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Weak Ferromagnetic Ground State in Copper(II) Linear Chains

CHRISTOPHER A. WHITE[a], MARIA C. DEROSA, GLENN P. A. YAP[a], N. P. RAJU[b], J. E. GREEDAN[b] and ROBERT J. CRUTCHLEY[a*]

[a]*Ottawa-Carleton Chemistry Institute, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario Canada K1S 5B6 and*
[b]*Brockhouse Institute for Materials Research, McMaster University, Hamilton Ontario, Canada L8S 4M1*

The linear chain Cu(II) compounds $[\{Cu(trpy)\}_2(\mu\text{-dicyd})]_n[BPh_4]_{2n}$, where trpy is 2,2′:6′,2″-terpyridine and $dicyd^{2-}$ is 1,3-dicyanamidobenzene dianion, and $[\{Cu(trpy)(CF_3SO_3)\}\{Cu(trpy)\}(\mu\text{-methyldicyd})]_n[CF_3SO_3]_n$, where $methyldicyd^{2-}$ is 1,3-dicyanamido-2-methylbenzene dianion, both possess a weak ferromagnetic ground state despite having dramatically different bridging geometries. We suggest that the topology of the bridging ligand induces spin canting superimposed onto a dominant antiferromagnetic exchange interaction between the Cu(II) ions of the chain.

Keywords copper(II); linear chains; spin canting.

The crystal structures of $[\{Cu(trpy)\}_2(\mu\text{-dicyd})]_n[BPh_4]_{2n}$ **1**, and $[\{Cu(trpy)(CF_3SO_3)\}\{Cu(trpy)\}(\mu\text{-methyldicyd})]_n[CF_3SO_3]_n$, **2** are shown in Figures 1 and 2 respectively. Axial and equatorial coordination sites can be identified by recognizing that the terpyridine ligand occupies equatorial coordination sites.

For **1**, each copper ion occupies a distorted square pyramid coordination sphere of nitrogen donor atoms that extend in an isolated linear chain of alternating copper pairs (closest Cu-Cu interchain

separation is 13 Å). The coordination mode of cyanamide is unusual but not without precedent. The crystal structure of $[\{Cu(bpy)(pcyd)\}_2(\mu\text{-}pcyd)_2]$, where pcyd is phenylcyanamido

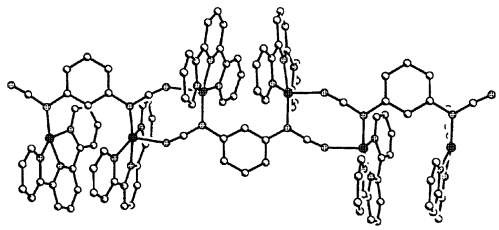

FIGURE 1 Ball and stick diagram showing the connectivity of atoms in complex **1**.

showed an identical coordination mode in which the cyanamido group bridges Cu(II) ions via the cyano and amido nitrogens [1]. For $[Cu_2(L)_2(\mu\text{-}NCNH)_2]^{2+}$ where L is N, N′, N″-trimethyl-1,4,7-triazacyclonone, the cyanamide bridging nitrogens occupy equatorial sites on Cu(II) ions which were antiferromagnetically coupled with μ_{eff} = 1.35 B.M. (298 K) [2] and an estimated J = -170 cm^{-1} [3]. The three-atom cyanamide bridge on **1** bonds to equatorial (via amido nitrogen) and axial (via cyano nitrogen) coordination sites of respective copper ions. Finally, the copper ions are crystallographically inequivalent.

For complex **2**, the cyanamide groups of $Medicyd^{2-}$ adopt different coordination geometries; one cyanamide group bridges two Cu(II) ions via its cyano nitrogen and the bonding to the copper ions is axial-equatorial, and the other cyanamido group bonds to one Cu(II) ion via its cyano nitrogen. Both Cu(II) ions possess a square pyramid coordination geometry. However, only one is coordinated by a triflate anion. The difference between the cyanamide coordination modes found in complex **1** and **2** is suggested to arise from the steric repulsion of the methyl group in $Medicyd^{2-}$ which prevents coordination of Cu(II) to the amide nitrogen.

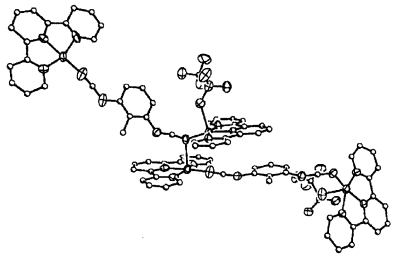

FIGURE 2 Drawing showing the connectivity of atoms in complex **2**. The triflate counter anion is not shown for clarity.

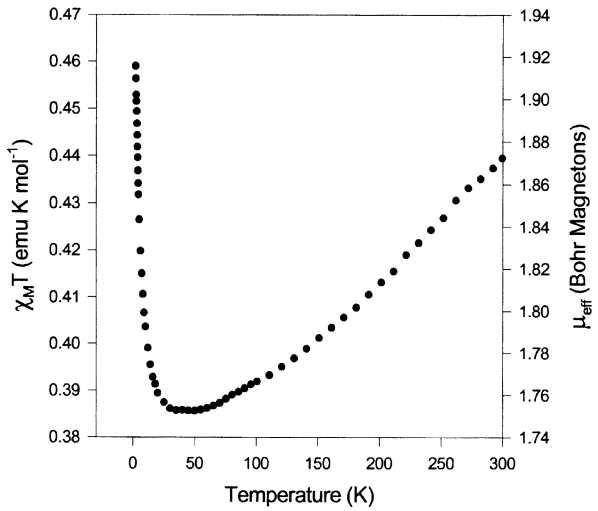

FIGURE 3 Plot of $\chi_M T$ versus T for complex **1**

Plots of $\chi_m T$ versus T of complex **1** and **2**, at 1 Tesla field strength, are shown in Figure 3 and 4, respectively. These plots each show a minimum similar to that seen for ferrimagnetic systems [4], homonuclear chains with either two different spin sublattices [5], an exotic stacking of the metal ions [6], double chains [7] or regular spin chains with alternating g-tensors [8]. Based on the crystal structures

of **1** and **2**, the latter case seemed a possible description. However, attempts to model our magnetic data according the method described in ref 8 were unsuccessful when using reasonable *g* values for Cu(II) ions.

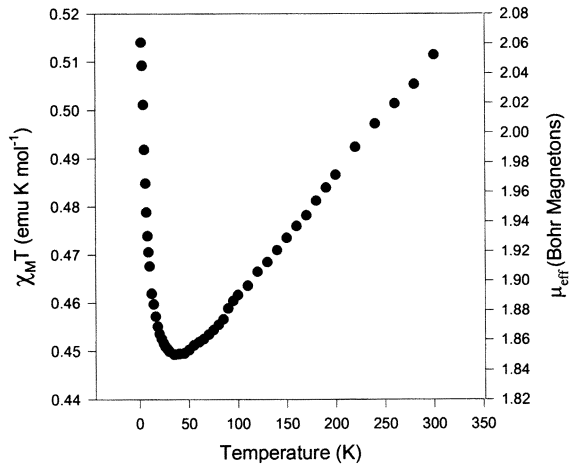

FIGURE 4 Plot of $\chi_M T$ versus T for complex **2**

Another possibility is that the magnetic properties of **1** and **2** arise in part from spin canting. Spin canting occurs when an antisymmetric interaction tends to orient the two local spins perpendicular to each other while an anisotropic interaction tends to orient them in an antiparallel direction. The non-compensating interaction of local spins propagates along the chain and yields a weak ferromagnetic ground state. Thus, as temperature is lowered, instead of a decreasing $\chi_M T$ versus T plot typical of an antiferromagnetic chain, a minimum is reached, indicating the population of the weakly ferromagnetic ground state. For **1**, a magnetization versus applied field study has shown no evidence of spontaneous magnetization down to our limit of 2 K. Indeed, no spontaneous magnetization is expected for a truly one-dimensional system at temperatures greater

than absolute zero [9]. Magnetization at 2 K approaches the value expected for a copper(II) compound, i.e. $N\beta g/2$ ($\approx$ 1 B.M.) at moderately high field strengths and the data are consistent with a weak antiferromagnetic interaction between Cu(II) ions. This apparently occurs despite the axial-equatorial coordination of the cyanamide group bridging the two copper ions. All the data suggest that the schematic for spin canting can be best represented as follows,

For **2**, a magnetization versus applied field study also shows no evidence of spontaneous magnetization. However, the data are more appropriately fitted to the Brillouin function for an S= 1 system, indicating a ferromagnetic interaction between Cu(II) ions in the chain. Ferromagnetic exchange likely occurs via the cyano-nitrogen atom which bridges axial and equatorial coordination sites of respective Cu(II) ions. Thus, spin canting in complex **2** can be best represented as follows,

Changing the auxiliary ligands on Cu(II) does not alter the observation of a weakly ferromagnetic ground state for the chain and suggests that this state is a consequence of the topology of the *meta*-dicyd^{2-} bridging ligand when bonded to Cu(II) ions. These studies and the effects of changing the nature of the metal ion, and counter ion will be presented in the near future.

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