 2.747(8) Å. The metals are separated by 3.652(1) Å in the dinuclear unit.

The structure of **2** is shown in Figure 2, while the selected bond lengths and angles are summarized in Table 3. It contains a dinuclear cation  $[Cu^{II}_{2}L^{1}_{2}]^{2+}$ , being located on a crystallographic inversion center and two  $[Cu^{I}_{2}(SCN)_{3}]^{-}$  anionic fragments. The asymmetric unit of it consists of half of the reported formula,  $[(Cu^{II}L^{1})Cu^{I}_{2}(SCN)_{3}]$ .



Figure 2. The coordination environment of complex 2 with ellipsoids at 30% probability. Symmetry transformation c = -1-x, -y, -z. Here, the Cu1 is divalent while Cu2 and Cu3 are monovalent.

The structure of dinuclear cation  $[Cu^{II}_{2}L^{1}_{2}]^{2+}$  is comparable to that of 1, except the axial positions of Cu(II) are occupied by S-coordinated SCN<sup>-</sup> ions located on the opposite sides of the basal plane. Thus, the environments of the both copper atoms are square pyramidal. The Addison parameter ( $\tau$ ) is 0.072 for the copper atom. Like 1, the basal plane around Cu1 is constructed by the chelating tridentate N atoms of Schiff base and the oximato oxygen (O11) of symmetry related ligand. The Cu–O and Cu–N bond distances are comparable to those observed in 1 (see Table 1). The r.m.s. deviation of the four basally coordinating atoms from the mean plane passing through them is 0.022 Å, while the metal atom is 0.184(1) Å from this plane towards the axially coordinating sulphur atom. The axial position is occupied by a S atoms (S1) of the  $\mu_{1,1,3}$ -SCN ligand from the anionic part with a Cu1–S1 distance of 2.713(2) Å. The Cu1…Cu1 separation in this dinuclear unit is 3.630 (1) Å.



**Figure 3**. Top: The 1D anionic chain,  $[Cu_2^I(SCN)_3]_n^n$  is formed by Cu(I) and SCN<sup>-</sup> along crystallographic '*c*' axis. Bottom: The railroad track-like 2D sheet of polymer **2**, constructed by the connection of 1D chains by dinuclear cationic units *via* S atom of thiocyanato ligand with in crystallographic '*ac*' plane. Cu(I) and Cu(II) have been represented by green and brown balls respectively.

The most interesting feature of the crystal packing of **2** is the formation of 1D anionic chains formulated as  $[Cu_2^I(SCN)_3]_n^n$  constructed by two independent copper(I) ions, Cu2 and Cu3 and three SCN<sup>-</sup> anions; one presents  $\mu_{1,3}$ -SCN bridging mode, while the rest two SCN<sup>-</sup> present a  $\mu_{1,1,3}$ -SCN coordination mode. The monovalent (Cu2) is tetrahedral with S<sub>3</sub>N chromophore, whereas the coordination environment around the other monovalent (Cu3) is trigonal planar with N<sub>2</sub>S chromophore. The tetrahedral environment around Cu2 is distorted as confirmed by the  $\tau_4$  index which is 0.882. The  $\tau_4$  index is defined as  $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$ , with  $\alpha$  and  $\beta$  (in °) being the two largest angles around the central metal in the

compound with  $\tau_4 = 0$  for a perfect square planar and  $\tau_4 = 1$  for a perfect tetrahedron.<sup>40</sup> The Cu<sup>I</sup>–S and Cu<sup>I</sup>–N distances vary in the ranges 2.280(1)–2.508(1) Å and 1.890(2)–1.948(2) Å, respectively. The Cu<sup>I</sup>-S distances (2.280(1)-2.508(1) Å) are noticeably shorter than the Cu<sup>II</sup>–S distances (2.713(2) Å). The Cu2····Cu3 separation is 5.441 Å. The monovalent Cu2 and Cu3 atoms of the asymmetric unit are connected by a  $\mu_{1,1,3}$ -SCN ligand via N1 and S1, respectively whereas those of two different units are linked by a  $\mu_{1,3}$ -SCN ligand through N3 and S3, respectively. Moreover, the Cu2 atoms of two different units form a  $Cu_2^{I}S_2$  dinuclear square grid by connecting the other  $\mu_{1,1,3}$ -SCN ligand through a pair of sulphur ends (S2) while the N-end (N2) connects the Cu3 atom of other unit. The shortest inter-atomic distance between two copper(I) within this dinuclear square grid is 2.823(1) Å which is slightly longer than the sum of the van der Waals radii of copper(I) (2.8 Å). Thus, the connections of monovalent copper ions by thiocyanato ligands furnish a 1D anionic chain. Finally, the railroad track-like 2D sheet is constructed by the connection of the resulting anionic chains through the divalent Cu(1) atom of dinuclear units via sulphur atom (S1) of  $\mu_{1,1,3}$ -SCN ligand which connects all three metal atoms in asymmetric unit (Figure 3). The Cu1-S1-Cu3 bridging angle is 113.98 (4)°. The SCN<sup>-</sup> coordination through nitrogen is practically linear with C–N–Cu<sup>I</sup> angles in the range 163.3(3)–168.8(3)°. In contrast, the coordination through sulphur is bent with  $C-S-Cu^{I}$  angles fall within the ranges  $98.3(1)-103.4(1)^{\circ}$ .

The structure of complex **3** is shown in Figure 4, while the selected bond length and angles are summarized in Table 4. The structure of **3** also contains a dinuclear cation  $[Cu^{II}_{2}L^{2}_{2}]^{2+}$ , being located on a crystallographic inversion center and two  $[Cu^{I}(SCN)_{2}]^{-}$  anionic fragments similar to **2**. The asymmetric unit of it consists of half of the reported formula,  $[(Cu^{II}L^{2})Cu^{I}(SCN)_{2}]$ . The structure of the dinuclear cation  $[Cu^{II}_{2}L^{2}_{2}]^{2+}$  is comparable to that of **1** and **2**. Thus, the basal plane of both the Cu1 atoms in the dinuclear fragments is formed by the Schiff base ligand and SCN<sup>-</sup> ligands complete the square pyramidal coordination geometry through S-coordination at the axial position from different sides of the basal planes. As expected, the bond lengths and angles between **2** and **3** show very small differences (Table 4). The r.m.s. deviation of these four donor atoms in the basal plane around the Cu1 center is 0.108 Å while the metal atom deviates 0.212(1) Å from this plane towards the axially coordinating sulphur atom. The Addison parameter of the Cu1 atom ( $\tau = 0.257$ ) indicates that it suffers less distortion from the square pyramidal geometry than that in **2**. The Cu1…Cu1 separation in this dinuclear unit is 3.693(1) Å.



Figure 4. The coordination environment of complex 3 with ellipsoids at 30% probability. Symmetry transformation c = x, -1/2-y, -1/2+z. Here, the Cu1 is divalent and the Cu2 is monovalent.

Like **2**, the crystal packing of **3** also forms the 1D anionic chains formulated as  $[Cu^{I}(SCN)_{2}]_{n}^{n}$ . However, unlike **2**, it is constructed by one independent copper(I) ion, Cu2 and by two SCN<sup>-</sup> anions. The monovalent Cu(2) atom has a tetrahedral coordination with S<sub>2</sub>N<sub>2</sub> chromophore. The  $\tau_4$  index (0.811) confirms its tetrahedral coordination. Like **2**, the Cu<sup>I</sup>–S and Cu<sup>I</sup>–N distances vary in the ranges 2.549(1)–2.591(1) Å and 1.925(3)–1.928(3) Å, respectively. Here, the 1D chain is formed by the connection of Cu2 atoms of two different units by a  $\mu_{1,3}$ -SCN and a  $\mu_{1,1,3}$ -SCN ligands *via* both S and N ends. This type of binding fashion comprises a 8-membered metallacyclic rings with Cu2···Cu2 separation of 5.371 Å. The resulting 1D chains are connected by the divalent Cu1 atom of dinuclear units through sulphur atom (S1) of  $\mu_{1,1,3}$ -SCN ligands to form a stair like 2D layer (Figure 5). Here, the Cu1–S1–Cu2 bridging angle is 138.93 (5)°. The SCN<sup>-</sup> coordination through nitrogen and sulphur are nearly linear and bent as are evident from C–N–Cu<sup>I</sup> (161.3(4) and 163.4(4)°) and C–S–Cu<sup>I</sup> (97.8(2) and 100.3(2)°) angles, respectively.



**Figure 5**. Top: The 1D anionic chain,  $[Cu^{I}(SCN)_{2}]_{n}^{n}$  is formed by Cu(I) and SCN<sup>-</sup> along crystallographic '*a*' axis. Bottom (Left): The stair like arrangement of 2D layer of **3** constructed by the connection of 1D chains by dinuclear cationic units *via* S atom of thiocyanato ligand with in crystallographic '*ac*' plane. Cu(I) and Cu(II) have been represented by green and brown balls respectively. Bottom (Right): Stair like arrangement of 2D layer of **3** when view along '*c*' axis. Here, brown colour indicates Cu atom and grey colour represents dummy atom.

The 2D coordination framework of complexes **2** and **3** are very different (Figures 3 and 5) although both are constructed by the connection of Cu<sup>I</sup>SCN based 1D chains *via* Cu(II) based dinuclear linkers. They have different stoichiometry and coordination environment around monovalent copper centers. Both trigonal planar and tetrahedral geometry around Cu(I) ions in **2** forms a unique 1D chain formulated as  $[Cu^{I}_{2}(SCN)_{3}]_{n}^{n}$  whereas, in the 1D chain,  $[Cu^{I}(SCN)_{2}]_{n}^{n}$  of **3**, Cu(I) adopts only trigonal planar geometry (Scheme 3). The different substitution in amine part of Schiff base ligands (L) has no significant influence on the molecular structure of the dinuclear linker of complexes **2** and **3**. However, the dinuclear Cu(II) unit in **3** is bulkier than that in complex **2** because the methyl groups of L<sup>1</sup> have been

replaced by ethyl groups in  $L^2$  (indicated by red circle in Figures 3 and 5). Thus, sterically less demanding dinuclear Cu(II) moieties of complex **2** are accommodated between 1D chains which are arranged in railroad track-like manner with the average inter-chain separation of 10.125 Å. On the other hand, presumably, in order to accommodate the bulkier dinuclear Cu(II) moieties of complex **3**, the 1D chains are organized like stairs with increased average inter-chain separation (10.864 Å).



**Scheme 3**. The different coordination environment around Cu(I) by SCN<sup>-</sup> produces Cu<sup>I</sup>SCN based different infinite chains (A and B) or layer (C). Complexes **2** and **3** are formed by chains B and A respectively.

It is important to mention that previously one 2D and one 3D mixed-valence Cu(I/II) coordination polymers have been reported where cationic Cu(II) moieties associate with Cu<sup>I</sup>SCN based anionic 1D chain and 2D layer (Scheme 3), respectively. The 2D polymer has been reported by Ray et. al.<sup>30</sup> In that structure, railroad track-like arrangement of 1D anionic chains  $[Cu^{I}(SCN)_{2}]_{n}^{n}$  from a 2D sheet as extended coordination framework host which traps the imidazolidinyl phenolate bridged cationic Cu(II) dinuclear units through H-bonding interaction. It should be noted that formation of 1D anionic chain occurred in similar way as in complex **3** but the arrangement of chains are different from **3**. As mentioned before, Mitra

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et. al. reported<sup>21</sup> the crystal structure of an isomeric 3D polymer that have identical molecular building block  $[(Cu^{II}L^1)_2Cu^I_4(SCN)_6]$  to 2D polymer, **2**. However, the different dimensionalities of these two isomers are due to the different structures of  $[Cu^I_2(SCN)_3]_n^{n-1}$ anionic fragment. In the 3D isomer, the SCN ligands coordinate to Cu(I) only in trigonal planar arrangement to form a 2D layers (Scheme 3C) which are interconnected by the oximato bridged dinuclear Cu(II) moieties,  $(Cu^{II}L^1)_2$  to construct a 3D network. On the other hand, in **2**, the 1D chains (Scheme 3B) which are produced with the help of trigonal planar and tetrahedral Cu(I), are connected by  $(Cu^{II}L^1)_2$  to form the 2D polymer.

#### Magnetic properties of the complexes

The temperature dependent magnetic susceptibilities for complexes **1**–**3** were investigated in the temperature ranges of 2–300 K and 2–30 K in applied fields of 7000 and 400 G, respectively. The direct current (dc) magnetic properties of complexes **1**–**3** in the form of a  $\chi_M T vs. T$  plot ( $\chi_M$  being the magnetic susceptibility per Cu<sub>2</sub><sup>II</sup> unit and *T* the absolute temperature) are shown in Figures 6–8. At room temperature,  $\chi_M T$  is equal to 0.19 emu mol<sup>-1</sup> K for **1**, 0.19 emu mol<sup>-1</sup> K for **2** and 0.15 emu mol<sup>-1</sup> K for **3**. These values are much lower than the expected for the sum of two non-interacting Cu<sup>II</sup> centers (0.75 emu mol<sup>-1</sup> K, S<sub>Cu</sub> =  $V_2$ ,  $g_{Cu} = 2.0$ ), providing evidence of strong antiferromagnetic interactions. For the three complexes, the  $\chi_M T$  product rapidly decreases to 100 K, reaching 0.002 emu mol<sup>-1</sup> K for **1**, 0.01 emu mol<sup>-1</sup> K for **2** and 0.02 emu mol<sup>-1</sup> K for **3**. For the three dinuclear Cu<sup>II</sup> complexes the  $\chi_M vs. T$  curve show a rapid increase of the  $\chi_M$  value below 100 K, due to the presence of small amount of paramagnetic impurities (Figures 6–8 (inset)). Their structures reveal that complex **1** contains two non-equivalent Cu<sup>II</sup> ions, while in complexes **2** and **3**, the two symmetry related Cu<sup>II</sup> ions are equivalents. In the three cases the two metal ions Cu<sup>II...</sup>Cu<sup>II</sup> are double bridged by two N<sub>i</sub>O oximato ligands.





**Figure. 6.** Plot of  $\chi_M T vs. T$  for **1**. The solid line represents the best fit to the experimental data. The  $\chi_M vs. T$  plot is shown in the inset.



**Figure 7.** Plot of  $\chi_M Tvs$ . *T* for **2**. The solid line represents the best fit to the experimental data. The  $\chi_M vs$ . *T* plot is shown in the inset.



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**Figure 8.** Plot of  $\chi_M T vs. T$  for **3**. The solid line represents the best fit to the experimental data. The  $\chi_M vs. T$  plot is shown in the inset.

The fit of the experimental data was performed using the Bleaney-Bowers equation for dinuclear Cu(II) complexes, derived from the Hamiltonian  $H = -J(S_1S_2)$ , and introducing a  $\rho$  term to evaluate the paramagnetic impurity.<sup>41</sup> Best fit parameters are J = -549.6 cm<sup>-1</sup>, g = 2.06,  $\rho = 0.9\%$  and  $R = 3 \times 10^{-6}$  for 1; J = -578.7 cm<sup>-1</sup>, g = 2.17,  $\rho = 2.2$  % and  $R = 3 \times 10^{-6}$ for 2 and J = -663.8 cm<sup>-1</sup>, g = 2.08,  $\rho = 3.9$  % and  $R = 4 \times 10^{-6}$  for 3. The best fit curves are plotted in Figures 6–8 along with the experimental data.

In the 2D polymers, the distances between the Cu(II) ions of the neighboring dinuclear units are more than 10 Å and 8 Å for complexes 2 and 3 respectively. So any possible interaction between the dinuclear Cu(II) units through the diamagnetic Cu<sup>I</sup>SCN chains was not considered. Even if this interaction is present, its corresponding coupling constant value should be several orders of magnitude less than the corresponding interaction between the Cu(II) ions through the oximato ligand.

The large number of dinuclear Cu(II) complexes doubly bridged by two N<sub>0</sub>O oximato ligands have been reported showing strong antiferromagnetic coupling,<sup>42-56</sup> usually displaying J values, in an absolute value, higher than  $-500 \text{ cm}^{-1}$  (even diamagnetism at room temperature in some cases), so the strong antiferromagnetic coupling for complexes 1-3 was not unexpected. Previous works, in this field, have shown that the mechanism of the interaction between the two Cu(II) ions and the double oximato-bridge depends on the good orbital overlap in  $Cu-(R=NO)_2-Cu$  core (R = different groups), as the most relevant factor.<sup>30,31</sup> The unpaired electron of each Cu(II) ion is located on the  $d_{x-y}^{2}$  magnetic orbital, so the planarity of the bridging region favors stronger antiferromagnetic coupling. According to the literature data, the structural parameters that affect the strength of the magnetic coupling, in Cu(II) dimers with double oximato ligands, are: the Cu–N and Cu–O distances, the Cu–O–N and Cu–N–O angles, the distance from the Cu(II) ion(s) to the average plane of the two NO bridges, the dihedral angle between the planes of each O-Cu-N unit and the average plane of the two NO bridges and the dihedral Cu-N-O-Cu angle. The structural values of the above mentioned parameters for complexes 1-3 are shown in Table 5. Magneto-structural studies in complexes with high absolute J values, that imply small values of the magnetic susceptibility along the temperature range, are not easy. Since theoretical

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calculations show that the most important parameter in determining the magnetic coupling must be the planarity of the Cu(NO)<sub>2</sub>Cu ring,<sup>53-56</sup> we have plotted the magnetic exchange, J, constants as function of the average Cu–N–O–Cu dihedral angle for several analogous complexes (Figure 9), since this angle reflects the planarity of this ring. Form this plot it is evident that there is an approximate linear relationship between the coupling constant and the dihedral Cu–N–O–Cu angle. In Figure 9, we have added the corresponding points to complexes 1–3. From this result, it should be concluded that the magnetic exchange in dinuclear Cu(II) complexes with double oximato ligands is in all cases very strong and antiferromagnetic but a simple relation between planarity and the J parameter is not at all consistent.



**Figure 9.** *J vs.* the average value of the Cu–N–O–Cu dihedral angle. The regression line is indicated.

#### Conclusions

We have synthesized and characterized three copper complexes (1-3) with oxime based mono-condensed Schiff base ligands. Complex 1 is a usual double-oximato bridged Cu(II) dimer while complexes 2 and 3 are two rare mixed-valence, Cu(I)-Cu(II) 2D coordination polymers obtained by *in situ* reduction of a part of Cu(II) with NaSCN at room temperature. The self-replication of the *in situ* generated Cu<sup>1</sup><sub>2</sub>(SCN)<sub>3</sub><sup>-</sup> (in 2) or Cu<sup>1</sup>(SCN)<sub>2</sub><sup>-</sup> (in 3) anionic fragments lead to the formation of Cu<sup>I</sup>NCS based 1D anionic chains which are linked by cationic dimers. The 1D chain of 2 is formed in an unprecedented manner. The structures of 1D chains are different due to the different stoichiometry of Cu(I) and thiocyanoto ligand and diverse coordination environment around copper(I) centers. The 1D chains are arranged railroad track-like in **2** and such arrangement is known but the stair like arrangement of 1D chains which is found in **3** is unique for such species. The different substitutions in amine part of Schiff base ligand in the Cu(II) dimers in **2** and **3** seems to be responsible for different organization of 1D chains. Thus, the present system reveals that a subtle change in the ligand system may lead to the formation of different network structures of mixed-valence Cu(I/II) coordination polymers. The magnetic coupling between the double oximato bridged intra-dimer Cu(II) is antiferromagnetic and very strong, in agreement with the structurally and magnetically characterized reported Cu(NO)<sub>2</sub>Cu dimers.

#### **Supporting Information**

 Figures of UV-Vis spectra, IR spectra (Figures S1–S4) and crystallographic data in CIF format for all three complexes (1–3). These material is available free of charge *via* the Internet at http://pubs.acs.org.

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32         33         34         35         36         37         38         39         40         41         42         43         44         45         46         47         48         50         51         52	
32         33         34         35         36         37         38         301         41         42         43         44         45         46         47         48         50         51         52         53	
32       33       34       35         33       34       35       36       37         38       30       41       42       44       46         41       42       44       45       46       51       52       53         50       51       53       54       54       54       54       54	
323       34       35       36         333       35       36       37       38         34       45       44       44       44         44       44       44       44       44         50       51       52       54       55	
323 34 35 36 37 38 9 41 42 34 45 46 47 8 9 51 52 53 55 56	
323       34       35       36       37       389       41       42       44       44       44       49       51       52       54       55       56       57	

Table 1.	Crystal	data and	structure	refinement	for com	plexes (	(1-3)	).
							· /	<i>.</i>

Complexes	1	2	3
Formula	C <sub>21</sub> H <sub>42.5</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>10.5</sub> Cl <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> Cu <sub>6</sub> N <sub>12</sub> O <sub>2</sub> S <sub>6</sub>	$C_{24}H_{40}Cu_4N_{10}O_2S_4$
М	745.09	1070.20	883.06
Crystal System	Orthorhombic	Triclinic	Monoclinic
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	PĪ	$P2_1/c$
a/Å	7.8532(4)	10.1247(3)	11.7972(6)
b/Å	18.8955(8)	10.3908(3)	13.8115(7)
c/Å	22.8742(10)	10.4233(6)	10.6670(5)
$\alpha / ^{\circ}$	90	96.318(2)	90
$\beta^{\circ}$	90	102.640(2)	98.116(2)
γ/°	90	115.983(1)	90
V/Å <sup>3</sup>	3394.3(3)	934.96(7)	1720.64(15)
Ζ	4	1	2
$D_c/g \text{ cm}^{-3}$	1.458	1.901	1.705
$\mu/\text{mm}^{-1}$	1.466	3.727	2.721
F (000)	1528	534	900
R(int)	0.047	0.022	0.050
Total Reflections	38758	12968	19183
Unique reflections	6018	3779	3057
$I > 2 \overline{\sigma(I)}$	4856	3342	2456
$R1^a$ , $wR2^b$	0.0631, 0.1922	0.0274, 0.0778	0.0381, 0.1022
Temp (K)	293	293	293
$GOF^c$ on $F^2$	1.04	1.07	1.04

 ${}^{a}\text{R1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, \ {}^{b}w\text{R2} \ (F_{o}^{2}) = \left[\sum [w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w \ F_{o}^{4}\right]^{\frac{1}{2}} \text{ and } {}^{c}\text{GOF} = \left[\sum [w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{params})\right]^{\frac{1}{2}}$ 

 Table 2. Bond distances (Å) and angles (°) for complex 1.

Cu(1)-O(31)	2.396(9)	Cu(2)–O(2)	2.747(8)
Cu(1)–O(21)	1.881(5)	Cu(2)–O(11)	1.870(4)
Cu(1)–N(12)	1.997(5)	Cu(2)–N(22)	1.999(5)
Cu(1)–N(15)	1.921(5)	Cu(2)–N(25)	1.905(6)
Cu(1)–N(18a)	2.104(7)	Cu(1)–N(28)	2.079(5)
O(31)–Cu(1)–O(21)	95.7(3)	O(2)–Cu(2)–O(11)	101.2(3)
O(31)–Cu(1)–N(12)	85.8(3)	O(2)–Cu(2)–N(22)	77.3(2)
O(31)–Cu(1)–N(15)	92.8(3)	O(2)–Cu(2)–N(25)	86.0(3)
O(31)–Cu(1)–N(18a)	101.5(3)	O(2)–Cu(2)–N(28)	101.8(3)
O(21)–Cu(1)–N(12)	104.8(2)	O(11)–Cu(2)–N(22)	105.8(2)
O(21)–Cu(1)–N(15)	170.6(2)	O(11)–Cu(2)–N(25)	171.2(3)
O(21)-Cu(1)-N(18a)	91.4(2)	O(11)–Cu(2)–N(28)	91.0(2)
N(12)-Cu(1)-N(15)	79.8(2)	N(22)–Cu(2)–N(25)	80.4(2)
N(12)-Cu(1)-N(18a)	161.7(2)	N(22)–Cu(2)–N(28)	163.0(2)
N(15)-Cu(1)-N(18a)	83.0(2)	N(25)-Cu(2)-N(28)	82.6(2)

Cu(1)–S(1)	2.713(2)	Cu(2)–S(2)	2.412(1)	Cu(3)-S(1)	2.358(1)			
Cu(1)–O(11)	1.890(2)	Cu(2)–S(3)	2.280(1)	Cu(3)–N(2)	1.890(2)			
Cu(1)–N(11)	2.007(2)	Cu(2) - N(1)	1.948(2)	Cu(3) - N(3)	1.898(3)			
Cu(1)–N(12)	1.942(2)	$Cu(2) - S(2)^{c}$	2.508(1)					
Cu(1)–N(13)	2.073(2)							
S(1)-Cu(1)-O(11)	93.31(7)	S(2)-Cu(2)-S(3)	112.33(3)	S(1)-Cu(2)-N(2)	112.68(9)			
S(1)-Cu(1)-N(11)	91.09(7)	S(2)-Cu(2)-N(1)	106.51(9)	S(1)-Cu(2)-N(3)	110.29(9)			
S(1)-Cu(1)-N(12)	99.58(10)	$S(2)-Cu(2)-S(2)^{c}$	110.01(3)	N(2)-Cu(2)-N(3)	136.98(13)			
S(1)-Cu(1)-N(13)	99.00(10)	S(3)-Cu(2)-N(1)	123.28(9)					
O(11)-Cu(1)-N(11)	106.03(8)	$S(3)-Cu(2)-S(2)^{c}$	102.79(4)					
O(11)-Cu(1)-N(12)	165.67(11)	$N(1)-Cu(2)-S(2)^{c}$	100.76(10)					
O(11)-Cu(1)-N(13)	89.07(9)							
N(11)-Cu(1)-N(12)	80.11(10)							
N(11)-Cu(1)-N(13)	161.37(10)							
N(12)-Cu(1)-N(13)	82.79(11)							
Symmetry transformation $c = -1 - x - y - z$								

Table 3. Bond distances (Å) and angles (°) around metal atoms for complex 2.

Symmetry transformation c = --1-x, -y, -z.

Table 4. Bond distances (Å) and angles (°) around metal atoms for complex 3.

Cu(1)-S(1)	2.720(1)	Cu(2)-S(1)	2.591(1)
Cu(1)-O(11)	1.896(2)	Cu(2) - S(2)	2.549(1)
Cu(1)–N(11)	2.020(3)	Cu(2) - N(2)	1.928(3)
Cu(1)–N(12)	1.944(4)	$Cu(2) - N(1)^{c}$	1.925(3)
Cu(1)–N(13)	2.120(3)		
S(1)-Cu(1)-O(11)	96.87(9)	S(1)-Cu(2)-S(2)	105.85(4)
S(1)-Cu(1)-N(11)	92.43(8)	S(1)-Cu(2)-N(2)	97.24(11)
S(1)-Cu(1)-N(12)	90.01(9)	$S(1)-Cu(2)-N(1)^{c}$	106.07(12)
S(1)-Cu(1)-N(13)	104.60(8)	S(2)-Cu(2)-N(2)	108.72(12)
O(11)-Cu(1)-N(11)	105.23(10)	$S(2)-Cu(2)-N(1)^{c}$	99.16(11)
O(11)-Cu(1)-N(12)	171.30(12)	$N(2)-Cu(2)-N(1)^{c}$	136.94(17)
O(11)-Cu(1)-N(13)	89.82(12)		
N(11)-Cu(1)-N(12)	79.68(12)		
N(11)-Cu(1)-N(13)	155.87(11)		
N(12)-Cu(1)-N(13)	83.28(13)		

Symmetry transformation c = x, -1/2 - y, -1/2 + z.

	Table	5.	Magnetic	and	structural	parameters	of	com	olexes	1-	-3.
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	1	2	3
$J(\mathrm{cm}^{-1})$	-549.6	-578.7	-663.8
$^{a}\theta(^{\circ})$	168.60 / 171.15	163.89	170.76
$^{b}\alpha(^{\circ})$	10.02 /6.20	23.65	14.00
$^{c}d(\text{\AA})$	0.229 / 0.175	0.325	0.191
Cu–O (Å)	1.887 /1.866	1.890	1.897
Cu–N (Å)	2.002/2.006	2.007	2.019
Cu–O–N (°)	122.87/123.70	122.11	124.20
Cu–N–O (°)	129.54/129.77	128.51	129.44

 $^{a}\theta$  = dihedral angle between the planes of each O–Cu–N unit and the average plane of the two NO bridges.<sup>b</sup> $\alpha$ = dihedral Cu-N-O-Cu angle. <sup>c</sup>d = distance from de Cu<sup>II</sup> atom(s) to the average plane of the two NO bridges.

## For Table of Contents Use Only

# Antiferromagnetic mixed-valence Cu(I)-Cu(II) 2D coordination frameworks constructed by double oximato bridged Cu(II) dimers and Cu<sup>I</sup>SCN based 1D anionic chains

#### Lakshmi Kanta Das, Carmen Diaz and Ashutosh Ghosh\*

One oximato bridged Cu(II) dimer and two rare mixed-valence Cu(I)-Cu(II) 2D coordination polymers as a railroad track-like 2D sheet and a stair like 2D layer have been synthesized using two oxime-based tridentate Schiff bases. *In situ* partial reduction of Cu(II) to Cu(I) is observed in presence of NaSCN at room temperature.

