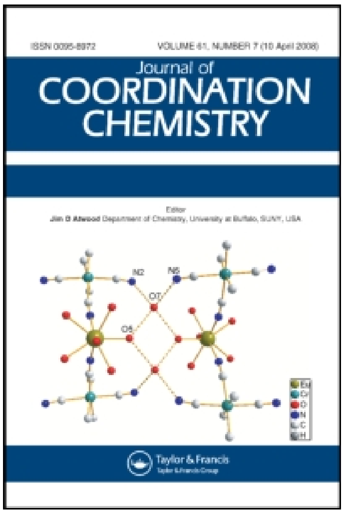

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and magnetic property of a one-dimensional copper(II) complex with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand

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To cite this Article Shi, Jing-Min , Zhang, Xia , Wu, Chang-Ju , Shi, Wei and Liu, Lian-Dong(2007) 'Synthesis, crystal structure and magnetic property of a one-dimensional copper(II) complex with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand', Journal of Coordination Chemistry, 60: 17, 1827 — 1832

To link to this Article: DOI: 10.1080/00958970701194082

URL: http://dx.doi.org/10.1080/00958970701194082

Journal of Coordination Chemistry
Vol. 60, No. 17, September 2007, 1827–1832

Synthesis, crystal structure and magnetic property of a one-dimensional copper(II) complex with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand

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(*Received 19 September 2006; revised 28 October 2006; in final form 30 November 2006*)

A one-dimensional polynuclear copper(II) complex $[Cu(\mu_{1,6}\text{-dmpzdo})(SCN)_2]_n$ (where dmpzdo = 2,5-dimethylpyrazine-1,4-dioxide) has been synthesized and its crystal structure determined by X-ray crystallography. The coordination geometry of Cu(II) atom is a square plane and each Cu(II) ion is connected by two $\mu_{1,6}$-dmpzdo bridging ligands, leading to the formation of a one-dimensional chain. ESR spectra indicate magnetic coupling between the bridged Cu(II) ions. The fitting of the variable-temperature magnetic susceptibility data (4–300 K) gave $2J = -68.69\,\text{cm}^{-1}$.

Keywords: Synthesis; Crystal structure; Copper(II) complex; Magnetic property

1. Introduction

Molecular magnetism attracts attention for molecular-based magnets and understanding biological function of some metallic proteins. Major advances have been made in theoretical study and application as new molecular-based materials [1].

To obtain strong magnetic coupling, judicious choice of coordinated atoms with large electron densities is crucial. Theoretical calculation has confirmed that electron densities of the O atom from aromatic N-oxides are larger than those of the N atom from the relevant N-containing heteroaromatics [2]. Pyrazine1,4-dioxide and its derivatives are such bridging ligands with O-donor atoms possessing larger electron density than the N-donor of pyrazine and its derivatives. The 3D complex $[Mn(N_3)_2(pzdo)]_n$ containing pyrazine-1,4-dioxide as bridging ligand [3] has displayed strong magnetic coupling. Among the reported complexes dealing with pyrazine-1,4-dioxide and its derivatives as bridging ligands are the binuclear Mn(II) complex [4], 1D Mn(II) complex [4], 2D Mn(II) and 2D Co(II) complexes [4, 5], 3D Co(II) complexes [6], 3D rare earth complexes [7] and a 1D Cu(II) complex [8]. Interest in the magneto-structural studies of

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701194082

multi-nuclear complexes with aromatic N-oxide as bridging ligands resulted in our synthesizing a few relevant complexes [9, 10]. In this article we present the crystal structure and the magnetic study of the new one-dimensional chain complex [Cu($\mu_{1,6}$-dmpzdo)$(SCN)_2]_n$.

2. Experimental

2.1. *Preparation*

2,5-Dimethylpyrazine-1,4-dioxide was prepared from 2,5-dimethylpyrazine by the literature method [10]; other chemicals are analytical grade and used without further purification.

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.2440 g, 6.59×10^{-4} mol) and dmpzdo (0.0923 g, 6.59×10^{-4} mol) were dissolved in 8 mL H_2O and the two solutions were mixed. The mixed solution was put into one side of an H-tube, and then NaSCN (0.1068 g, 1.32×10^{-3} mol) was dissolved in 20 mL methanol and placed in the other side of the H-tube. Deep brown single crystals were obtained after the mixed solution was allowed to stand for one month at room temperature (found: C 30.25, H 2.19, N 17.62, Cu 19.55%. $C_8H_8CuN_4O_2S_2$ requires C 30.04, H 2.52, N 17.52, Cu 19.87%).

2.2. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 10 KOe in the temperature range of 4–300 K on a SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

2.3. *X-ray crystal structure determination*

The determination of the crystal structure at 25°C was carried out on an X-ray diffractometer, Bruker Smart-1000 CCD using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). A crystal with dimensions $0.21 \times 0.12 \times 0.10\ mm^3$ were selected and subsequently glued to the tip of a glass fiber. Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). The crystal belongs to monoclinic space group $P2_1/c$ with $a = 5.7396(11)$ Å, $b = 14.607(3)$ Å, $c = 6.9028(14)$ Å, $\beta = 98.925(3)^\circ$, $V = 571.7(2)$ Å^3, $Z = 2$, empirical formula $C_8H_8CuN_4O_2S_2$, molecular weight 319.845, $D_c = 1.858\ g\,cm^{-3}$, $F(000) = 322$, θ range 2.79–27.04°, completeness = 0.986. A total of 3347 reflections were collected and 1241 were independent ($R_{int} = 0.025$), of which 1061 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final refinement including hydrogen atoms converged to $R=0.0412$, $wR=0.1052$, the goodness-of-fit $S=1.094$, $(\Delta\rho)_{\max}=0.610\,\mathrm{e\,Å^{-3}}$, $(\Delta\rho)_{\min}=-0.366\,\mathrm{e\,Å^{-3}}$ and $(\Delta/\sigma)=0.000$. The deposition number of the crystal at the CCDC is 253121.

3. Results and discussion

3.1. *Infrared spectrum*

The peaks at 2111 and 2101 $\mathrm{cm^{-1}}$ are from vibrations of thiocyanate ligand, while the peaks at 1665, 1625 and 1401 $\mathrm{cm^{-1}}$ may be attributed to the vibrations of the C=N and C=C bonds of pryrazine.

3.2. *Crystal structure*

Figure 1 shows the coordination diagram for the complex with the atom numbering scheme. It displays that atom Cu1 is coordinated by O1, O1A, N2 and N2A atoms, in which N2 and N2A atoms are from two $\mathrm{NCS^-}$ terminal ligands and O1 and O1A atoms come from two bridging ligands and atom Cu1 lies on an inversion center. The coordination data, bond lengths: Cu1–N2, 1.915(3) Å and Cu1–O1, 2.032(3) Å, and the associated angles: N2–Cu1–O1, 91.90(11)° and N2–Cu1–O1A, 88.10(11)°, indicate that Cu1 is a slightly distorted square-planar coordination environment, and Cu1 and its associated four coordinated atoms are strictly located on a plane. Figure 1 also displays that each dmpzdo coordinates to two Cu(II) ions with Cu(II)$\cdots$Cu(II) separation of 8.264 Å forming a one-dimensional chain. All non-hydrogen atoms of dmpzdo are located on a plane, and the dihedral angle between the square plane and dmpzdo plane is 99°, almost perpendicular to each other. Comparing the coordination parameters with those of the reported 1D complex $\{[\mathrm{Cu}(\mu_{1,6}\text{-dmpzdo})(\mathrm{dmpzdo})_2]\cdot(\mathrm{ClO_4})_2\}_n$, the Cu–O bridge bond length and the separation of Cu$\cdots$Cu(II) in the present complex is shorter than that of the 1D Cu(II) complex, and there is the difference of the dihedral angles mentioned above.

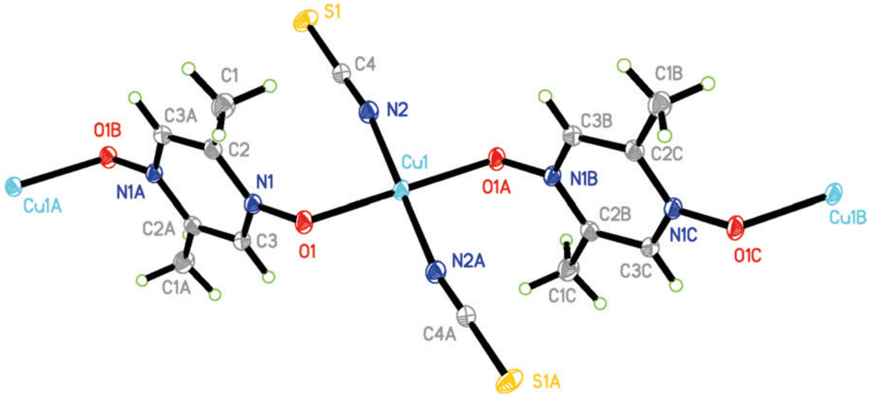

Figure 1. Coordination diagram of the title complex with the atom numbering scheme.

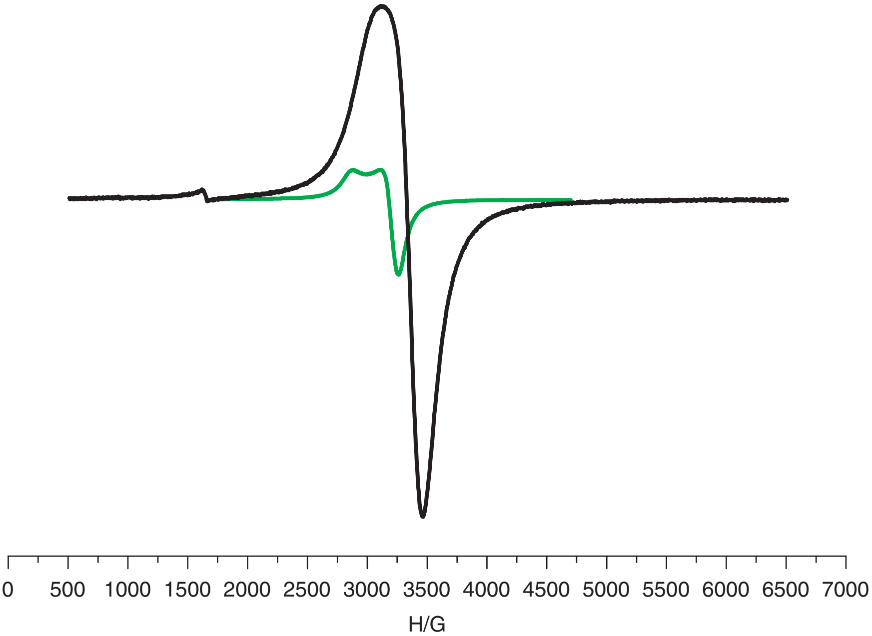

Figure 2. ESR spectra of the title complex at room temperature (black curve) and at 77 K (green curve).

3.3. *ESR spectra*

Polycrystalline powder ESR spectra of this complex were recorded in X-band at both room temperature and 77 K and are shown in figure 2. At room temperature two bands are observed and one corresponds to the transition $\Delta M_s = \pm 1$, located at $g_\| = 2.18$ (3110 Gauss), $g_\perp = 1.96$ (3462 Gauss). The other very weak band appears at about 1600 Gauss, which is attributed to the $\Delta M_s = \pm 2$ forbidden transitions and the appearance of the half-field band confirms a magnetic interaction between the bridged copper(II) ions [12, 13]. At 77 K two close neighboring bands are also observed at 2885 Gauss and 3122 Gauss and the two bands are attributed to the transitions $\Delta M_s = \pm 1$. This phenomenon has been observed in one-dimensional Cu(II) complexes [14].

3.4. *Magnetic property*

Figure 3 shows the plots of χ_M *versus* T and μ_{eff} *versus* T for the complex, where χ_M is the molar magnetic susceptibility per mononuclear unit, and μ_{eff} is the magnetic moment per Cu(II) ion; the data have been corrected for diamagnetism. At room temperature μ_{eff} is 1.61 μ_B which is slightly smaller than the expected value for an isolated Cu(II) ion (1.73 μ_B for $g_{\text{av}} = 2$). The μ_B value decreases gradually with decreasing temperature from 1.61 μ_B at 300 K, reaching a minimum 0.33 μ_B at 5 K. This magnetic behavior indicates an anti-ferromagnetic interaction between the μ-dmpzdo bridged Cu(II) ions. In order to evaluate the coupling intensity the experimental magnetic data have been fitted using uniform one-dimensional equation (2),

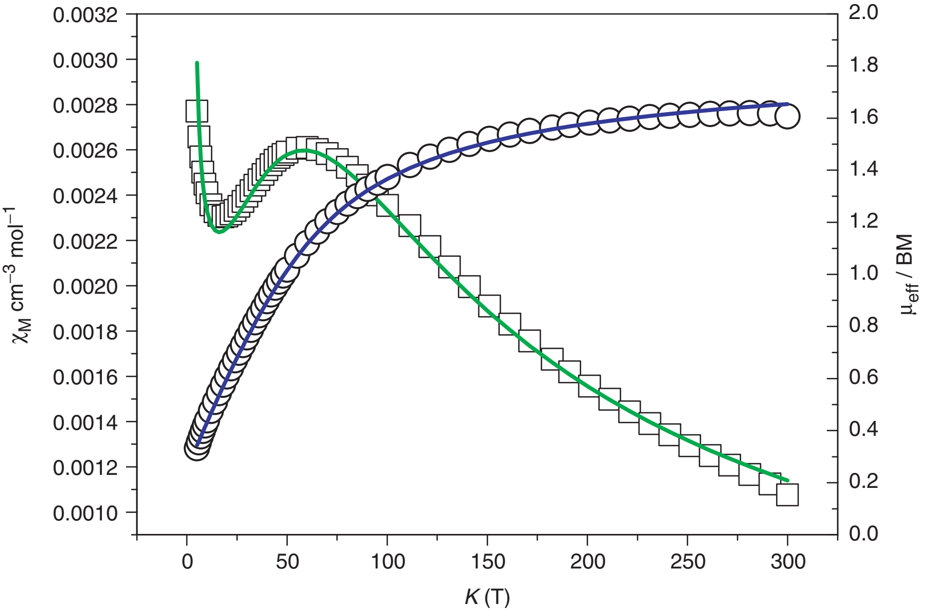

Figure 3. Plots of χ_M (open square for experimental data, green line for the fitted value) and μ_{eff} (open circle for experimental data, blue line for the fitted value) *vs.* *T*.

derived from the Bonner–Fisher calculation [15] based on the isotropic Heisenberg Hamiltonian (1):

$$\hat{H} = -2J\,\Sigma\,\hat{S}_{\mathrm{Cui}}\hat{S}_{\mathrm{Cui+1}} \tag{1}$$

$$\chi_{\mathrm{M}} = \left[\frac{Ng^2\beta^2}{\kappa T - J'}\right]\frac{[A + Bx^2]}{[1 + Cx + Dx^3]} \tag{2}$$

$$A = 0.2500;\ B = 0.18297;\ C = 1.5467;\ D = 3.4443$$
$$x = -J/\kappa T$$

where J is the Heisenberg exchange constant between the $\mu_{1,6}$-dmpzdo bridged copper(II) ions, $\hat{S}_{\mathrm{Cui}}$ and $\hat{S}_{\mathrm{Cui+1}}$ are spin operators corresponding to Cu(II), J' is the magnetic coupling of the non-bridged Cu(II) ions. The theoretical model gave a good fit with the experimental results. The agreement factors are $R = 4.3 \times 10^{-4}$ [R is defined as $R = \Sigma(\chi_{\mathrm{obsd.}} - \chi_{\mathrm{Calcd}})^2/(\chi_{\mathrm{obsd.}})^2$], $g = 2.12$, $2J = -68.69\,\mathrm{cm}^{-1}$, $J' = 1.91\,\mathrm{cm}^{-1}$. The $2J$ value suggests that there exists a moderate anti-ferromagnetic interaction between the $\mu_{1,6}$-dmpdzo bridged copper(II) ions. The absolute $2J$ value of the present complex is smaller than that ($2J = -98.88\,\mathrm{cm}^{-1}$) of $\{[\mathrm{Cu}(\mu_{1,6}\text{-dmpzdo})(\mathrm{dmpzdo})_2]\cdot(\mathrm{ClO_4})_2\}_n$ [8], which may be attributed to the different structural factors. Compared with complexes with pyrazine as bridging ligand, the distance between the bridged Cu(II) ions in this complex is larger [16–18], and the magnetic interaction of the present complex is larger than that of the Cu(II) complexes with pyrazine as a bridging ligand.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20271043) and the Natural Science Foundation of Shandong Province of China (Y2005B25).

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