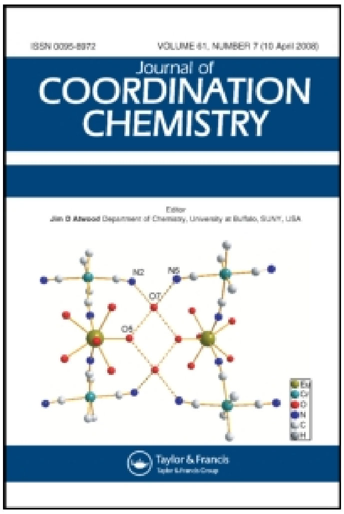

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Crystal Structure and Magnetic Properties of A One-Dimensional Polymer $[Mn(im2\text{-}py)(tp)(H_2O)_2]\cdot 1.25H_2O$

Licun Li[a]; Songyan Liu[a]; Daizheng Liao[a]; Zonghui Jiang[a]; Shiping Yan[a]; S. S. Turner[b]
[a] Department of Chemistry, Nankai University, Tianjin, P. R. China [b] Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, London, UK

**To cite this Article** Li, Licun , Liu, Songyan , Liao, Daizheng , Jiang, Zonghui , Yan, Shiping and Turner, S. S.(2003) 'Crystal Structure and Magnetic Properties of A One-Dimensional Polymer $[Mn(im2\text{-}py)(tp)(H_2O)_2]\cdot 1.25H_2O$', Journal of Coordination Chemistry, 56: 5, 383 — 388

**To link to this Article: DOI:** 10.1080/0095897031000092403

**URL:** http://dx.doi.org/10.1080/0095897031000092403

*J. Coord. Chem.*, 2003, Vol. 56, No. 5, pp. 383–388

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# CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A ONE-DIMENSIONAL POLYMER [Mn(im2-py)(tp)($H_2O$)$_2$] · 1.25$H_2O$

LICUN LI[a,]*, SONGYAN LIU[a], DAIZHENG LIAO[a], ZONGHUI JIANG[a,]*,
SHIPING YAN[a] and S.S. TURNER[b]

[a]*Department of Chemistry, Nankai University, Tianjin 300071, P. R. China;*
[b]*Davy-Faraday Research Laboratory, The Royal Institution of Great Britain,*
*21 Albemarle, Street London, W1S 4BS, UK*

*(Received 30 September 2002)*

A new manganese(II) complex [Mn(im2-py)(tp)($H_2O$)$_2$] · 1.25$H_2O$ (im2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and tp = terephthalato dianion) has been synthesized and characterized structurally and magnetically. The crystal structure consists of neutral chains of manganese(II) ions linked by the terephthalate ligand. Variable temperature magnetic susceptibility data exhibit a weak antiferromagnetic coupling between the manganese(II) ion and the imino nitroxide radical.

*Keywords:* Imino nitroxide; Manganese(II) complex; Crystal structure; Magnetic coupling

## INTRODUCTION

There has been increasing interest in molecular-based magnetic materials, in which the combination of metal ions and organic radicals are used to construct assembled systems [1,2]. Metal-radical complexes with pyridyl-substituted nitroxide radicals have been intensively studied in recent years [3–10]. These radicals are especially attractive because of their donor atoms and their ability to assemble extended coordination geometries with changing magnetic coupling. Heterospin systems consisting of organic free radicals and paramagnetic metal ions constitute one of the most promising design strategies for high Curie-temperature molecular-based magnets [1,11,12]. Meanwhile, the terephthalato ligand is a versatile ligand with good binding ability as manifested by the formation of polymeric structure system [13–15]. We present here the structure of a one-dimensional manganese(II)-radical complex [Mn(im2-py)(tp)($H_2O$)$_2$] · 1.25$H_2O$ (**1**) (im2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and tp = terephthalato dianion) with terephthalato bridging ligand, and its magnetic properties.

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*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000092403

## EXPERIMENTAL

### Physical Measurements

Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 instrument. Variable temperature magnetic susceptibilities of polycrystalline samples in a gelatin capsule were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

### Syntheses

All reagents were of analytical grade and used without further purification. The ligand 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (im2-py) was prepared according to reported methods [16].

#### *[Mn(im2-py)(tp)($H_2O$)$_2$]·1.25$H_2O$*

An aqueous solution (10 cm$^3$) of $K_2$tp (0.072 g, 0.3 mmol) was added to a mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.065 g, 0.3 mmol) and im2-py (0.065 g, 0.3 mmol) in 15 cm$^3$ of $H_2O$. The solution was stirred for 1.5 h and filtered. The filtrate was kept at room temperature for five days to yield well-formed yellow crystals of [Mn(im2-py)(tp)($H_2O$)$_2$]·1.25$H_2O$. (1) Yield: 70%. *Anal.* Calcd. for $C_{20}H_{26.5}N_3O_{8.25}Mn$(%): C, 47.17; H, 5.31; N, 11.78. Found C, 47.89; H, 5.51; N, 11.14.

### Crystallographic Data and Structure Determination

A yellow crystal (0.15 × 0.01 × 0.05 nm) was selected and mounted on a glass fibre. All measurements were made on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 4537 reflections including 3896 independent reflection ($R_{\text{int}} = 0.0921$) was collected in the $1.78 < \theta < 25.03°$ range at room temperature. The structure was solved by direct methods using the SHELXS97 program [17]. A full-matrix least-squares refinement on $F^2$ was carried out using SHELXL97 [18] and the goodness-of-fit on $F^2$ was 1.058. Final agreement factors are $R_1 = 0.0815$ $wR_2 = 0.1240$ ($I > 2\sigma(I)$). Maximum and minimum peaks in the final difference Fourier synthesis were 0.442 and −0.478 eÅ$^{-3}$, respectively. Crystallographic data and refinement parameters are listed in Table I. Final atomic coordinates for non-hydrogen atoms are given in Table II.

## RESULTS AND DISCUSSION

### Description of the Crystal Structure

The structure of **1** is shown in Fig. 1. Selected bond distances and angles are given in Table III. In **1**, each terephthalato dianion binds two manganese(II) ions in bis-monodentate mode leading to a one-dimensional chain structure. The im2-py radical ligand coordinates to the Mn(II) ions *via* the pyridyl-and imino-N atoms to form a planar five-membered chelate ring; the two Mn–N bondlengths are 2.321(8) and 2.261(9) Å for

TABLE I Crystallographic data and data-collection parameters for Complex **1**

| | |
|---|---|
| Formula | $C_{20}H_{26.5}N_3O_{8.25}Mn$ |
| Formula weight | 495.88 |
| Temperature/K | 293(2)K |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$/Å | 10.020(8) |
| $b$/Å | 10.573(8) |
| $c$/Å | 12.888(10) |
| $\alpha$/° | 113.582(14) |
| $\beta$/° | 93.966(15) |
| $\gamma$/° | 110.037(14) |
| $V$/Å$^3$ | 1141.4(15) |
| $Z$ | 2 |
| μ/mm$^{-1}$ | 0.630 |
| $F$(000) | 517 |
| Measured/independent reflections | 4537/3896 [$R_{\text{int}} = 0.092$] |
| $R$ | 0.082 |
| $R_w$ | 0.124 |

TABLE II Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å $\times 10^3$] for Complex **1**

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{\text{eq}}$ |
|---|---|---|---|---|
| Mn(1) | 3775(2) | 2766(2) | 3130(1) | 32(1) |
| N(1) | 1353(8) | 1704(10) | 2112(6) | 31(2) |
| N(2) | 2974(9) | 225(9) | 2307(6) | 42(2) |
| N(3) | 1201(11) | −2034(11) | 1326(7) | 55(3) |
| O(1) | −26(10) | −3058(10) | 751(9) | 132(4) |
| O(2) | 3018(7) | 2773(7) | 4627(5) | 44(2) |
| O(3) | 3837(7) | 2730(8) | 6242(6) | 53(2) |
| O(4) | 6050(6) | 3445(7) | 3842(5) | 39(2) |
| O(5) | 7146(7) | 3976(8) | 2556(5) | 60(2) |
| O(6) | 3843(6) | 5002(6) | 3721(5) | 35(2) |
| O(7) | 4381(7) | 2752(8) | 1484(5) | 72(2) |
| O(8) | 3234(11) | 3687(10) | 8357(7) | 7993) |
| O(9) | 5993(17) | 5939(18) | 9676(12) | 84(5) |
| C(1) | 569(11) | 2464(11) | 2075(7) | 36(3) |
| C(2) | − 875(13) | 1791(15) | 1550(9) | 54(3) |
| C(3) | − 1570(12) | 306(15) | 1072(8) | 55(4) |
| C(4) | − 781(12) | − 564(12) | 1061(8) | 52(3) |
| C(5) | 681(11) | 210(12) | 1629(8) | 31(3) |
| C(6) | 1629(11) | − 555(11) | 1750(8) | 32(3) |
| C(7) | 2453(12) | − 2383(12) | 1542(10) | 50(3) |
| C(8) | 3679(12) | − 805(12) | 2310(9) | 51(3) |
| C(9) | 2044(16) | − 3438(17) | 2033(12) | 181(8) |
| C(10) | 2729(15) | − 3252(16) | 362(10) | 130(6) |
| C(11) | 4099(16) | − 459(14) | 3540(10) | 145(8) |
| C(12) | 5003(15) | − 447(14) | 1774(15) | 175(9) |
| C(13) | 2841(11) | 2291(11) | 5383(9) | 37(3) |
| C(14) | 1367(11) | 1107(10) | 5185(8) | 36(3) |
| C(15) | 172(11) | 894(11) | 4437(8) | 41(3) |
| C(16) | 1174(10) | 212(11) | 5778(8) | 40(3) |
| C(17) | 7166(10) | 3940(11) | 3486(10) | 42(3) |
| C(18) | 8623(10) | 4490(11) | 4294(8) | 36(3) |
| C(19) | 8772(10) | 3976(11) | 5111(9) | 46(3) |
| C(20) | 9843(10) | 5529(11) | 4166(8) | 42(3) |

$U_{\text{eq}}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

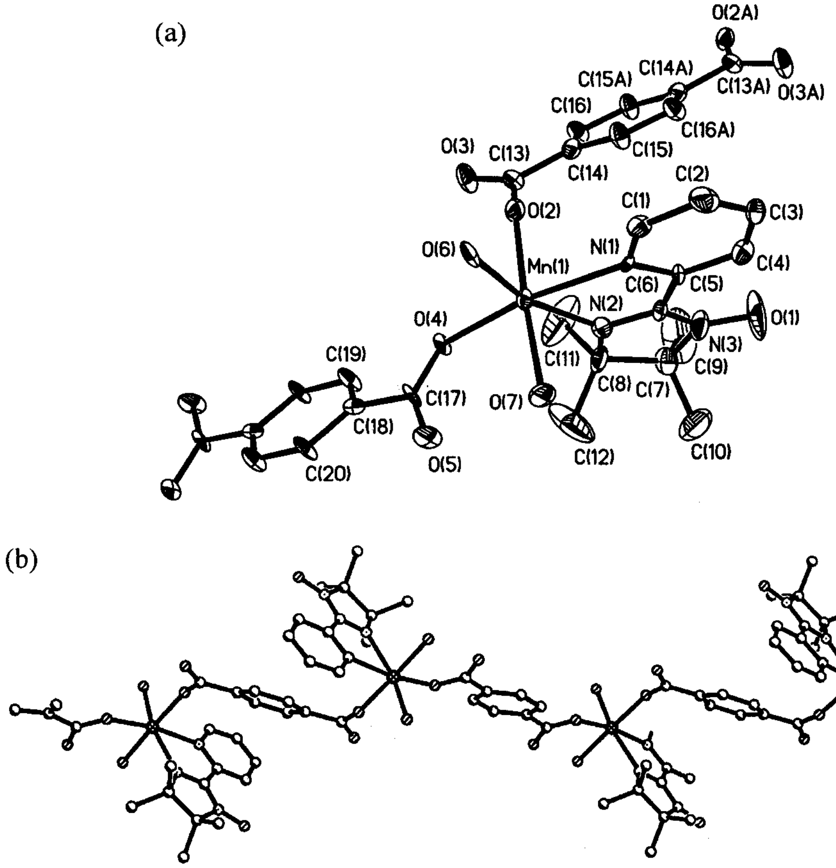

FIGURE 1 (a) ORTEP view of the coordination geometry around Mn(II) in **1**; (b) perspective view of an infinite one-dimensional chain in **1**.

TABLE III Selected bondlengths (Å) and angles (°) for Complex **1**

| | | | |
|---|---|---|---|
| Mn(1)–O(2) | 2.119(6) | Mn(1)–O(4) | 2.148(6) |
| Mn(1)–O(6) | 2.149(6) | Mn(1)–O(7) | 2.243(7) |
| Mn(1)–N(2) | 2.261(9) | Mn(1)–N(1) | 2.321(8) |
| N(3)–O(1) | 1.246(10) | O(2)–C(13) | 1.265(10) |
| O(2)–Mn(1)–O(4) | 97.4(2) | O(2)–Mn(1)–O(6) | 86.8(2) |
| O(4)–Mn(1)–O(6) | 96.5(2) | O(2)–Mn(1)–O(7) | 174.8(3) |
| O(4)–Mn(1)–O(7) | 87.6(2) | O(6)–Mn(1)–O(7) | 91.3(2) |
| O(2)–Mn(1)–N(2) | 90.3(3) | O(4)–Mn(1)–N(2) | 101.0(3) |
| O(6)–Mn(1)–N(2) | 162.5(3) | O(7)–Mn(1)–N(2) | 90.0(3) |
| O(2)–Mn(1)–N(1) | 88.4(3) | O(4)–Mn(1)–N(1) | 170.6(3) |
| O(6)–Mn(1)–N(1) | 91.3(3) | O(7)–Mn(1)–N(1) | 86.9(2) |
| N(2)–Mn(1)–N(1) | 71.4(3) | C(13)–O(2)–Mn(1) | 150.9(7) |

Mn(1)–N(1) and Mn(1)–N(2), respectively. Two water molecules coordinate to Mn(1), O(6) and O(7) at 2.149(6) and 2.268(9) Å. Mn–O(carboxylate) bond distances are 2.119(6) and 2.148(6) Å for Mn(1)–O(2) and Mn(1)–O(4), respectively, in agreement with those reported for other carboxylato-containing manganese(II) complexes

[19,20]. Thus the manganese(II) ion has a distorted octahedral coordination environment. The equatorial plane is formed by two nitrogen atoms (N(1), N(2)) from im2-py, one oxygen atom (O(4)) from tp and one oxygen atom (O(6)) from a water molecule. Dihedral angles between the basal plane and the phenyl rings for two tp ligands are 48.8 and 57.5°, respectively. For im2-py, the NO group ligand has N–O 1.246(10) Å, as is generally observed [21–23]. The dihedral angle between the nitroxide group (O(1)–N(3)–C(6)–N(2)) and the pyridyl ring is 2.8° and the nitroxide group forms a dihedral angle of 3.4° with the Mn(II) ion basal plane; these three planes are almost coplanar.

## Magnetic Properties

The magnetic susceptibility of Complex **1** was measured in the temperature range 2–300 K. Plots of $\chi_M$ and $\mu_{eff}$ *versus* $T$ are shown in Fig. 2. At room temperature, the effective magnetic moment $\mu_{eff}$ is equal to 6.07 $\mu_B$, which is slightly smaller than that expected for non-interacting $S_{Mn} = 5/2$ and $S_{Rad} = 1/2$ spins (6.16 $\mu_B$). The $\mu_{eff}$ value decreases with decreasing temperature and reaches a steady state around 20 K. At 7 K the value is 4.85 $\mu_B$, corresponding to $S = 4/2$. Further cooling causes a further decrease of $\mu_{eff}$, showing intermolecular antiferromagnetic interactions. The magnetic analysis was carried out with the susceptibility equation based on the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}\hat{S}_R$, where $J$ is the exchange integral between the Mn(II) ion and the im2-py radical. Considering intermolecular magnetic coupling, the parameter $\theta$ was included in the equation.

$$\chi_M = \frac{N\beta^2}{k(T-\theta)}\left[\frac{28g_3^2 + 10g_2^3\exp(-6J/KT)}{7 + 5\exp(-6J/KT)}\right]$$

$$g_2 = (7g_{Mn} - g_R)/6, \quad g_3 = (5g_{Mn} + g_R)/6$$

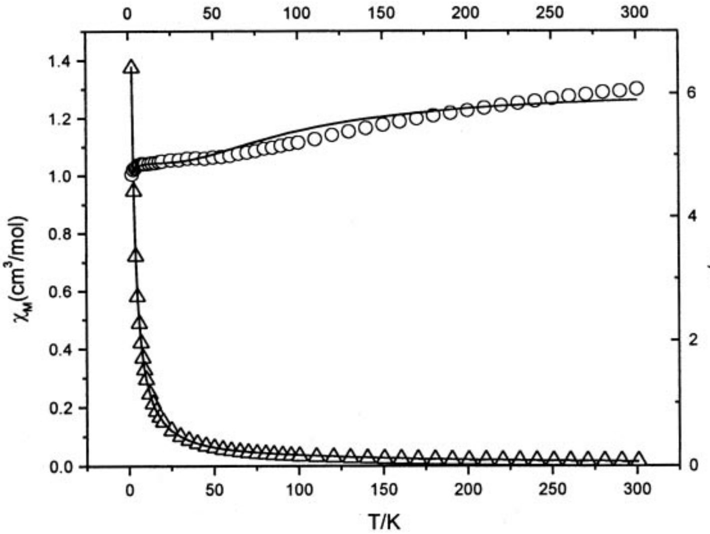

FIGURE 2 Plots of $\chi_M(\Delta)$ and $\mu_{eff}(\circ)$ of 1 *versus* $T$. The solid line corresponds to the best theoretical fit.

Least-squares fitting of the experimental data led to $J = -18.82\,\mathrm{cm}^{-1}$, $g_{\mathrm{Mn}} = 2.0$, $g_{\mathrm{R}} = 2.0$ (fixed), $\theta = -0.20\,\mathrm{K}$, $R = 3.27 \times 10^{-5}$ ($R$ is defined as $\sum[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calc}}]^2 / \sum[(\chi_{\mathrm{M}})_{\mathrm{obs}}]^2$).

The fitting results show that exchange coupling between Mn(II) and im2-py is weakly antiferromagnetic, consistent with other reported manganese(II)-imino nitroxide complexes [23]. This can be understood by an orbital symmetry argument. Owing to the coplanarity of the imino nitroxide moiety with the Mn(II) ion basal plane, the magnetic orbital of the im2-py radical with $\pi$ symmetry gives effective $\pi$ overlap with one of the $\pi$ orbitals, and is orthogonal to the other $\pi$ and two $\sigma$ orbitals of the manganese(II) ion. This will result in a weak antiferromagnetic interaction as observed.

## Acknowledgments

This project was supported by the National Science Foundation of China (Nos. 20271029, 20171025).

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