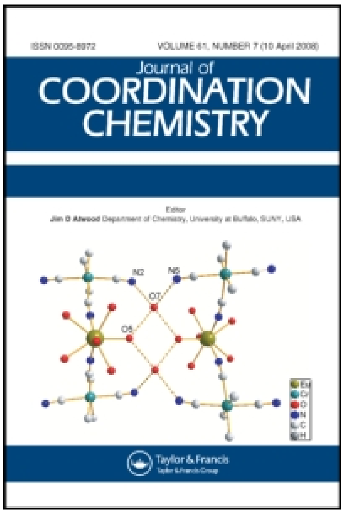

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and magnetism of a three-dimensional Mn(II) coordination polymers 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]; L.-D. Liu[a]
[a] Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China [b] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

To cite this Article Shi, J.-M. , Zhang, F.-X. , Wu, C.-J. , Yi, L. and Liu, L.-D.(2007) 'Synthesis, crystal structure and magnetism of a three-dimensional Mn(II) coordination polymers with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand', Journal of Coordination Chemistry, 60: 14, 1473 — 1478

To link to this Article: DOI: 10.1080/00958970701429629

URL: http://dx.doi.org/10.1080/00958970701429629

Journal of Coordination Chemistry
Vol. 60, No. 14, 15 July 2007, 1473–1478

Taylor & Francis
Taylor & Francis Group

Synthesis, crystal structure and magnetism of a three-dimensional Mn(II) coordination polymers with 2,5-dimethylpyrazine-1,4-dioxide as bridging ligand

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

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

(*Received 24 April 2006; revised 11 June 2006; in final form 13 June 2006*)

A novel three-dimensional Mn(II) coordination polymer, $\{[\mathrm{Mn}(\mu_{1,6}\text{-dmpzdo})_3]\cdot(\mathrm{ClO}_4)_2\}_n$, has been synthesized with 2,5-dimethylpyrazine-1,4-dioxide (dmpzdo) as a 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 $a = 11.6672(14)$, $b = 11.6672(14)$, $c = 16.652(4)$ Å. In the complex each Mn(II) is coordinated by six $\mu_{1,6}$-dmpzdo bridging ligands and each $\mu_{1,6}$-dmpzdo bridging ligand coordinates two Mn(II) ions, forming a three-dimensional structure. The variable temperature (4–300 K) magnetic susceptibility data gave the magnetic coupling constant $2J = -0.30\,\mathrm{cm}^{-1}$.

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

1. Introduction

Molecular magnetism has attracted considerable attention, and major advances have been made in theoretical description and application as new molecular-based materials [1]. Special attention has been paid to the design and construction of coordination polymers to study their magnetic properties and develop high T_c molecular-based magnets [2].

In order to obtain strong magnetic coupling judicious choice of coordinated atoms with large electron densities is crucial. Calculation has confirmed that the electron densities on the O atom from aromatic N-oxides are larger than those of the N atom from the relevant N-containing heteroaromatics [3]. Pyrazine-1,4-dioxide and its derivatives are such bridging ligands and the O-donor atoms possess larger electron density than the N-donor atom of pyrazine and its derivatives; strong magnetic interactions in the 3D complex $[\mathrm{Mn}(\mathrm{N}_3)_2(\mathrm{pzdo})]_n$ containing pyrazine-1,4-dioxide and azido as mixed bridging ligand have been reported [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],

---

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

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701429629

3D Co(II) complexes [7] and 3D rare earth complexes [8], but no three-dimensional Mn(II) complex has been published. Interest in the magneto-structure studies of multinuclear complexes with pyrazine-1,4-dioxide and its derivatives as bridging ligands resulted in synthesis, characterization and magnetic study of the title complex. In this paper we present the crystal structure and the magnetic study of the three-dimensional complex $\{[\mathrm{Mn}(\mu_{1,6}\text{-dmpzdo})_3]\cdot(\mathrm{ClO}_4)_2\}_n$.

2. Experimental

2.1. *Preparation*

2,5-Dimethylpyrazine-1,4-dioxide was prepared from the 2,5-dimethylpyrazine by the literature method [9]; other chemicals are analytical grade and used without further purification.

The three-dimensional complex $\{[\mathrm{Mn}(\mu_{1,6}\text{-dmpzdo})_3]\cdot(\mathrm{ClO}_4)_2\}_n$ was prepared as follows: Dmpzdo (0.2745 g, 1.96×10^{-3} mol) in 5 mL H_2O was added into a 10 mL CH_3CN solution containing $\mathrm{Mn(ClO_4)_2\cdot 6H_2O}$ (0.2403 g, 6.64×10^{-4} mol) and the mixed solution was stirred for a few minutes; orange single crystals were obtained after the solution was allowed to stand for one week at room temperature (Yield: 85%). Anal. Calcd for $C_{18}H_{24}Cl_2MnN_6O_{14}$ (Fw: 674.27): C, 32.06; H, 3.59; N, 12.47; Mn, 8.15%. Found: C, 32.19; H, 3.75; N, 12.59; Mn, 8.69%.

2.2. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 $\mathrm{cm^{-1}}$ 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 $0.29\times0.25\times0.18\ \mathrm{mm^3}$ 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, Bruker Smart-1000 CCD, using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Correction for *Lp* factor was 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 of the crystal at CCDC is 278004. The relevant structure parameters are given in table 1.

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

Empirical formula	$C_{18}H_{24}Cl_2MnN_6O_{14}$
CCDC deposit no.	278004
Formula weight	674.273
Temperature (K)	298
Crystal size (mm^3)	$0.29 \times 0.25 \times 0.18$
Crystal system	Trigonal
Space group	*R*-3
a (Å)	11.6672(14)
b (Å)	11.6672(14)
c (Å)	16.652(4)
α (°)	90.00
β (°)	90.00
γ (°)	120.00
Volume (Å^3)	1963.1(6)
Z	3
Density (calculated) ($Mg\,m^{-3}$)	1.711
Absorption coefficient (mm^{-1})	0.790
θ_{min}, θ_{max} (°)	2.36, 25.35
Completeness (%)	1.00 ($\theta = 25.35°$)
Goodness-of-fit on F^2	1.19
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.1017$
R indices (all data)	$R_1 = 0.0478$, $wR_2 = 0.1027$
$(\Delta/\sigma)_{max}$	0.000
Largest diff. peak and hole (e Å^{-3})	0.316, −0.217

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

Mn1–O3	2.1665(19)		
O3B–Mn1–O3A	86.25(7)	O3–Mn1–O3B	93.75(7)
O3D–Mn1–O3C	86.24(7)	O3D–Mn1–O3A	86.24(7)
O3D–Mn1–O3B	93.75(7)	O3d–Mn1–O3	93.75(7)
O3E–Mn1–O3C	93.75(7)	O3E–Mn1–O3A	93.75(7)
O3E–Mn1–O3B	86.25(7)	O3E–Mn1–O3	86.25(7)
O1E–Co1–O1B	87.60(5)	O3A–Mn1–O3C	93.75(7)

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

3. Results and discussion

3.1. *Infrared spectrum*

The peaks at 1641, 1614, 1523, 1453 and 1362 cm^{-1} may be attributed to the vibrations of the C=N and C=C bonds of pryrazine rings, and the strong and broad bands for perchlorate appeared at 1145, 1116 and 1086 cm^{-1}.

3.2. *Crystal structure*

3.2.1. Crystal data. $C_{18}H_{24}Cl_2MnN_6O_{14}$, M = 674.27, trigonal, space group *R*-3, $a = 11.6672(14)$ Å, $b = 11.6672(14)$ Å, $c = 16.652(4)$ Å, $Z = 3$, $V = 1963.1(6)$ Å^3, $D_c = 1.711\,g\,cm^{-3}$, $F(000) = 1035$, μ(Mo-Kα) = 0.790 mm^{-1}. Selected bond distances and angles are listed in table 2.

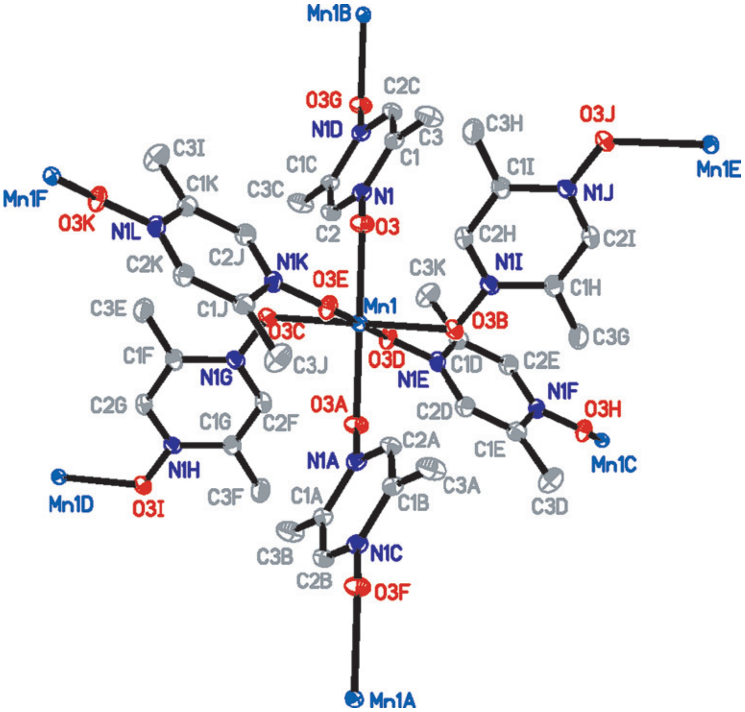

Figure 1. Coordination diagram of the complex with atom numbering scheme.

3.2.2. Crystal structure. Figure 1 shows the complex with atom numbering scheme and table 2 gives the data dealing with coordinated bond lengths and angles. Mn1 is coordinated by six O atoms from six $\mu_{1,6}$-dmpzdo ligands in the coordination geometry slightly distorted octahedral. Each Mn(II) ion is surrounded by six other Mn(II) ions with separation distance of 8.728 Å. Adjacent Mn(II) ions at this distance are joined by $\mu_{1,6}$-dmpzdo ligands forming a three-dimensional structure. In *a* and *b* directions there exist microporous channels, and perchlorate anions are trapped in the channels by Coulomb forces as shown in figure 2.

3.3. *Magnetism*

Figure 3 shows a plot of μ_{eff} *versus* T for the complex. The magnetic moment value per Mn(II) at 300 K is 5.94 μ_{B} decreasing with temperature drop to a minimum of 3.39 μ_{B} at 4.85 K. The data of the variable-temperature magnetic susceptibilities were fitted with the model developed by Rushbrook and Wood and used by Ma [4] for a Heisenberg antiferromagnet based on a simple cubic lattice with the Hamiltonian operator $H = -2J\Sigma \boldsymbol{S}_i\boldsymbol{S}_j$, and the relevant fitting formula is as follows.

$$\chi_{\mathrm{M}} = \left[\frac{35Ng^2\beta^2}{12kT}\right]\left[1+\sum C_nX^n\right]$$

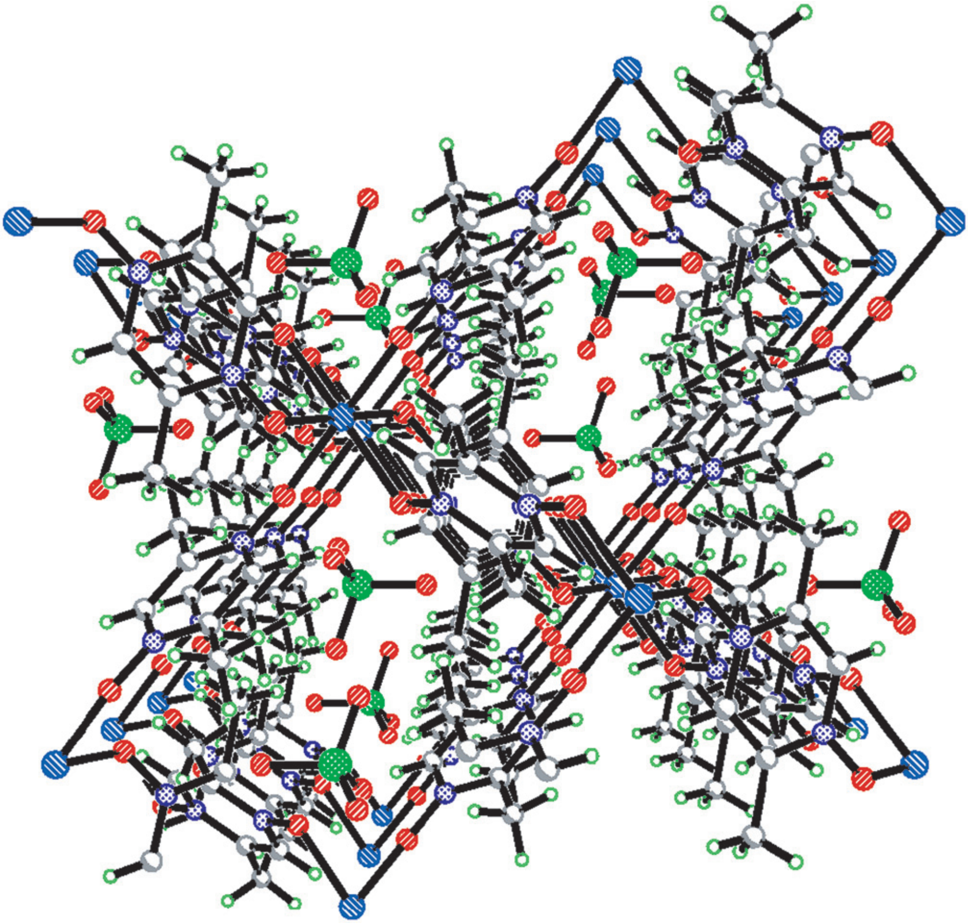

Figure 2. The channels of the crystal, viewed from the *a* direction.

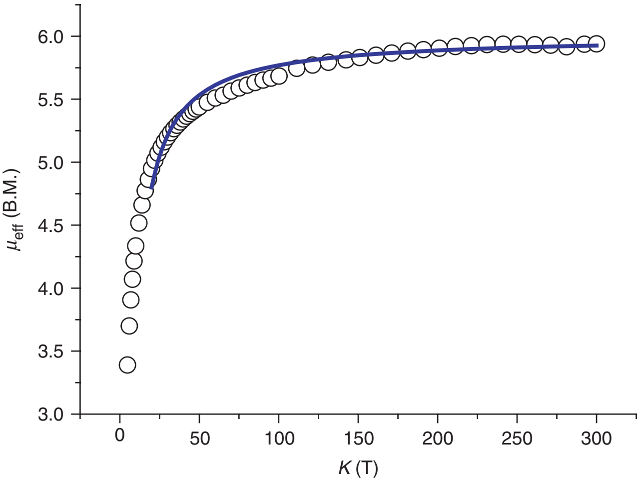

Figure 3. Plots of μ_{eff} (open circle for the experimental values and blue line for the theoretical values) *vs*. *T*.

with $X = \mathrm{J}/kT$, $C_1 = 35$, $C_2 = 221.67$, $C_3 = 608.22$, $C_4 = 26049.66$, $C_5 = 210986$, $C_6 = 8014980$. The best fitting of the magnetic data above 18 K gives the agreement factor $R = 9.77 \times 10^{-4}$ [R is defined as $R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{Calcd}})^2/(\chi_{\mathrm{obsd}})^2$], $J = -0.15\,\mathrm{cm}^{-1}$, $g = 2.03$, indicating a very weak antiferromagnetic coupling between the bridged Mn(II) ions. The interaction is similar to the magnetic interactions of the two-dimensional Mn(II) and Co(II) complexes with pyrazine-1,4-dioxide as bridging ligands [6], implying similar magnetic coupling function.

Acknowledgements

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

References

[1] W. Wernsdorfer, R. Sessoli. *Science*, **284**, 133 (1999).
[2] S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003).
[3] Z.-M. Su, J.-K. Feng, A.-M. Ren, S.-Q. Zhang, J.-Z. Sun. *Chem. J. Chin. Univ.*, **21**, 590 (2000).
[4] B.-Q. Ma, H.-L. Sun, S. Gao, G. Su. *Chem. Mater.*, **13**, 1946 (2001).
[5] H.-L. Sun, S. Gao, B.-Q. Ma, G. Su, S.R. Batten. *Cryst. Growth. Des.*, **5**, 269 (2005).
[6] H.-L. Sun, B.-Q. Ma, S. Gao, G. Su. *J. Chem. Soc., Chem. Commun.*, 2586 (2001).
[7] H.-L. Sun, Z.-M. Wang, S. Gao. *Inorg. Chem.*, **44**, 2169 (2005).
[8] H.-L. Sun, S. Gao, B.-Q. Ma, F. Chang, W.-F. Fu. *Microp. Mesop. Mater.*, **73**, 89 (2004).
[9] P.G. Simpon, A. Vinciguerra, J.V. Quagliano. *Inorg. Chem.*, **2**, 282 (1963).