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Synthesis and Crystal Structure of One-Dimensional Copper(II) Coordination Polymer Bridged by Pyrazine Derivative

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The one-dimensional copper(II) coordination polymers $[Cu(tdpd)(pda)]_n$ (**1**) (H_2tdpd = 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile, pda = 1,2-phenylenediamine) has been synthesized and characterized. Compound **1** is a linear chain of copper(II) ions bridged by $tdpd^{2-}$ dianion with terminal pda ligand. Magnetic susceptibility measurement shows antiferromagnetic couplings between the copper(II) ions.

Keywords coordination polymer; copper; pyrazine derivative

INTRODUCTION

The formation of coordination networks constructed from *exo* ligands (ligands with coordination sites outwardly oriented) and metal cations are currently attracting much attention. The formation of such networks may take place in the crystalline phase through self-assembly processes based on the reversible coordination of metal cations by *exo* ligands. The iterative binding process leads to the assembling cores acting as structural nodes of the network. The dimensionality of coordination networks is defined by the number of translation operating on the assembling core. The dimensionality depends, on one hand, on the topological and coordination features of the organic *exo* ligand and, on the other hand, on the stereochemical requirements of the metal. Although the majority of reported coordination networks are formed using bis-monodentate *exo* ligands such as pyrazine or 4,4'-bipyridine,[1] examples coordination networks formed by polydentate ligands have been published.[2]

The construction of novel networks based on coordination compounds requires a careful selection of the polydentate ligand. We have focused on the pyrazine derivative 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile (H_2tdpd). The $tdpd^{2-}$ dianion is a potentially hexadentate ligand. We have previously shown that it can construct coordination polymers with triangular and rectangular lattices by coordination bonds.[3]

Following our work in this field we report the synthesis and characterization of novel one-dimensional $tdpd^{2-}$ derivatives with formula $[Cu(tdpd)(pda)]_n$ (**1**) (pda = 1,2-phenylenediamine). The use of the bidentate pda ligand helps stabilize the one-dimensional systems.

EXPERIMENTAL

Synthesis of $[Cu(tdpd)(pda)]_n$ (**1**)

An aqueous solution (10 ml) of copper(II) acetate monohydrate (1 x 10^{-4} mol) and H_2tdpd (1 x 10^{-4} mol) was transferred to a glass tube, and then an ethanolic solution (5 ml) of pda (1 x 10^{-4} mol) was poured into

the tube without mixing the two solutions. Green plate crystals began to form in one week. One of these crystals was used for X-ray crystallography. Physical measurements were conducted on a polycrystalline powder that was synthesized as follows: an aqueous solution (100 ml) of copper acetate monohydrate (1×10^{-3} mol) and H_2tdpd (1×10^{-3} mol) was added to a 1×10^{-3} mol amount of pda dissolved in an ethanol (50 ml). Upon stirring the mixture, the green powder appeared immediately. The identity of the magnetic and X-ray batches has been confirmed by their powder X-ray diffraction patterns. Crystal data: $C_{12}H_8CuN_6O_2$, monoclinic, $P2_1/a$ (no. 14), $a = 9.7929(5)$, $b = 11.1946(6)$, $c = 11.4320(4)$ Å, $\beta = 92.321(4)°$, $U = 1252.24(9)$ Å^3, $Z = 4$, green plate crystal (0.30 x 0.30 x 0.10 mm), 2851 total reflections ($2\theta_{max} = 148.66°$), 2307 observed [$I > 2\sigma(I)$], 190 variables, $R = 0.044$, $wR_2 = 0.124$, goodness of fit = 1.10. Diffraction data were collected on an Enraf Nonius CAD-4 diffractometer equipped with graphite-monochromated Cu-Kα radiation. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation) and refined with full-matrix least-squares technique (SHELXL-93).[4]

Physical Measurements

The magnetic susceptibility data were recorded over the temperature range from 2 to 300 K at 0.5 T with a SQUID susceptometer (Quantum Design. San Diego, CA). All data were corrected for diamagnetism which was calculated from Pascal's constants. The temperature-independent paramagnetism was assumed to be 60×10^{-6} cm^3·mol^{-1}.

RESULTS AND DISCUSSION

Description of the Structure

An ORTEP drawing of the structure around the copper atom in **1** with the atom numbering scheme is shown in Figure 1(a). The copper atom displays a five-coordinate square-pyramidal configuration with two

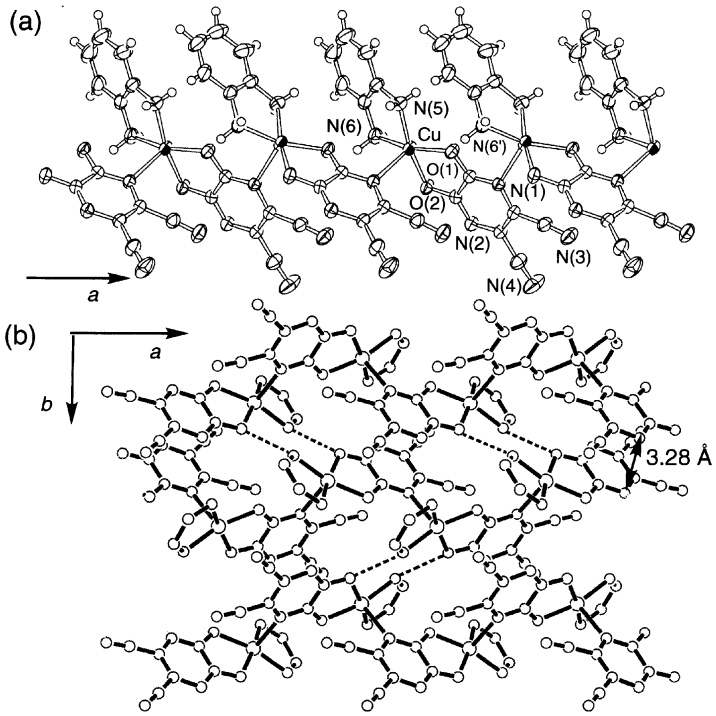

FIGURE 1 Crystal structure of compound **1**: (a) labeling scheme (ORTEP, 50% probability); (b) view of the two-dimensional structure on the *ab* plane. Hydrogen atoms and aromatic rings of pda are omitted for clarity. Dashed lines represent hydrogen bonds.

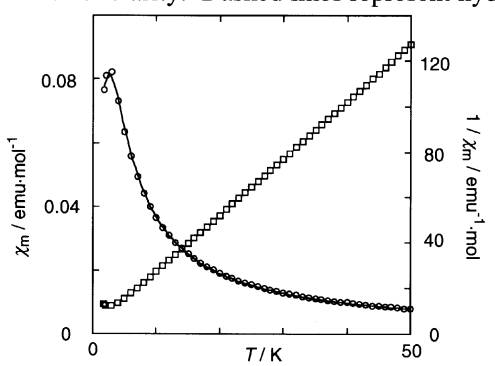

FIGURE 2 Plot of the temperature dependence of χ_m and $1/\chi_m$ for compound **1**. Solid curves represent the best fit to Heisenberg type chain mobel with interchain interactions.

equatorial nitrogen atoms of pda molecule and two oxygen atoms of tdpd^{2-} dianion and one apical nitrogen atom of another tdpd^{2-} dianion (Cu-O(1) 1.966(2); Cu-O(2) 1.952(2); Cu-N(5) 1.991(2); Cu-N(6) 2.006(2); Cu-N(1') 2.440(2) Å). The copper atom deviates by 0.26 Å from the basal plane of two nitrogen and two oxygen atoms. The percentage of trigonal distortion from square pyramidal geometry is described by the parameter τ, defined as $[(\alpha - \beta) / 60] \times 100$, where α and β are angles between the donor atoms forming the plane in a square pyramidal geometry ($\tau = 0$ for an ideal square-pyramidal geometry, while $\tau = 100$ % for the ideal trigonal bipyramidal geometry).[5] The τ parameter for complex **1** (9.0 %) indicates, indeed, that the coordination geometry at the copper atoms is best described as distorted square pyramidal. The tdpd^{2-} dianions bind the two metal ions through O(1), O(2) and N(1). These units self-assemble to form one-dimensional chains. The pda ligand acts as a bidentate ligand. Of particular interest in this structure is the presence of an extended network of intrachain hydrogen bonds enhancing the stability of the one-dimensional chain. There are the hydrogen bonds between the nitrogen atom of the pda ligand and the coordinated oxygen atom of tdpd^{2-} dianion (O(1)-N(6'), 3.00 Å) (Figure 1(a)). The one-dimensional chain is connected by hydrogen bonds (O(2)-N(6'), 3.00 Å) and π-π stacking interactions (N(1)-N(2'), 3.28 Å), forming two-dimensional sheets (Figure 1(b)).

Magnetic Properties

The magnetic susceptibility of **1** was measured over the temperature of 2-300 K (Figure 2). The χ_m decreases at lower temperature. The plot of $1/\chi_m$ vs. T obeys the Curie-Weiss law with a negative Weiss constant of $\theta = -2.1$ K, indicating a weak antiferromagnetic interaction in the chain. The data were analyzed by using the Heisenberg linear chain theory to give $J = -1.6$ cm^{-1} and $g = 2.18$. The computed curve dose not give a satisfactory match to the experimental data. The fact suggests that significant interchain interactions through the hydrogen bonds and π-π stacks are operative. In order to take them into account, we have incorporated a standard mean-field correction.[6] A good fit is achieved

when interchain interactions (J') are considered in the Heisenberg type chain expression : the values of J, J', and g are -1.9 cm^{-1}, 1.8 cm^{-1}, and 2.04, respectively. The fit is not good enough to take them as realistic values, but these values are indicative of the relative strength of the interactions.

CONCLUSION

In this study, we have synthesized novel one-dimensional copper(II) coordination polymer bridged by the $tdpd^{2-}$ dianions. The presence of an extended network of intrachain hydrogen bonds enhances the stability of the one-dimensional chain. The thermal variation of the magnetic susceptibility has been interpreted in terms of the occurrence of antiferromagnetic coupling between the copper(II) ions.

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