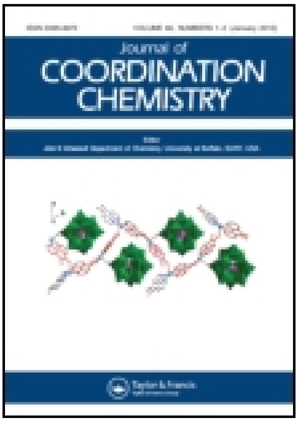

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Synthesis, crystal structure and magnetism of a one-dimensional Mn^{II} chain with a single $\mu_{1,3}$-azido as bridge ligand

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Synthesis, crystal structure and magnetism of a one-dimensional Mn^{II} chain with a single $\mu_{1,3}$-azido as bridge ligand

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A new 1-D Mn^{II} chain, $[Mn(\mu_{1,3}\text{-}N_3)(phenCl)_2]_n \cdot (ClO_4)_n$ (phenCl = 2-chloro-1,10-phenanthroline), was synthesized with single $\mu_{1,3}$-azido as bridge and 2-chloro-1,10-phenanthroline as coligand, and its crystal structure determined by X-ray crystallography. In the complex, Mn^{II} is located in a distorted octahedral geometry, and azide is an end-end bridge, linking two Mn^{II} ions with separation of 5.7356(10) Å, forming a 1-D chain. In the crystal, there are two kinds of π-π stacking between adjacent chains. The fitting of the variable-temperature (2.00–320 K) magnetic susceptibilities gave an anti-ferromagnetic interaction of $J = -5.99\,\text{cm}^{-1}$ ($H = -J\Sigma S_i S_{i+1}$), among the stronger magnetic interaction in Mn^{II} complexes with azido as single end-end bridge. Reported experimental results do not confirm clearly the magneto-structural correlations revealed by theoretical calculations.

Keywords: Magnetism; Manganese(II) complex; Crystal structure; Azido ligand

1. Introduction

Molecular magnetism has attracted considerable attention and major advances have been made in theoretical description and applications as new molecular-based materials [1,2]. Azide is a versatile bridge, and a large number of complexes have been prepared and their magnetic coupling properties studied. Key factors [3–6] that tune the magnetic coupling sign and strength have been obtained with end-end bridging showing an anti-ferromagnetic interaction, while end-on bridging creates ferromagnetic coupling, although exceptions [7–9] have been reported. These magneto-structural correlations are obtained by studying a large number of azide-bridged complexes with different coligands because the structures of azide-

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bridged complexes are sensitive to coligand [10]. Compared with Cu^{II} and Ni^{II} azide-bridged complexes, very few Mn^{II} complexes with azide as a single end-end bridge have been reported [11–19] and magneto-structural factors are not clearly understood. Therefore, we synthesize a single end-end azido-bridging Mn^{II} complex and 2-chloro-1,10-phenanthroline as coligand, and report its crystal structure and magnetism.

2. Experimental

2.1. *Materials*

2-Chloro-1,10-phenanthroline was prepared according to the literature [20]; other chemicals are analytical grade and used without purification.

2.2. *Synthesis of* $\{[Mn(\mu_{1,3}\text{-}N_3)(phenCl)_2)]\cdot ClO_4\}_n$

NaN_3 (0.0206 g, 0.317 mM) was dissolved into 5 mL·H_2O and then added into 15 mL methanol solution containing $Mn(ClO_4)\cdot 6H_2O$ (0.0695 g, 0.192 mM) and phenCl (0.0424 g, 0.197 mM). The mixed solution was stirred for a few minutes and yellow single crystals were obtained after the filtrate was allowed to stand at room temperature for one week. IR (cm^{-1}): 2102(s), 2068(s), 1620(s), 1582(m), 1502(m), 1403(s), 1146(s), 1099(s). Anal. Calcd. for $C_{24}H_{14}Cl_3MnN_7O_4$ (Fw: 625.71): C, 46.07; H, 2.26; N, 15.67; Mn, 8.78%. Found: C, 46.31; H, 2.37; N, 15.29; Mn, 9.24%.

2.3. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer from 4000 to 500 cm^{-1} using KBr disks. C, H, and N analyses were carried out on a Perkin-Elmer 240 instrument and Mn content was measured on an atomic spectrophotometer model Z-8000. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 1 k Oe from 2.00 to 320 K on a MPMS-7SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

2.4. *X-ray crystallography*

A yellow single crystal with dimensions 0.34 × 0.28 × 0.16 mm was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25 °C on an X-ray diffractometer and Model Bruker Smart-1000 CCD, using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) from $2.60 < 2\theta < 50.04°$. A total of 10,334 reflections were collected, of which 4393 were independent ($R_{int} = 0.033$), and 3563 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for Lp factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were placed in calculated positions and refined as riding. The programs for structure solution and refinement were SHELXS-97 and SHELXTL, respectively (Bruker, 2001). Crystallographic data and structural refinement parameters are provided in table 1.

Table 1. Crystal data and structural refinement.

Empirical formula	$C_{24}H_{14}Cl_3MnN_7O_4$
Crystal system	Monoclinic
Space group	$P2_1c$
Unit cell dimensions (Å, °)	
a	15.688(2)
b	17.425(3)
c	9.1260(14)
β	92.219(2)
Volume (Å^3), Z	2492.9(7), 4
Calculated density (g cm^{-3})	1.667
Absorption coefficient (mm^{-1})	0.900
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0610$, $wR_2 = 0.1609$
Goodness-of-fit on F^2	1.044
Largest difference peak and hole (e·Å^{-3})	0.873 and −0.590

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the coordination diagram and atom numbering scheme. The data in table 2 display that coordination bond lengths are 2.187(4)–2.308(3) Å and the associated angles change from 72.40(12)° to 168.60(13)°. Mn1 assumes a distorted octahedral geometry. Figure 1 also shows that azide is a $\mu_{1,3}$-azido bridge connecting adjacent Mn^{II} ions with separation distance of 5.7356(10) Å, forming a single $\mu_{1,3}$-azide bridged 1-D Mn^{II} chain along the *c* axis as shown in figure 2. In the chain, the N6-N5-Mn1 and N6A-N7A-Mn1 angles are 127.9(3)° and 128.3(3)°, respectively, and the torsional angle of Mn1-N5-N6-N7-Mn1A is 104.1°. The non-hydrogen atoms of 2-chloro-1,10-phenanthroline define an approximate plane within 0.0510 Å (for Cl1 ligand) and 0.0677 Å (for Cl2 ligand) with a maximum deviation of –0.1101(23) Å for Cl1 (for Cl1 ligand) and –0.01351(25) Å for Cl2

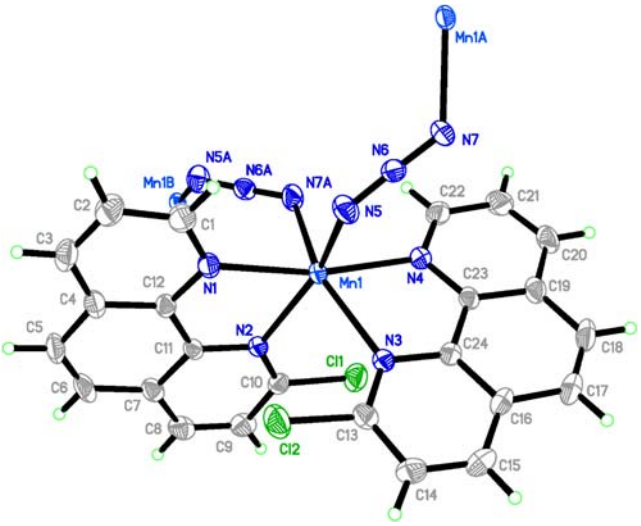

Figure 1. Coordination diagram of the complex with atom numbering scheme.

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

Mn1-N5	2.187(4)	Mn1-N7A	2.191(4)	Mn1-N4	2.264(3)
Mn1-N1	2.272(4)	Mn1-N2	2.303(3)	Mn1-N3	2.308(3)
N1-Mn1-N2	72.40(12)	N4A-Mn1-N3	72.84(12)	N7A-Mn1-N4	85.13(14)
N5-Mn1-N1	86.11(14)	N7A-Mn1-N1	86.25(14)	N5-Mn1-N4	88.07(14)
N5-Mn1-N3	88.63(14)	N2-Mn1-N3	89.89(11)	N7A-Mn1-N2	91.14(14)
N5-Mn1-N7A	100.15(16)	N41-Mn1-N2	115.21(13)	N1-Mn1-N3	116.76(12)
N5-Mn1-N2	155.05(14)	N7A-Mn1-N3	156.05(14)	N4-Mn1-N1	168.60(13)

Symmetry code: N7A: x, $-y+1/2$, $z+1/2$.

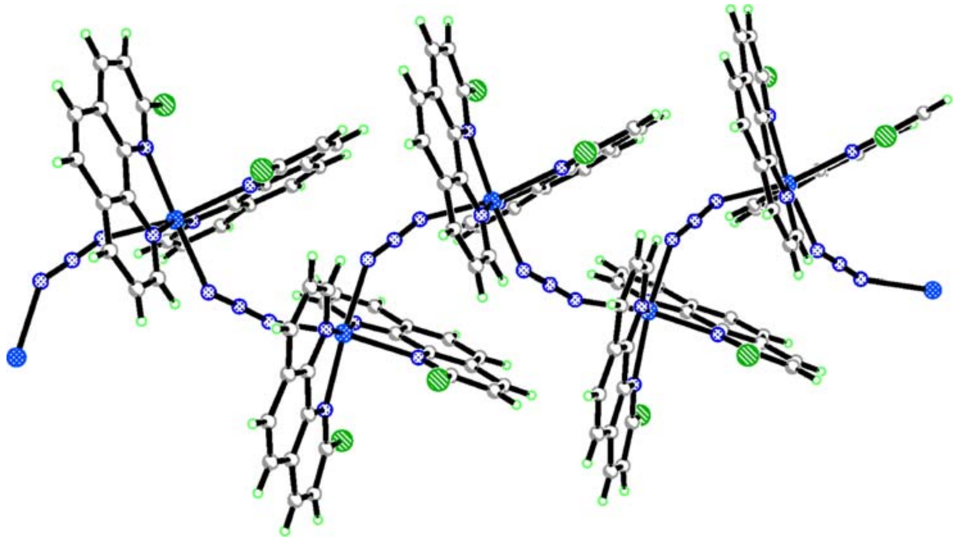

Figure 2. Uniform 1-D chain with single $\mu_{1,3}$-azide as bridging ligand.

(for Cl2 ligand). In the crystal, there are two slipped π-π stackings [21] between adjacent chains termed PS-1 and PS-2, respectively, as shown in figures 3 and 4, respectively, which involve 2-chloro-1,10phenanthroline ring and its symmetry-related counterpart, with interplanar distances of 3.498 Å for PS-1 and 3.378 Å for PS-2. In PS-1 and PS-2, the separation distance of non-bonded atom pairs C5 C7A (C7 C5A) and C16 C18A (C18 C16A) are 3.572(7) Å and 3.467(7) Å, respectively. In addition, compared with a reported Mn^{II} complex [22], minor difference of the coligands resulted in different structures.

3.2. *Magnetic study*

Variable-temperature (2.00–320 K) magnetic susceptibilities are shown in figure 5, where χ_M is the molar magnetic susceptibility per mononuclear Mn^{II} unit and μ_{eff} is the magnetic moment per mononuclear Mn^{II}. The μ_{eff} value at 320 K is 5.62 B.M., which is slightly smaller than that of uncoupled mononuclear Mn^{II} (5.92 B.M. for $g_{av} = 2$) at room temperature. The μ_{eff} values slowly decrease as temperature drops until 90.0 K with $\mu_{\mathrm{eff}} = 4.57$ B.M., and then the mu_{eff} values decrease sharply with temperature drop, reaching minimum

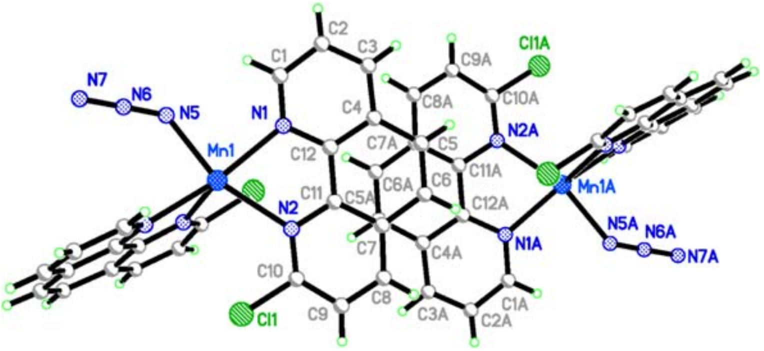

Figure 3. PS-1 π-π stacking from the adjacent chains.

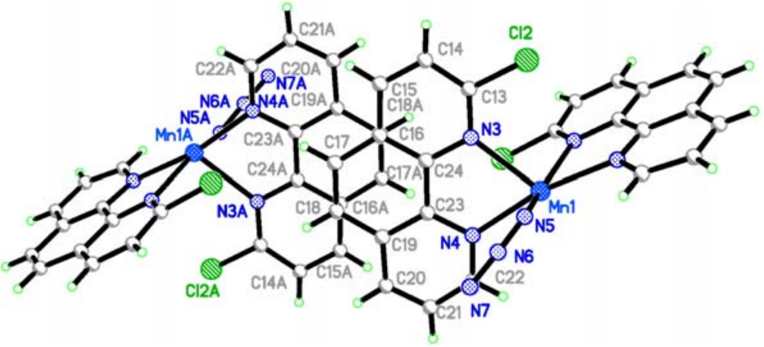

Figure 4. PS-2 π-π stacking from the adjacent chains.

0.68 B.M. at 2.00 K, which indicates that there is an anti-ferromagnetic interaction between adjacent $\mathrm{Mn^{II}}$ ions. The fitting formula (2) [23] of a uniform 1-D $\mathrm{Mn^{II}}$ chain, which was obtained based on the isotropic Hamiltonian, as presented in equation (1), was used to fit the experimental susceptibility data.

$$H = -J\Sigma S_i S_{i+1} \tag{1}$$

$$\chi_M = \frac{Ng^2\beta^2 S(S+1)}{3\kappa(T-\theta)}\frac{1+u}{1-u}(1-\rho) + \frac{Ng^2\beta^2}{3\kappa T}S(S+1)\rho \tag{2}$$

Equation (2) gave a good fit to the experimental data as shown in figure 5, and the relevant fitting parameters are $g = 2.05 \pm 0.00$, $J = -5.99 \pm 0.02\,\mathrm{cm^{-1}}$, $\theta = -2.74 \pm 0.11\,\mathrm{K}$, $\rho = 0.00736 \pm 0.00023$, and agreement factor $R = \Sigma(\chi_{\mathrm{obsd}-}\chi_{\mathrm{calcd}})^2/(\chi_{\mathrm{obsd}})^2 = 4.0 \times 10^{-5}$. The value of $J = -5.99\,\mathrm{cm^{-1}}$ can be attributed to the magnetic coupling of azide-bridged $\mathrm{Mn^{II}}$ and the value of $\theta = -2.74\,\mathrm{K}$ may be ascribed to the PS-1 and PS-2 π-π stacking magnetic coupling pathways.

On single end-end azide-bridged $\mathrm{Mn^{II}}$ complexes, calculations [24] reveal that magnetic interaction is always anti-ferromagnetic and two geometric parameters, the Mn-N-N angle and the Mn-N-N-N-Mn dihedral angle τ, are dominant for the magnetic coupling strength.

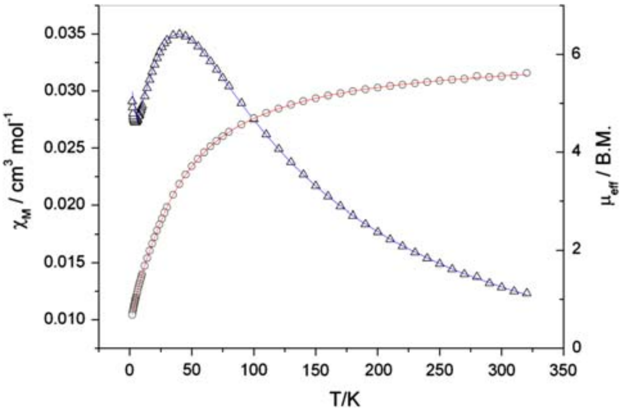

Figure 5. Plots of χ_M (the open triangle for the experimental data and the blue curve for the fitting values) and μ_{eff} (the open circle for the experimental data and the red curve for the fitting value) versus T for the Mn^{II} complex.

The anti-ferromagnetic coupling strength features a maximum for Mn-N-N angles close to 110° and should be a minimum near 160°. The Mn-N-N-N-Mn dihedral angle τ affords the same qualitative results: a planar location of Mn^{II} ions and bridged azido anion should lead to a maximum anti-ferromagnetic interaction, but a larger dihedral angle τ should result in a weaker anti-ferromagnetic coupling. Table 3 shows the magneto-structural data for binuclear Mn^{II} and 1-D Mn^{II} complexes with single end-end azide as bridge [11–19], with very strong magnetic coupling strength relative to most complexes in the literature. The data of table 3 indicate that it is hard to confirm clearly the magneto-structural correlations [24] mentioned above. It is necessary to synthesize more Mn^{II} complexes with single $\mu_{1,3}$-azide as bridge and to study their magnetic properties in order to understand the magneto-structural correlations.

Table 3. Known magneto-structural data for binuclear Mn^{II} and 1 D Mn^{II} complexes with single end-end azido anion as bridged ligand.

Complex	Mn-N-N (°)	Mn-N$_3$-Mn (°)	J (cm^{-1})	Ref.
(1) $\{[Mn(\mu_{1,3}\text{-}N_3)L1](NO_3)\}_n$	158.9/159.0	170.4	−1.02	[11]
(2) $[Mn(\mu_{1,3}\text{-}N_3)L2(N_3)_2]BPh_4\cdot 0.5H_2O$	133.9/124.0	127.2	−2.29	[12]
(3) $[Mn_2(\mu_{1,3}\text{-}N_3)L1(H_2O)(NO_3)](NO_3)_2$	155.1/149.9	156.9	−1.72	[11]
(4) $[Mn(\mu_{1,3}\text{-}N_3)L3(Cl)(H_2O)_2]_n\cdot nH_2O$	127.6/159.8	180.0	−3.5	[13]
(5) $[Mn_2(\mu_{1,3}\text{-}N_3)L4]_n(ClO_4)_{3n}$[a]	162.9	180	−3.6	[14]
(6) $[Mn(\mu_{1,3}\text{-}N_3)(N_3)(H_2O)(L5)_2]_n$	142.6/137.3	180	−4.4	[15]
(7) $[Mn(\mu_{1,3}\text{-}N_3)(L6)_2]_n(ClO_4)_n$	136.7/151.5	25.6	−4.7	[16]
(8) $[Mn(\mu_{1,3}\text{-}N_3)L7]_n(PF_6)_n$	125.2/118.8	53.2	−4.8	[17]
(9) $[Mn_2(\mu_{1,3}\text{-}N_3)(N_3)_2(L8)_2]\cdot(ClO_4)$	141.2	180	−5.98	[18]
(10) $[Mn(\mu_{1,3}\text{-}N_3)(L9)_2]_n(ClO_4)_n$	161.3/124.3	85.96	−6.60	[19]
(11) $[Mn(\mu_{1,3}\text{-}N_3)(PhenCl)_2]_n\cdot(ClO_4)_n$	127.9/128.3	104.1	−5.99	This work

L1: 2,4,6-tris[{N-methyl-N-(pyridine-2-yl)methylidene}hydrazine]-1,3,5-triazine; L2: 1,10-phenanthroline; L3: 4,4'-dipyridyl-N,N'-dioxide; L4: M,N'-bis(pyridine-2-yl)]ethane-1,2-diamine; L5: quinazoline; L6: pyridine-2-carbaldehyde-imine; L7: 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo{12.3.1}-octadeca1,(18),2,12,14,16-pentane; L8: tris(6-methyl-2-pyridylmethyl)amine; L9: 4-methoxy-N(pyridine-2-ylmethylene)aniline; [a] From the magnetic coupling point of view, it is a binuclear complex.

4. Conclusion

A new 1-D Mn^{II} chain with single $\mu_{1,3}$-azide as bridge has been synthesized. Compared to similar Mn^{II} complexes, the present complex displays stronger anti-ferromagnetic interaction between bridged Mn^{II} ions. Analysis for limited magneto-structural data of Mn^{II} complexes indicates that anti-ferromagnetic coupling strengths do not correlate simply with Mn-N-N angle and Mn-N-N-N-Mn dihedral angle. In order to understand magneto-structural correlations of this system, a large number of Mn^{II} complexes with single $\mu_{1,3}$-azide as bridge should be prepared and the relevant magnetic properties should be studied.

Supplementary material

CCDC 892769 contains detailed information of the crystallographic data for this article and these data can be obtained free charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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