Origin of Ferromagnetic Coupling in a Dicyanamide-bridged One-dimensional Cu(II) Complex

Hui-Zhong Kou* and Yi He
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

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A dicyanamide-bridged 1D chain complex has been characterized structurally and magnetically. The Cu(II) ion exhibits a distorted trigonal bipyramidal (tbp) geommetry with the axial positions ocuppied by the benzimidazole nitrogen atom and the unidentate dca nitrogen atom. The ferromagnetic nature of the complex has been assigned to be due to the π–π contacts rather than the μ-1,5 dca bridges.

Dicyanamide anion, dca^-, is a versatile bridging ligand connecting two or more metal ions with three nitrogen atoms.[1–8] The coordination modes of dca are interesting and rich. The magnetic coupling between the metal ions through the dca bridges has been extensively investigated, which were stimulated by the observation of magnetic ordering in some three-dimensional dca-bridged transition metal complexes.[1,8] It has been documented that the 1,5-bridging mode gives rise to longer intermetallic separations, which is unfavourable for intermetallic magnetic coupling. Naturally, the strength of the magnetic exchange also relates to the extent of delocalization of the magnetic orbitals to the bridging dca ligands. As far as the dca–Cu(II) complexes are concerned, negligibly small antiferromagnetic or weak ferromagnetic interaction through the μ-1,5-bridging mode have been reported.[4,7] These inconsistencies prompted us to study dca-bridged Cu(II) complexes with the hope of getting insight into the magneto-structural correlationship. In this letter, we report a dca-bridged 1D Cu(II) complex, $[Cu(Hambi)(dca)_2]\cdot H_2O$ (**1**) (Hambi = 2-aminomethylbenzimidazole).

To an aqueous solution (10 mL) of $Cu(ClO)_2\cdot 6H_2O$ (0.1 mmol) and Hambi·2HCl[9] (0.1 mmol) was added $NaN(CN)_2$ (0.2 mmol) in water (5 mL). Slow evaporation of the resultant light blue solution gave needle-like single crystals. Yield: 40%. Anal. Calcd for $C_{12}H_{11}CuN_9O$: C, 39.95; H, 3.07; N, 34.94%. Found: C, 39.79; H, 2.87; N, 34.83%. IR: ν_{max}/cm^{-1} 2312s, 2282s, 2251s, and 2178s (C≡N).

The structure[10] of **1** contains neutral chains, which run parallel to the *a* axis, as illustrated in Figure 1. The coordination sphere of the Cu(II) ion is approximately trigonal bipyramidal (tbp) with three nitrogen atoms (N2, N5, and N7a) of two bridging dca ligands and one Hambi ligand. The axial positions are occupied by two nitrogen atoms (N1 and N8) of the terminal dca ligand and Hambi ligand, respectively. The $Cu–N_{equatorial}$ bond distances range from 2.036(2) to 2.181(3) Å, whereas the $Cu–N_{axial}$ bond distances are 1.952(3) and 1.957(2) Å, less than that of the equatorial bonds, giving a depressed tbp coordination sphere. The N1–Cu1–N8 linkage deviates slightly from linearity (170.77(10)°). The bridging dca ligands coordinate to Cu(II) in a μ-1,5 fashion. The adjacent Cu(II)···Cu(II) separation through the dca bridges is 7.479(1) Å. The closest interchain Cu(II)···Cu(II) distance is 6.569(1) Å.

Figure 2 shows the packing of the chains in the unit cell. The amide nitrogen atoms of the bridging dicyanamide ligands are hydrogen-bonded to the N atoms of benzimidazole of the adjacent chain, giving rise to a two-dimensional layer. Two layers are connected through π–π interaction between the conjugated benzimidazole cycles of the Hambi ligands. Additionally, these double layers are hold together via hydrogen bonds of the types N–H···O and O–H···N (unidentate dca ligands). The distances of two adjacent aromatic cycles are approximately 3.57 and 3.58 Å. The π–π contacts of the benzimidazole cycles generate one-dimensional packing along the *a* axis. The Cu(II)···Cu(II) distances across the interacting Hambi ligands are 7.435(1) and 8.520(1) Å, respectively.

The room-temperature EPR spectrum displays three transitions corresponding to $g_1 = 2.044$, $g_2 = 2.105$, and $g_3 = 2.270$ ($g_{av} = 2.14$). The signals are typical of a Cu(II) complex in a tbp coordination environment, indicative of the d_{z^2} ground state in Cu(II).

A plot of $\chi_m T$ vs T is shown in Figure 3. The gradual rise in

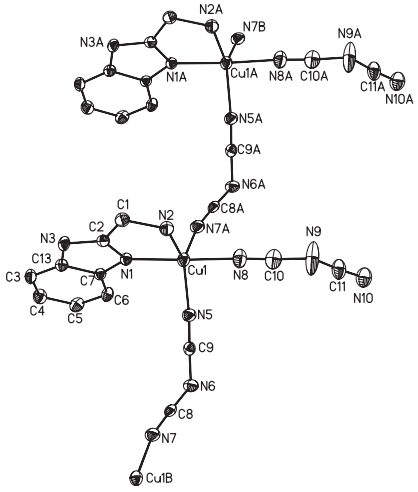

Figure 1. ORTEP plot of chain-like complex (**1**).

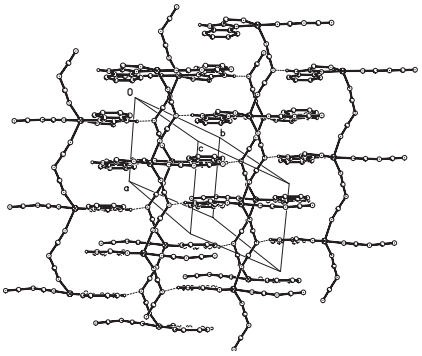

Figure 2. Cell packing diagram showing the π–π contacts.

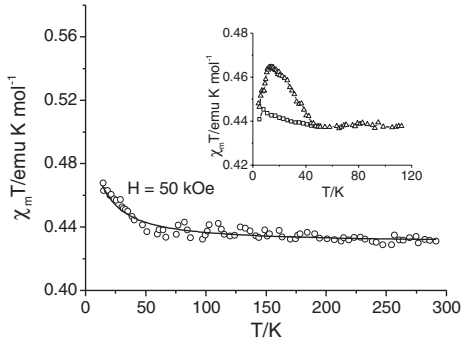

Figure 3. Magnetic behavior of complex **1**. Solid lines are the best fits based on the parameters described in the text. Inset: Temperature dependence of $\chi_m T$ in different fields of 10 kOe (□) and 20 kOe (△).

$\chi_m T$ as T decreases is characteristic of a magnetic system with a dominant ferromagnetic interaction. In order to verify the ferromagnetic nature of **1**, the magnetic measurements in applied magnetic fields of 10 kOe and 20 kOe were performed. The curves support the above supposition (Inset of Figure 3).

For a Cu(II) ion in a tbp coordination geometry, the unpaired electron lies mainly in d_{z^2} orbital, which directs to the axial nitrogen atoms in complex **1**. The little delocalization of the orbital towards the equatorial nitrogen atoms leads to a comparatively weak magnetic interaction through the μ-1,5 dca bridges. Thus the comparatively strong ferromagnetic interaction can be attributed to the magnetic coupling through the π–π contacts, whereas the weak antiferromagnetic interaction is due to the magnetic exchange through the μ-1,5 dca bridges.

Considering that the paramagnetic Cu(II) ions are connected by the π–π contacts to form a one-dimensional chain, we tried to evaluate the magnetic coupling by using a 1D chain model. The magnetic exchange through the μ-1,5 dca bridges was considered negligibly small. We have accordingly analyzed the magnetic data through the numerical expression proposed by Baker et al.[11] for a ferromagnetically coupled uniform chain including an intermolecular interaction term. The best fit parameters obtained are: $J = +0.83\,\mathrm{cm}^{-1}$, $g = 2.14$, $J' = -0.33\,\mathrm{cm}^{-1}$ ($z = 4$, the number of the next-nearest neighbors around the chain). As discussed above, the positive exchange constant (J) suggests the existence of ferromagnetic interaction through the π–π contacts.

It is worth mentioning that the ferromagnetic interaction in the previously reported dca-bridged Cu(II) complexes is assumed to be due to the μ-1,5 dca bridges, although similar π–π contacts are present in one of the complexes Cu(phen)(dca)$_2$.[7b,c] The present research emphasizes that the μ-1,5 dca bridge propagates very weak magnetic interaction, antiferromagnetic in most cases. The ferromagnetic coupling observed in Cu(phen)(dca)$_2$ is likely to be due to the π–π contacts rather than the dca bridging.

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10 Crystal data: $C_{12}H_{11}CuN_9O$, fw = 360.84, triclinic, $a = 7.479(1)$, $b = 9.082(2)$, $c = 11.737(2)$ Å, $\alpha = 78.98(3)^\circ$, $\beta = 0.42(3)^\circ$, $\gamma = 68.47(3)^\circ$, $V = 723.9(2)$ Å^3, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo Kα) = 1.529 mm^{-1}, 6977 reflections measured ($1.57 \leq \theta \leq 25.04^\circ$) and 5096 considered unique ($R_{int} = 0.0326$). The final $wR(F^2)$ was 0.0741 (all data), with conventional $R(F)$ 0.0520 for 216 parameters. CCDC-218199 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 deposit@ccdc.cam.ac.uk).

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