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Inorganic Chemistry Communications 8 (2005) 1169–1172

INORGANIC CHEMISTRY COMMUNICATIONS

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Synthesis and magnetic property of a dual μ-[N(CN)$_2$] bridged copper(II) supramolecule with dinuclear unit

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Received 14 July 2005; accepted 10 September 2005
Available online 2 November 2005

Abstract

A dicyanamide (dca) Cu(II) supramolecular complex constructed by hydrogen-bond interactions and weak Cu–N bond interactions has been prepared and the structure was determined by X-ray diffraction analysis. The magnetic studies indicate that strong antiferromagnetic interactions exist between two Cu(II) ions of the dca-bridged dimer.

Keywords: Dicyanamide; Supramolecule; Crystal structure; Magnetic material

Dicyanamide-bridged 1D to 3D extended systems are attracting much attention in the field of crystal engineering and the design of inorganic coordination polymers, because of their fascinating structures and long-range magnetic ordering in the binary α-M(dca)$_2$ (dca = dicyanamide) compounds [1]. More generally, dca is also a very interesting ligand due to the presence of three potential donor centers and varieties of possible bridging fashions [2]. Interesting types of structures such as rutile-like networks and interpenetration have been already observed in dca bridged compounds. However, in most of the dca-bridged coordination polymers reported, dca acts both as network-constructed factor and as counter-anion to balance the charge on the metal. Neutral monodentate, chelated and bridging ligands have been used as coligands, for the construction of multiform topologies and architectures with potential applications as functional materials, while the examples of ionic ligand as coligand are limited [3]. Herein, a novel Cu(II) supramolecular complex was reported, which is constructed by two anion ligands, dca and pcl (Hpcl = picolinic acid).

The title complex [Cu(N(CN)$_2$)(C$_6$H$_4$NO$_2$)(H$_2$O)]$_2$ was prepared by mixing the methanol solution of CuCl$_2 \cdot$ 2H$_2$O (0.5 mmol) 10 mL and aqua solution of picolinic acid (0.5 mmol) 10 mL, and stirring for 30 min at room temperature. The aqua solution of sodium dycyanamide (0.5 mmol) 10 mL dropped into the above mixture, and adjusted the pH value to 5 using 10% NaOH aqua solution, further stirring for 30 min. Blue-green solution was filtered and standing at room temperature, and block blue-green crystals were obtained and washed with methanol solution (yield 78%). At the same time, a few of blue crystals of Cu(pcl)$_2$ (determined by X-ray diffraction analysis) were obtained as by-product, which can be separated from the title complex manually, due to the differences in the color and shape of the crystals.

The single X-ray crystallographic analysis [4] reveals that the Cu(II) anion is surrounded by three N atoms from a pcl ligand and two dca ligands, two O atoms from a pcl ligand and an aqua molecule as depicted in Fig. 1. The dca ligand has a dual μ$_{1,5}$-coordination fashion, and two dca molecules link two Cu(II) into a porous dinuclear unit, while the pcl ligand coordinates to the metal ion with a bidentate mode using the N atom of pyridine ring and the O atom of the carboxylate group. The N1, N2, N4A and O1 atoms are in the equatorial plane (average devia-

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doi:10.1016/j.inoche.2005.09.022

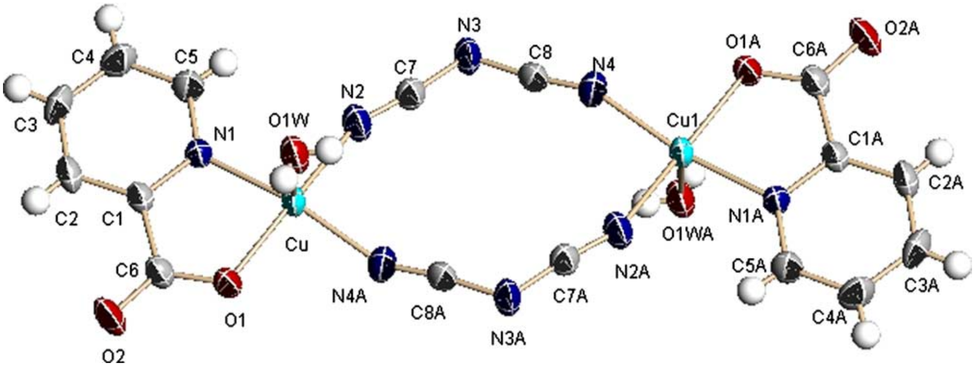

Fig. 1. The coordination environment of Cu(II) in the title complex, thermal ellipsoids are shown in 50% probability.

tion: 0.0201) and the deviation of Cu(II) from the above plane is 0.1691 Å. The O1W atom occupies the axial position. The bond distances of Cu–N1, Cu–N2, Cu–N4A and Cu–O1 are 1.986(3), 1.979(3), 1.984(3) and 1.955(2) Å respectively, in which both of the two Cu–N (dca) bonds distances are with slightly difference, and also nearly to the corresponding value in some Cu–dca systems reported [5]. The O1W atom occupies the axial position, and the bond distance of Cu–O1W is somewhat longer with the value of 2.257(3) Å. The bond angles of N1–Cu–N2, N2–Cu–N4A, N4A–Cu–O1 are in the range of 82.59(10)–91.49(12)°, and those of N1–Cu–N4A and N2–Cu–O1 are 167.92(14)° and 171.14(13)° respectively. The angles of the bond N1–Cu–O1W, N2–Cu–O1W, N4A–Cu–O1W, and O1–Cu–O1W are in the range of 93.45(11)–95.87(11)°, indicating the distorted square–pyramidal environment of the Cu(II) anion. The bond distances of N3–C7 and N3–C8 are 1.297(5) and 1.301(5) Å, while the bond angle of C7–N3–C8 is 118.8(3)°, lightly smaller than 120°, indicating the N3 atom of the dca ligand has hybrid sp^2 orbitals. The dca ligand has an end to end coordination mode and links two Cu(II) anions forming a porous structure with dinuclear unit.

In this system, there exist weak interactions between the Cu–Cu and Cu–N4 (from the dca ligand of the symmetric unit) of two adjacent dinuclear units, with the distance of 3.856 and 3.353 Å, respectively. Besides of the weak bond interactions, there are hydrogen-bond interactions between the O1w(aqua) ··· O2(carboxylate) with the distance of 2.782 Å, forming a one dimensional chain. The chains are also assembled by the hydrogen-bond interactions between O1w(aqua) ··· O2(carboxylate) with the distance of 2.766 Å. Viewing down the *c* axis, it is interesting to find that the hydrogen-bond interactions constructed by two O atoms of aqua molecules and two O atoms of carboxylate groups, link into a regular square plane as shown in Fig. 2. The title complex forms a channel-like supramolecular structure (Fig. 3), due to the construction of normal coordination bonds along with the hydrogen-bond interactions and the weak interactions of the Cu–Cu and Cu–N4 bonds.

Variable temperature magnetic susceptibilities were determined in the temperature range of 4–300 K on a Quantum Design MPMS SQUID magnetometer at the applied magnetic field of 10 T. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants [6]. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = \sqrt{8\chi_{\text{M}}T}$, where χ_{M} is the magnetic susceptibility per Cu(II) moiety. The plots of the molar magnetic susceptibility versus T and the effective magnetic moment μ_{eff} versus T for the title complex are shown in

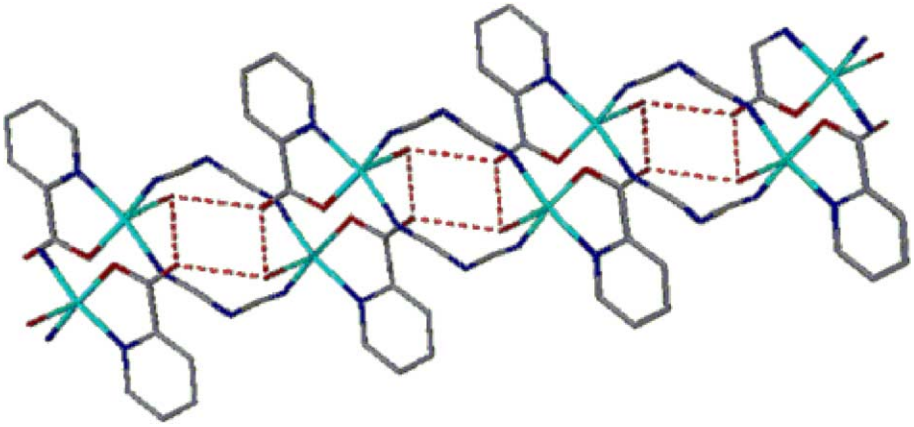

Fig. 2. A perspective view down the *c*-axis of the hydrogen-bond interactions.