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Poly[chlorido(μ_3-1,2,4-triazolato)-manganese(II)]

Yu-Xiang Gao,* Li-Bin Wang and Xiang-Rong Hao

Department of Chemistry, Tonghua Teachers' College, Tonghua 134002, People's Republic of China
Correspondence e-mail: yxgao_tonghua@yahoo.com.cn

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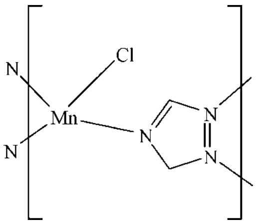
Key indicators: single-crystal X-ray study; *T* = 293 K; mean σ(N–N) = 0.007 Å; *R* factor = 0.034; *wR* factor = 0.147; data-to-parameter ratio = 15.9.

The title compound, $[Mn(C_2H_2N_3)Cl]_n$, has been prepared by the hydrothermal reaction of manganese(II) chloride and 1,2,4-triazole. The Mn^{II} cation is surrounded by three N atoms belonging to three different triazolate ligands and a Cl atom, and exhibits a slightly distorted tetrahedral coordination geometry. A polymeric layer is formed by the triply bridging nature of the 1,2,4-triazolate ligand bonded to three different Mn^{II} atoms through its three N atoms. The layer contains both binuclear units and tetranuclear macrocyclic units. In the binuclear unit, two Mn atoms are bridged by two nearly coplanar triazolate groups through the 1,2-positions, affording a six-membered ring around an inversion center. Each binuclear unit is further connected to four parallel units through the other four N atoms of the triazolate groups. Four adjacent units, which are pairwise parallel, afford 16-membered tetranuclear macrocyclic units. In each of these, the two nearest-neighbor Mn atoms are bridged by a single triazolate group through the 1,4-positions.

Related literature

For background information, see: Evans *et al.* (2001); Evans & Lin (2001); Honma *et al.* (2001); Jannasch (2003); Javaid *et al.* (2001); Sudik *et al.* (2005); Kitaura *et al.* (2002); Ngo *et al.* (2004); Rowsell *et al.* (2004); Sanchez *et al.* (2003); Vioux *et al.* (2004). For isostructural compounds, see: Krober *et al.* (1995); Ouellette *et al.* (2006).



Experimental

Crystal data

$[Mn(C_2H_2N_3)Cl]$
M_r = 158.46
Monoclinic, $P2_1/n$
a = 6.277 (2) Å
b = 9.6631 (10) Å
c = 8.6724 (10) Å
β = 99.7833 (18)°
V = 518.34 (18) Å^3
Z = 4
Mo *Kα* radiation
μ = 2.92 mm^{-1}
T = 293 (2) K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: none
4328 measured reflections
1032 independent reflections
931 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.147
S = 1.00
1032 reflections
65 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.88 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.98 e Å^{-3}

Data collection: *APEX2* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2116).

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supplementary materials

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Poly[chlorido(μ_3-1,2,4-triazolato)manganese(II)]

Y.-X. Gao, L.-B. Wang and **X.-R. Hao**

Comment

Hybrid organic-inorganic materials occupy a prominent position by virtue of their applications to catalysis, optical materials, membranes, and sorption (Ngo *et al.*, 2004; Evans *et al.*, 2001; Vioux *et al.*, 2004; Sanchez *et al.*, 2003; Evans & Lin, 2001; Jannasch, 2003; Javaid *et al.*, 2001; Honma *et al.*, 2001; Sudik *et al.*, 2005; Rowsell *et al.*, 2004; Kitaura *et al.*, 2002). The design of organic-inorganic hybrid materials is conceived of the metal, metal cluster, or metal oxide substructure as a node from which rigid or flexible multitopic organic ligands radiate to act as tethers to adjacent nodes in the bottom-up construction of complex extended architectures. While a variety of organic molecules have been investigated as potential tethers, materials incorporating multitopic carboxylates and pyridine ligands have witnessed the most significant development. However, ligands offering alternative tether lengths, different charge-balance requirements, and orientations of donor groups may afford advantages in the design of materials. One such ligand is 1,2,4-triazole, a member of the polyazaheteroaromatic family of compounds, which exhibit an extensively documented ability to bridge metal ions to afford polynuclear compounds. Triazole is an attractive ligand for the design of novel hybrid materials because of the unusual structural diversity associated with the di- and trinucleating properties of the neutral and anionic ligand forms, respectively. Here, the title complex, (I), obtained from 1,2,4-triazole and manganese(II) chloride under hydrothermal reaction is reported, which is isostructural to previously reported ones (Ouellette *et al.*, 2006; Krober *et al.*, 1995).

The coordination polyhedron of the manganese atom is shown in Fig. 1 and can be described as a slightly distorted tetrahedron. The manganese cation is surrounded by three crystallographically independent nitrogen atoms belonging to three different triazolato ligands, and a chlorine atom. The Mn—N bond lengths are in the range 2.005–2.006 Å, very close to each other. The Mn—C1 bond length is 2.218 Å. The bond angles around the manganese atom are in the range 106.21 to 113.28°. Polymeric layers, as shown in Fig. 2, are formed due to the triply bridging nature of the 1,2,4-triazolato ligand. The 1,2,4-triazolato ligand is simultaneously bonded to three different manganese atoms through its three nitrogen atoms, and its symmetry is very close to C_{2v}. A layer contains both binuclear units and tetranuclear units. In the binuclear unit two manganese atoms are bridged by two nearly coplanar triazolato groups through the 1,2-positions, affording a six-membered ring around an inversion center; the Mn···Mn separation within the binuclear unit is equal to 3.756 Å. The chlorine atoms bonded to the metals of a binuclear unit point out in opposite parallel directions. Each binuclear unit is further connected to four parallel units through the four positions of the triazolato groups. Four adjacent units, which are pairwise parallel, afford sixteen-membered tetranuclear macrocyclic units. In each of these the two nearest-neighbor manganese atoms are bridged by a single triazolate group through the 1,4 positions with Mn···Mn separations of 5.703 and 5.734 Å.

Experimental

All chemicals were used as purchased from Shanghai Chemical Co. Ltd. A mixture of manganese(II) sulfate monohydrate (0.5 mmol), potassium hydroxide (0.5 mmol), 1,2,4-triazole (0.5 mmol) and water (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was kept at 413 K for 2 d, and then cooled to room temperature. Pink crystals of (I) were obtained in a yield of 36%. Anal. Calc. for $C_2H_2ClN_3Mn$: C 15.15, H 1.26, N 26.51%; Found: C 15.12, H 1.27, N 26.55%.

Refinement

H atoms were placed in calculated positions with a C—H bond distance of 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

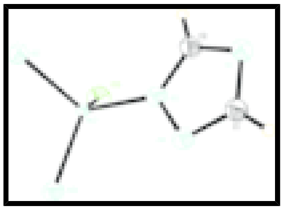

Fig. 1. The asymmetric unit of the title compound with additional atoms to complete the co-ordination of Mn, showing 30% probability displacement ellipsoids. Atoms labeled with i are at the symmetry position($2 - x$, $1 - y$, $2 - z$).

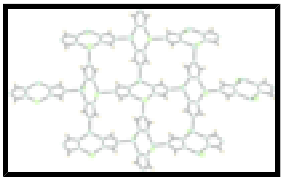

Fig. 2. View of a layer showing both the binuclear units and the tetranuclear macrocyclic units.

Poly[chlorido(μ_3-1,2,4-triazolato)manganese(II)]

Crystal data

$[Mn(C_2H_2N_3)Cl]$
$M_r = 158.46$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 6.277$ (2) Å
$b = 9.6631$ (10) Å
$c = 8.6724$ (10) Å
$\beta = 99.7833$ (18)°
$V = 518.34$ (18) Å^3
$Z = 4$

$F_{000} = 308$
$D_x = 2.031$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1032 reflections
$\theta = 3.1$–26.0°
$\mu = 2.92$ mm^{-1}
$T = 293$ (2) K
Cube, pink
0.10 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 293(2)$ K
φ and ω scans
Absorption correction: none
4328 measured reflections
1032 independent reflections

931 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.5$°
$\theta_{min} = 3.2$°
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.083P)^2 + 3.8904P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.88$ e Å^{-3}
1032 reflections	$\Delta\rho_{min} = -0.98$ e Å^{-3}
65 parameters	Extinction correction: SHELXTL (Bruker, 2001), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.073 (9)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.2120 (12)	0.7540 (7)	0.9382 (7)	0.0447 (17)
H1	0.1646	0.8101	1.0126	0.054*
C2	0.2601 (11)	0.6687 (7)	0.7288 (7)	0.0408 (15)
H2	0.2520	0.6529	0.6221	0.049*
Cl2	0.8066 (3)	0.4464 (2)	0.6732 (2)	0.0558 (6)
Mn1	0.54405 (12)	0.41947 (7)	0.81490 (8)	0.0179 (4)
N1	0.1569 (9)	0.7723 (6)	0.7860 (6)	0.0398 (12)
N2	0.3417 (9)	0.6475 (6)	0.9727 (6)	0.0416 (13)
N3	0.3735 (9)	0.5915 (5)	0.8358 (6)	0.0383 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.061 (4)	0.038 (4)	0.033 (3)	0.014 (3)	0.001 (3)	−0.003 (3)
C2	0.058 (4)	0.038 (4)	0.025 (3)	0.005 (3)	0.004 (3)	0.002 (2)
Cl2	0.0578 (12)	0.0639 (12)	0.0499 (11)	−0.0046 (9)	0.0213 (8)	0.0023 (9)

Mn1	0.0244 (5)	0.0159 (5)	0.0126 (5)	0.0004 (3)	0.0009 (3)	−0.0014 (2)
N1	0.050 (3)	0.034 (3)	0.034 (3)	0.004 (2)	0.003 (2)	0.002 (2)
N2	0.056 (3)	0.039 (3)	0.028 (3)	0.006 (3)	0.002 (2)	−0.003 (2)
N3	0.048 (3)	0.038 (3)	0.027 (2)	0.003 (2)	0.001 (2)	−0.004 (2)

Geometric parameters (Å, °)

C1—N2	1.315 (8)	Mn1—N2$^{\rm i}$	1.969 (5)
C1—N1	1.318 (8)	Mn1—N1$^{\rm ii}$	2.001 (5)
C1—H1	0.930	Mn1—N3	2.002 (5)
C2—N3	1.304 (8)	N1—Mn1$^{\rm iii}$	2.001 (5)
C2—N1	1.334 (8)	N2—N3	1.350 (7)
C2—H2	0.930	N2—Mn1$^{\rm i}$	1.969 (5)
Cl2—Mn1	2.232 (2)		
N2—C1—N1	112.3 (6)	N3—Mn1—Cl2	114.16 (18)
N2—C1—H1	123.8	C1—N1—C2	102.2 (5)
N1—C1—H1	123.8	C1—N1—Mn1$^{\rm iii}$	124.9 (5)
N3—C2—N1	113.9 (5)	C2—N1—Mn1$^{\rm iii}$	132.9 (4)
N3—C2—H2	123.0	C1—N2—N3	107.0 (5)
N1—C2—H2	123.0	C1—N2—Mn1$^{\rm i}$	125.7 (4)
N2$^{\rm i}$—Mn1—N1$^{\rm ii}$	106.1 (2)	N3—N2—Mn1$^{\rm i}$	127.3 (4)
N2$^{\rm i}$—Mn1—N3	107.7 (2)	C2—N3—N2	104.6 (5)
N1$^{\rm ii}$—Mn1—N3	108.8 (2)	C2—N3—Mn1	130.2 (4)
N2$^{\rm i}$—Mn1—Cl2	111.59 (18)	N2—N3—Mn1	125.0 (4)
N1$^{\rm ii}$—Mn1—Cl2	108.15 (18)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+1/2, *y*−1/2, −*z*+3/2; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2.

Fig. 1

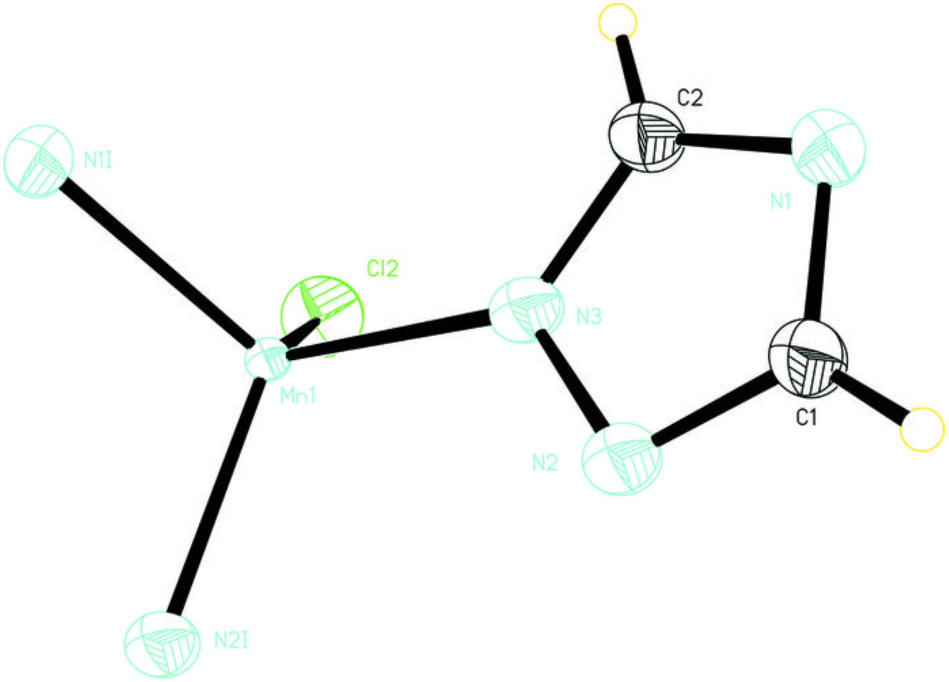

Fig. 2