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A novel three-dimensional coordination polymer: poly[di-μ_3-acetato-di-μ_2-acetato-di-μ_3-hydroxido-octa-μ_3-triazolato-heptamanganese(II)]

Zhe-Hui Weng,[a,b] Zi-Lu Chen[b] and Fu-Pei Liang[b]*

[a]College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China, and [b]College of Chemistry and Chemical Engineering, Guangxi Normal University, Yucai Road 15, Guilin 541004, People's Republic of China
Correspondence e-mail: fliangoffice@yahoo.com

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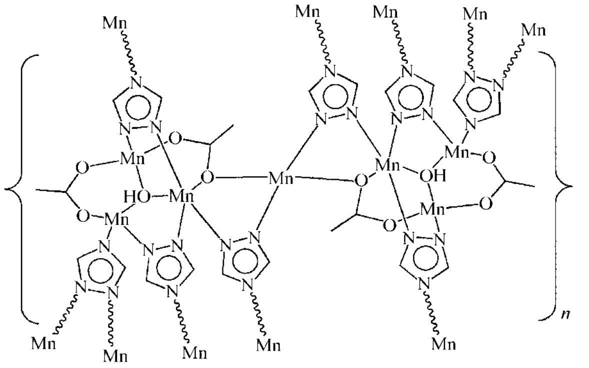
The title compound, $[\mathrm{Mn_7(C_2H_2N_3)_8(C_2H_3O_2)_4(OH)_2}]_n$, is composed of centrosymmetric heptanuclear building units with the central Mn atom on an inversion center. In the building block, three $\mathrm{Mn^{II}}$ ions are held together by one μ_3-hydroxide group, two μ_2-triazolate (trz) ligands and two μ_2-acetate groups, forming an $\mathrm{Mn_3}$ cluster. Two $\mathrm{Mn_3}$ clusters are bridged by an Mn atom *via* two μ_2-trz ligands and two μ_2-O atoms from two acetate ions to construct a heptanuclear building block. The heptanuclear building units, lying parallel to each other along the *b* direction, form one-dimensional ladder-like chains and are further interlinked, resulting in a three-dimensional framework through $\mathrm{Mn-N_{trz}}$ bonds.

Comment

The synthesis of metal–organic coordination polymeric complexes has developed rapidly in recent years owing to their fascinating variety of topologies as well as their potential applications in many fields, such as catalysis, electrical conductivity, luminescence, magnetism and nonlinear optics (Cao *et al.*, 2002; Janiak, 2003). Ligands used in the construction of polymers to bridge metals usually contain oxygen or nitrogen donors, in which multitopic carboxylate and pyridine ligands are most extensively exploited as linkers. However, more and more attention is being paid to ligands that could offer alternative tether lengths, different charge-balance requirements and orientations of donor groups, and 1,2,4-triazole is one such ligand (Ouellette *et al.*, 2006). 1,2,4-Triazole and its derivatives are very interesting ligands that can bridge as well as chelate metals, with 1,2-bridging (Milios *et al.*, 2006) or 1,2,4-bridging forms (Ouellette *et al.*, 2006). It can also be used as a monodentate ligand (Li *et al.*, 2007), and most complexes with this ligand exhibit antiferromagnetic coupling (Zhou *et al.*, 2005; Ding *et al.*, 2006).



(I)

On the other hand, Mn-based complexes have been widely reported over the past two decades, one of the most important

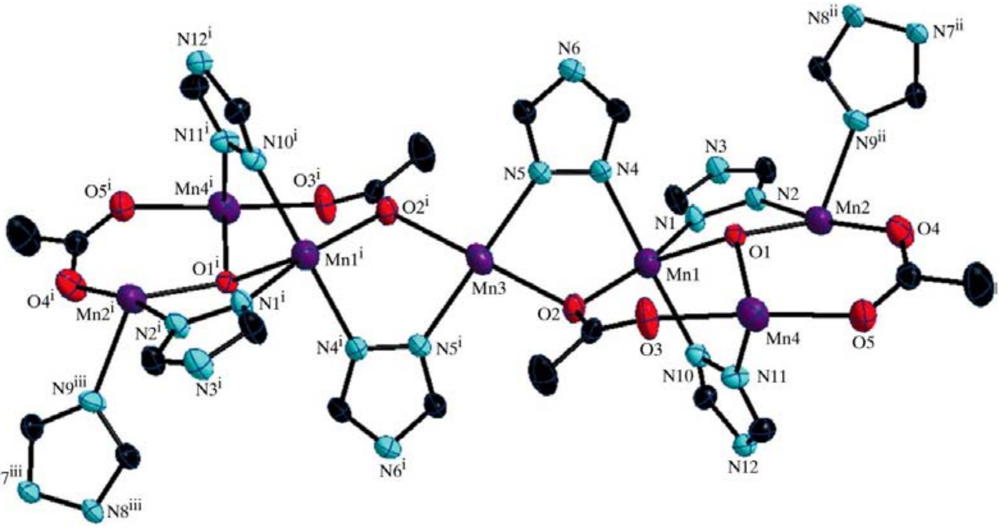


Figure 1
The $\mathrm{Mn^{II}}$ coordination environment in the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and all H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$.]

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reasons for this interest being their paramagnetic nature. Many exhibit large ground spin states (Jones *et al.*, 2004), many of which are thought to be the origin of the magnetic bistability displayed by single-molecule magnets (Laye & McInnes, 2004).

With this in mind, we decided to introduce Mn^{II} into the triazole ligand, considering that such metal–organic frameworks would exhibit unusual magnetic exchanging behavior (Tangoulis *et al.*, 1998). The title complex, (I), was obtained by solvothermal reaction of 1,2,4-triazole (Htrz) with $Mn(CH_3COO)_2\cdot4H_2O$ at 423 K or with $Mn(CH_3COCHCOCH_3)_2$ at 443 K.

Single-crystal structure analysis reveals that complex (I) is composed of heptanuclear $[Mn_7(trz)_8(CH_3COO)_4(OH)_2]$ building units, which are further interlinked through bonds formed by Mn and N atoms into a three-dimensional polymer. The heptanuclear Mn building unit, consisting of two $[Mn_{3.5}(trz)_4(CH_3COO)_2(OH)]$ subunits with atom Mn3 lying on an inversion center, is centrosymmetric (Fig. 1 and Table 1).

In the asymmetric unit of (I), atoms Mn1, Mn2 and Mn4 are held together by three distinct bridging systems to form an Mn_3 cluster, *viz.* (i) two μ_2-bridging acetate ligands, with Mn—O distances of 2.114 (3) (Mn2—O4), 2.181 (3) (Mn4—O5), 2.162 (3) (Mn4—O3) and 2.399 (3) Å (Mn1—O2), which are within the range 1.857–2.443 Å reported by Ouellette *et al.* (2006); (ii) two 1,2-bridging trz ligands, with an Mn4—N11 distance of 2.206 (3) Å, Mn—N10 of 2.211 (4) Å, Mn1—N1 of 2.247 (4) Å and Mn2—N2 of 2.213 (3) Å, which are slightly longer than those reported by Milios *et al.* (2006); and (iii) the O atom of the tridentate hydroxy group, lying out of the plane defined by the Mn_3 triangle by 0.6953 Å, with distances from each of the Mn atoms of 2.232 (3) (Mn1), 2.107 (3) (Mn2) and 2.230 (3) Å (Mn4), and these are also longer than those in related compounds (Ouellette *et al.*, 2006; Milios *et al.*, 2006). Two Mn_3 clusters are bridged by atom Mn3 *via* two μ_2-trz ligands and two μ_2-O atoms from two acetate ions to construct a heptanuclear building block, with an Mn3—O2 distance of 2.226 (3) Å, Mn1—N4 of 2.224 (4) Å and Mn3—N5 of 2.178 (4) Å. To the best of our knowledge, this kind of heptanuclear building block is unprecedented.

In the asymmetric unit of (I), the four Mn^{II} ions have two different coordination modes. Mn1, Mn3 and Mn4 are six-coordinated in a slightly distorted octahedron with coordination angles in the ranges 80.55 (12)–128.03 (14) or 166.36 (14)–180.00°. Atom Mn2 possesses a twisted trigonal–bipyramidal geometry, with equatorial N9^{ii}, O1 and N12^{iv} atoms and axial O4 and N2 atoms. The N2—Mn2—O1, N2—Mn2—N12^{iv} and N2—Mn2—N9^{ii} angles are 88.12 (12), 87.90 (13) and 86.51 (13)°, respectively (see Table 1 for symmetry codes).

The heptanuclear units are aligned along the *b* direction parallel to each other in a shoulder-to-shoulder fashion, and both sides of the two adjacent units are connected by two trz ligands, resulting in the formation of one-dimension ladder-like chains along the *b* axis (Fig. 2). Each chain is further interlinked with four other chains by coordination of the remaining N atoms of the trz ligands to the Mn^{II} ions in neighboring chains. This leads to the construction of a three-dimensional framework (Fig. 3).

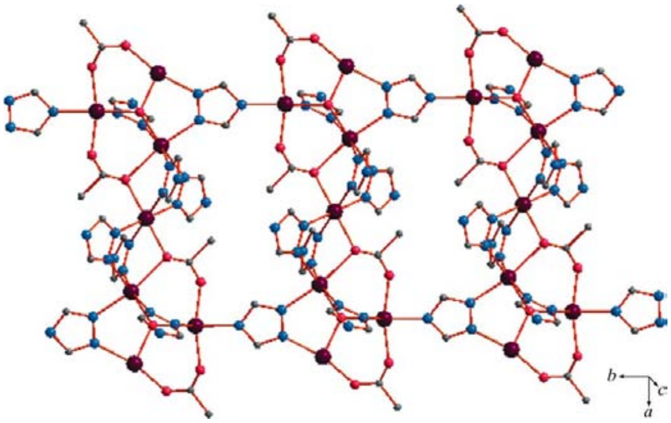

Figure 2
The ladder-like one-dimensional chain of (I) along the *b* axis.

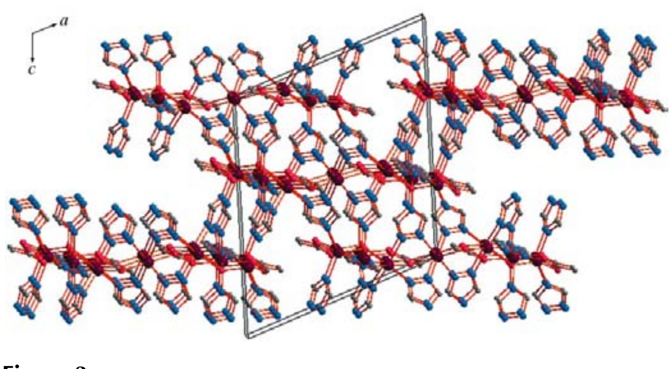

Figure 3
The three-dimensional packing of (I).

Experimental

The synthesis of complex (I) was achieved by two methods. In the first, a solution of Htrz (60.1 mg, 0.87 mmol), $Mn(CH_3COO)_2\cdot4H_2O$ (245.3 mg, 1 mmol), triethylamine (0.1 ml), CH_3CN (8 ml), EtOH (8 ml) and water (1 ml) was stirred briefly before being moved into a 25 ml autoclave and heated at 423 K for 4 d, followed by slow cooling to room temperature. The product was washed with EtOH and water, and colorless block-shaped crystals suitable for X-ray diffraction were collected and dried in air (80 mg, 66% yield). In the second method, a solution of Htrz (70.1 mg, 1.01 mmol), $Mn(CH_3COCHCOCH_3)_2$ (253 mg, 1 mmol), NaOH (40 mg, 1 mmol), CH_3CN (3 ml), EtOH (9 ml) and water (3 ml) was stirred briefly before being moved into a 25 ml autoclave and heated at 443 K for 3 d, followed by slow cooling to room temperature. The product was washed with EtOH and water, and colorless block-shaped crystals suitable for X-ray diffraction were collected and dried in air (65 mg, 43% yield).

Crystal data

$[Mn_7(C_2H_2N_3)_8(C_2H_3O_2)_4(OH)_2]$
$M_r = 1199.30$
Monoclinic, $P2_1/n$
$a = 14.677$ (2) Å
$b = 9.2626$ (15) Å
$c = 16.990$ (3) Å
$\beta = 109.717$ (2)°
$V = 2174.3$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.05$ mm^{-1}
$T = 298$ (2) K
0.22 × 0.20 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.662$, $T_{\max} = 0.723$

10662 measured reflections
3788 independent reflections
2800 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.113$
$S = 1.07$
3788 reflections
298 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 1.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Mn1—N10	2.211 (4)	Mn3—N5	2.178 (4)
Mn1—N4	2.224 (4)	Mn3—O2	2.226 (3)
Mn1—O1	2.232 (3)	Mn3—N8	2.248 (3)
Mn1—N1	2.247 (4)	Mn4—O3	2.162 (3)
Mn1—N7	2.305 (3)	Mn4—O5	2.181 (3)
Mn1—O2	2.399 (3)	Mn4—N11	2.206 (3)
Mn2—O1	2.107 (3)	Mn4—O1	2.230 (3)
Mn2—N12$^{\rm iv}$	2.191 (3)	Mn4—N6$^{\rm v}$	2.240 (4)
Mn2—N2	2.213 (3)	Mn4—N3$^{\rm vi}$	2.258 (4)
Mn2—N9$^{\rm ii}$	2.234 (3)		

Symmetry codes: (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{2}$; (iv) $-x+2, -y+1, -z$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y-1, z$.

The H atom of the hydroxide group was located in an electron-density map and was refined with distance restraints [O—H = 0.84 (6) Å]. The other H atoms were refined as riding on their parent C atoms [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3119). Services for accessing these data are described at the back of the journal.

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