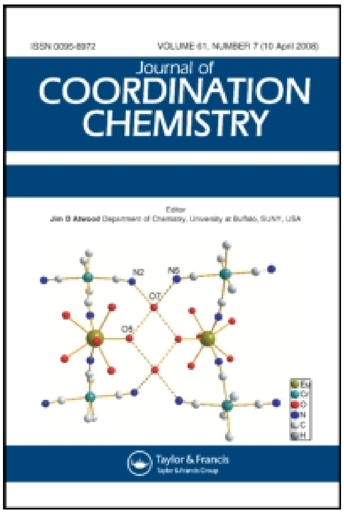

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Synthesis, crystal structure and magnetism study on a three-dimensional Co(II) coordination polymer with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand

J.-M. Shi[a]; F.-X. Zhang[a]; C.-J. Wu[a]; L. Yi[b]; J.-P. Ma[a]
[a] Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China [b] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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Synthesis, crystal structure and magnetism study on a three-dimensional Co(II) coordination polymer with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand

J.-M. SHI*†, F.-X. ZHANG†, C.-J. WU†, L. YI‡ and J.-P. MA†

†Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China
‡Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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A three-dimensional Co(II) coordination polymer, $\{[Co(\mu_{1,6}\text{-dmpzdo})_3]\cdot(ClO_4)_2\}_n$, has been synthesized with 2,5-dimethylpyrazine-1,4-dioxide (dmpzdo) as bridging ligand and its crystal structure determined by X-ray crystallography. The complex crystallizes in a trigonal system with a space group *R*-3 and $a = 11.5935(10)$, $b = 11.5935(10)$, $c = 16.344(3)$ Å. In the complex each Co(II) is coordinated by six $\mu_{1,6}$-dmpzdo bridging ligands and each $\mu_{1,6}$-dmpzdo bridging ligand coordinates two Co(II) ions; in this way a three-dimensional structure was formed. The variable temperature (4–300 K) magnetic moment data imply that a weak anti-ferromagnetic coupling between $\mu_{1,6}$-dmpzdo bridged Co(II) ions exists.

Keywords: Magnetism; Crystal structure; Multi-nuclear complex; Pyrazine N-oxide

1. Introduction

Molecular magnetism has attracted considerable attention because it contributes to the understanding of the biological function of some metallic proteins and is also relevant to the preparation of molecular-based magnets [1, 2].

In order to obtain strong magnetic coupling judicious choice of coordinated atoms with large electron densities is crucial. Theoretical calculations have confirmed that the electron densities on the O atom of aromatic N-oxides are larger than those of the N atom from the relevant N-containing heteroaromatics [3]. Pyrazine1,4-dioxide and its derivatives are such bridging ligands and its O-donor atoms possess larger electron density than that of the N-donor atom of pyrazine and its derivatives, leading to strong magnetic interactions in the 3D complex $[Mn(N_3)_2(pzdo)]_n$ containing pyrazine-1,4-dioxide and azido as mixed bridging ligands [4]. The reported complexes dealing with pyrazine-1,4-dioxide and its derivatives as bridging ligands include binuclear Mn(II) complex [5], 1D Mn(II) complex [5], 2D Mn(II) and 2D Co(II) complexes [5, 6], 3D Co(II) complexes [7] and 3D rare earth complexes [8].

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*Corresponding author. Tel.: 86-531-86180743. Fax: 86-531-86180017. Email: shijingmin@beelink.com

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We have interest in magneto-structural studies of multi-nuclear complexes with pyrazine-1,4-dioxide and its derivatives as bridging ligands and have synthesized a series of complexes [9] and studied their magnetism. In this article, we present the crystal structure and the magnetic study of the three-dimensional net complex $\{[Co(\mu_{1,6}\text{-dmpzdo})_3]\cdot(ClO_4)_2\}_n$.

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.

The three-dimensional complex $\{[Co(\mu_{1,6}\text{-dmpzdo})_3]\cdot(ClO_4)_2\}_n$ was prepared as follows: Dmpzdo (0.2632 g, 1.88×10^{-3} mol) in 5 mL H_2O was added into 10 mL CH_3CN containing $Co(ClO_4)2\cdot6H_2O$ (0.2467 g, 6.74×10^{-4} mol) and the solution was stirred for a few minutes. Red single crystals were obtained after the solution was allowed to stand for one week at room temperature (Yield: 82%). Anal. Calcd for $C_{18}H_{24}Cl_{l2}CoN_6O_{14}$ (Fw: 678.26): C, 31.87; H, 3.57; N, 12.39; Co, 8.69%. Found: C, 31.95; H, 3.81; N, 12.75; Co, 8.98%.

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 susceptibility measurements were performed using a crushed single crystal sample in the temperature range of 4–300 K with a SQUID magnetometer and applied magnetic field of 3 K Oe. 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*

A single crystal of dimensions $0.27\times0.23\times0.16$ mm was selected and subsequently glued to the tip of a glass fiber. Determination of the crystal structure at 25°C was carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD using graphite-monochromatic Mo-Kα radiation ($\lambda=0.71073$ Å). Corrections for *Lp* factor 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 deposition number at the CCDC is 283719. The relevant structure parameters are given in table 1.

Table 1. Crystal data and structure refinement of the complex.

Empirical formula	$C_{18}H_{24}Cl_2CoN_6O_{14}$
CCDC deposit no.	283719
Formula weight	678.26
Temperature (K)	298
Crystal size (mm^3)	$0.27 \times 0.23 \times 0.16$
Crystal system	Trigonal
Space group	*R*-3
a (Å)	11.5935(10)
b (Å)	11.5935(10)
c (Å)	16.344(3)
α (°)	90.00
β (°)	90.00
γ (°)	120.00
Volume ($Å^3$)	1902.5(4)
Z	3
Density (Calcd) ($Mg\,m^{-3}$)	1.776
Absorption coefficient (mm^{-1})	0.971
θ_{min}, θ_{max} (°)	2.3805, 27.600
Completeness (%)	0.992 ($\theta = 27.00°$)
Goodness-of-fit on F^2	1.067
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0301$, $wR_2 = 0.0784$
R indices (all data)	$R_1 = 0.0313$, $wR_2 = 0.0791$
$(\Delta/\sigma)_{max}$	0.000
Largest diff. peak and hole ($e\,Å^{-3}$)	0.326, −0.211

3. Results and discussion

3.1. *Infrared spectrum*

The peaks at 1639, 1617, 1527, 1454 and 1362 cm^{-1} may be attributed to the vibrations of the C=N and C=C bonds of pryrazine rings, whereas the strong and broad band for perchlorate ion appeared at 1147 and 1088 cm^{-1}.

3.2. *Crystal structure*

3.2.1. Crystal data. $C_{18}H_{24}Cl_2CoN_6O_{14}$, $M = 678.26$, trigonal, space group *R*-3, $a = 11.5935(10)$, $b = 11.5935(10)$, $c = 16.344(3)$ Å, $Z = 3$, $V = 1902.5(4)$ $Å^3$, $D_c = 1.776\,g\,cm^{-3}$, $F(000) = 1041$, $\mu(\text{Mo-K}\alpha) = 0.971\,mm^{-1}$. Selected bond distances and the associated angles are listed in table 2.

3.2.2. Crystal structure. Figure 1 shows the coordination diagram of the complex with atom numbering scheme and table 2 gives the data dealing with the bond lengths and the associated angles. Co1 is coordinated by six O atoms which come from six $\mu_{1,6}$-dmpzdo ligands and the coordination geometry is slightly distorted octahedron. Each Co(II) is surrounded by six Co(II) ions with the separation distance 8.630 Å and adjacent Co(II) ions with this distance are joined by $\mu_{1,6}$-dmpzdo bridge ligand, and which forms a three-dimensional structure. In *a* and *b* directions there exist microporous channels, and the perchlorate counter anions are trapped in the channels by Coulomb forces as shown in figure 2. The structure of this complex is almost

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Co1–O1	2.0935(12)		
O1C–Co1–O1A	92.40(5)	O1–Co1–O1C	87.60(5)
O1B–Co1–O1A	87.60(5)	O1B–Co1–O1	92.4(5)
O1D–Co1–O1A	87.60(5)	O1D–Co1–O1C	87.60(5)
O1D–Co1–O1	92.40(5)	O1D–Co1–O1B	92.40(5)
O1E–Co1–O1A	92.40(5)	O1E–Co1–O1C	92.40(5)
O1E–Co1–O1	87.60(5)	O1E–Co1–O1B	87.60(5)

Symmetry codes: (A): $-x+2/3$, $-y+4/3$, $-z+1/3$; (B): $-y+1$, $x-y+1$, z; (C): $y-1/3$, $-x+y+1/3$, $-z+1/3$; (D): $-x+y$, $-x+1$, z; (E): $x-y+2/3$, $x+1/3$, $-z+1/3$.

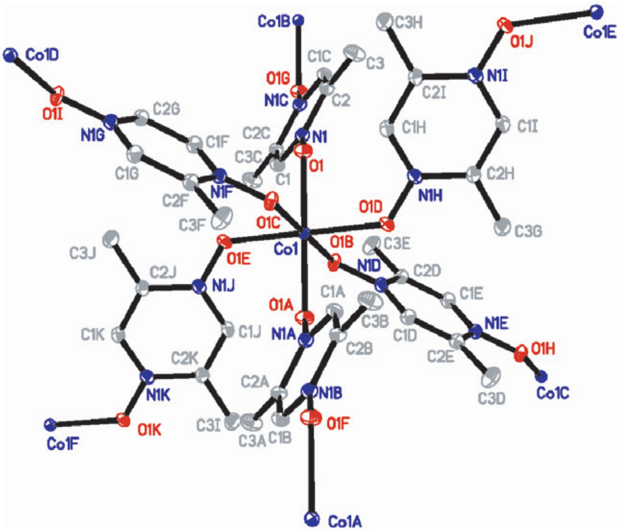

Figure 1. Coordination diagram of the complex with the atom numbering scheme.

identical with that of $\{[Mn(\mu_{1,6}\text{-dmpzdo})_3]\cdot(ClO_4)_2\}_n$ [11] except for minor differences in unit cell dimensions.

3.3. *Magnetism*

The magnetic moment value of the complex at 298.8 K is 4.65 μ_B per Co(II) unit, larger than that of mononuclear Co(II) at room temperature. The magnetic moment values decrease with decreasing temperature and reach a minimum of 3.35 μ_B at 5.05 K as shown in figure 3, indicating that there is antiferromagnetic coupling between the bridged Co(II) ions. Because no fitting model or fitting formula is available for three-dimensional Co(II) complexes, the variable-temperature susceptibility data were fitted to the Curie–Weiss law with $C = 2.76\,\text{cm}^3\,\text{mol}^1$ and $\theta = -8.35$ K; when the data were fitted with a binuclear Co(II) formula it gave $J = -1.64\,\text{cm}^{-1}$. All of these indicate that there is a weak antiferromagnetic interaction between the bridged Co(II) ions.

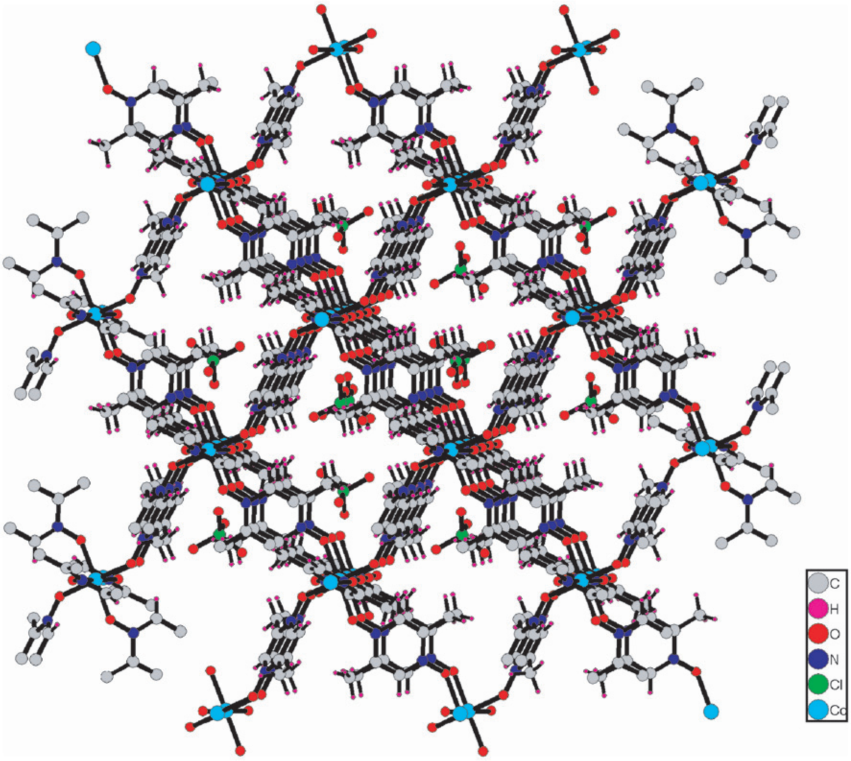

Figure 2. The channels of the crystal, viewed from *b* direction.

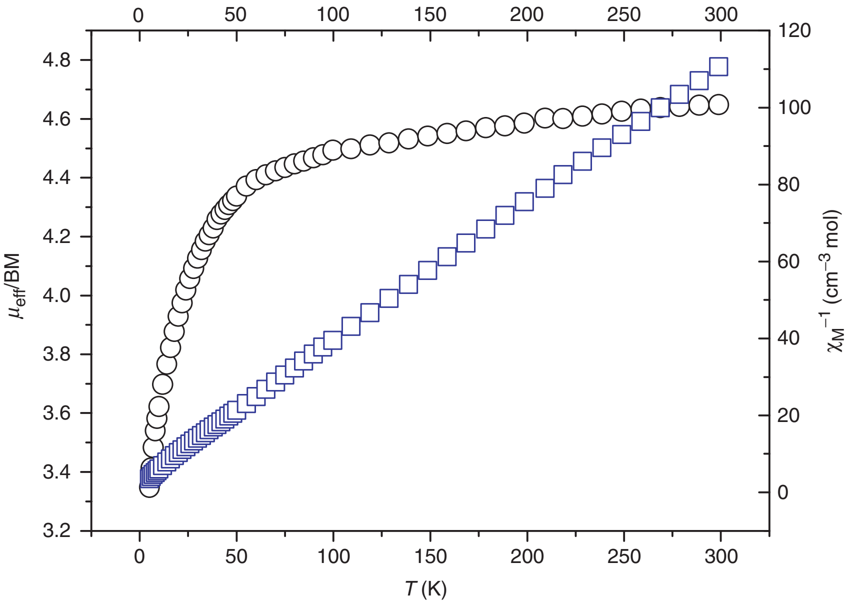

Figure 3. Plots of μ_{eff} (open black circle for the experimental values) and χ_M^{-1} (open blue square) *vs*. T for the complex.

Acknowledgments

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