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Acta Cryst. (1999). C**55**, 742–744

[Tris(2-pyridyl-κN-methyleneamino-κN-ethyl)amine-κN]manganese(II) diperchlorate

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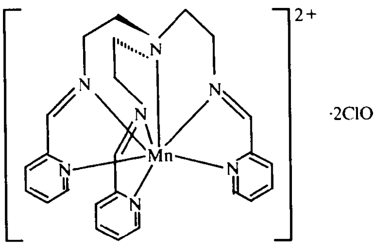
(*Received 14 September 1998; accepted 15 December 1998*)

Abstract

The Mn^{II} complex of a tripodal ligand containing one tertiary N atom, three pyridine N atoms and three Schiff base moieties derived from the condensation of tris(2-aminoethyl)amine (tren) and pyridinecarboxaldehyde, *i.e.* $[Mn(py_3tren)](ClO_4)_2$ [py_3tren is tris(2-pyridylmethyleneaminoethyl)amine, $C_{24}H_{27}N_7$], is a seven-coordinate monocapped trigonal antiprism with C_3 symmetry.

Comment

Tripodal metal complexes of transition metals and their derivatives have been widely investigated (Riley *et al.*, 1991; Sanyal *et al.*, 1995). Many potentially tripodal heptadentate ligands have been reported; most of them are imine-type ligands resulting from the condensation of tren, $N(CH_2CH_2NH_2)_3$, and various aromatic aldehydes or ketones (Kirchner *et al.*, 1987; Alcock *et al.*, 1980; Sim & Sinn, 1978). X-ray crystal structures of the BF_4^- and PF_6^- salts of $[M(py_3tren)]^{2+}$ [py_3tren is tris(2-pyridylmethyleneaminoethyl)amine] demonstrated that the distances between the metal atom and the bridgehead N atom are longer than the sum of the van der Waals radii (Kirchner *et al.*, 1987). These are described as a trigonal antiprism distorted towards a trigonal prism. To date, many seven-coordinate complexes of tripodal ligands, such as $[Mn(pyo_3tren)]^{2+}$ [pyo_3tren is tris(2-pyridyl-*N*-oxidemethyleneaminoethyl)amine; Gou *et al.*, 1993] and Mn–TPAA [TPAA is tris(2-pyridylmethylaminoethyl)amine; Deroche *et al.*, 1996], have been reported. In the course of preparing polyamine intermediates for macrocyclic condensation reactions, we obtained the title complex, (I).



(I)

The title complex crystallizes in a trigonal system with space group *P*31*c*. The manganese ion is coordinated by seven N atoms from py_3tren, the hemispheric coordination being best described as a monocapped trigonal antiprism of $[MnN_7]$, in which the bridgehead N atom is bonded to the metal atom. The three imine N atoms and the three pyridine N atoms form two ideal equilateral triangles between which the Mn atom is located. The two triangles, parallel to each other, are staggered by 48.0°, so the geometry is twisted from an ideal antitrigon (60°) by 12° towards a trigonal prism. There are equal bite angles N2—Mn1—N3 of 71.6 (2)° and equal bite distances between the chelating imine N2 and pyridine N3 atoms (N2···N3) of 2.716 Å. The complex

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cation has C_3 symmetry, the C_3 axis passing through the metal and N1 atoms. The Mn1—N2 and Mn1—N3 distances are 2.250 (6) and 2.390 (5) Å, respectively, while the Mn1—N1 bond length is 2.524 (9) Å, which is much less than the sum of the van der Waals radii of the two atoms.

The structure of this manganese complex is different from that of [Mn(py$_3$tren)](BF$_4$)$_2$ (Kirchner *et al.*, 1987), although the complex cation is the same. The distance between the metal atom and the bridgehead N atom of the latter complex (which has C_2 symmetry) is 2.79 Å (slightly less than the sum of their van der Waals radii) and the corresponding Mn1—N2 and Mn1—N3 distances are shorter than those of (I) by 0.049 and 0.073 Å. The two equilateral triangles are mutually staggered by 42.96°, so it is only described as 'pseudo-heptacoordinated'.

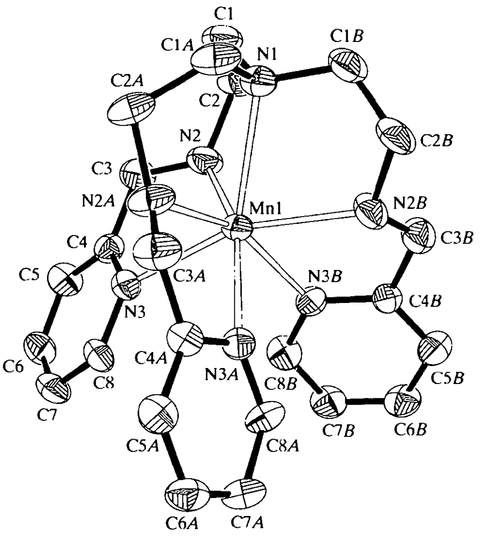

Fig. 1. The structure of the complex cation of (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

Experimental

2-Pyridinecarboxaldehyde (0.117 g, 1 mmol) was added to a solution of tren (0.146 g, 1 mmol). After stirring for 30 min at room temperature, Mn(ClO$_4$)$_2$ (1 mmol) was added and the solution was refluxed for 2 h. The yellow precipitate was filtered, washed with a small amount of dry ethanol and dried over P$_2$O$_5$ in a vacuum. Block-shaped yellow crystals suitable for X-ray structure analysis were obtained from a CH$_3$CN–EtOH (1:1) solution.

Crystal data

[Mn(C$_{24}$H$_{27}$N$_7$)](ClO$_4$)$_2$
M_r = 667.37
Trigonal
$P31c$
a = 10.068 (3) Å
c = 16.728 (6) Å
V = 1468.5 (8) Å^3
Z = 2
D_x = 1.509 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5.24–12.49°
μ = 0.690 mm^{-1}
T = 293 (2) K
Block
0.40 × 0.30 × 0.30 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.761, $T_{\max}$ = 0.800
2960 measured reflections
1131 independent reflections (plus 101 Friedel-related reflections)

791 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.078
$\theta_{\max}$ = 27.50°
$h = -1 \rightarrow 12$
$k = -13 \rightarrow 1$
$l = -1 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: 7.59%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.127
S = 1.052
1232 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.352 e Å^{-3}
$\Delta\rho_{\min}$ = −0.371 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Mn1	2/3	1/3	0.02401 (7)	0.0451 (4)
N1	2/3	1/3	0.1753 (5)	0.056 (2)
N2	0.4996 (7)	0.4070 (7)	0.0640 (3)	0.066 (2)
N3	0.4514 (6)	0.2214 (6)	−0.0639 (3)	0.0482 (12)
C1	0.5392 (10)	0.3537 (10)	0.2019 (4)	0.072 (2)
C2	0.5195 (9)	0.4647 (9)	0.1481 (4)	0.069 (2)
C3	0.3587 (8)	0.3273 (10)	0.0338 (4)	0.070 (2)
C4	0.3491 (7)	0.2642 (8)	−0.0463 (4)	0.0494 (14)
C5	0.2349 (9)	0.2422 (9)	−0.1005 (4)	0.066 (2)
C6	0.2318 (8)	0.1816 (9)	−0.1748 (4)	0.065 (2)
C7	0.3346 (9)	0.1361 (9)	−0.1924 (4)	0.066 (2)
C8	0.4445 (8)	0.1598 (8)	−0.1354 (4)	0.060 (2)
Cl1	1/3	2/3	−0.0424 (2)	0.0733 (9)
O12	1/3	2/3	0.0405 (7)	0.145 (6)
O11	0.1873 (8)	0.5497 (8)	−0.0683 (5)	0.125 (3)
Cl2	0	0	0.1187 (2)	0.0818 (11)
O22	0	0	0.0354 (5)	0.098 (3)
O21	−0.0069 (12)	0.1291 (10)	0.1484 (5)	0.138 (3)

A correction for linear isotropic decay was applied during data reduction (Siemens, 1994). All H atoms were introduced at calculated positions and refined using a riding model.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The authors would like to thank the National Natural Science Foundation of China for a grant (No. 29401003). S-HG is grateful to the State Department of Education for a special grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1054). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 744–748

catena-Poly[triphenyltin-μ-(*N*,*N*-diethylthiocarbamoylthioacetato-*O*:*O*′)], *catena*-poly[triphenyltin-μ-(*N*-methyl-*N*-phenylthiocarbamoylthioacetato-*O*:*O*′)] and triphenyl(*N*,*N*-tetramethylenethiocarbamoylthioacetato-*O*)tin

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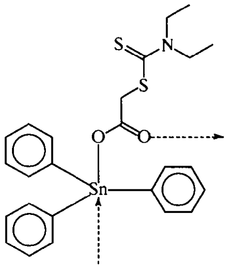
(*Received 29 July 1998; accepted 11 January 1999*)

Abstract

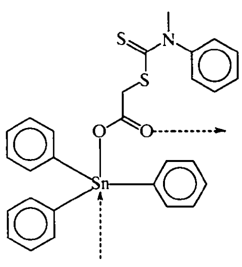
Carboxylate bridges link the two independent molecules of triphenyltin *N*,*N*-diethylthiocarbamoylthioacetate, (I), and the four independent molecules of triphenyltin *N*-methyl-*N*-phenylthiocarbamoylthioacetate, (II), into linear chains whose Sn atoms show *trans*-trigonal-bipyramidal coordination, *i.e.* (I) is *catena*-poly[triphenyltin-μ-(*N*,*N*-diethylthiocarbamoylthioacetato-*O*:*O*′)], $[Sn(C_6H_5)_3(\mu\text{-}C_7H_{12}NO_2S_2)]_n$, and (II) is *catena*-poly[triphenyltin-μ-(*N*-methyl-*N*-phenylthiocarbamoylthioacetato-*O*:*O*′)], $[Sn(C_6H_5)_3(\mu\text{-}C_{10}H_{10}NO_2S_2)]_n$. Triphenyltin *N*,*N*-tetramethylenethiocarbamoylthioacetate {or triphenyl(*N*,*N*-tetramethylenethiocarbamoylthioacetato-*O*)tin, $[Sn(C_6H_5)_3(C_7H_{10}NO_2S_2)]$} exists as a monomeric tetrahedral molecule.

Comment

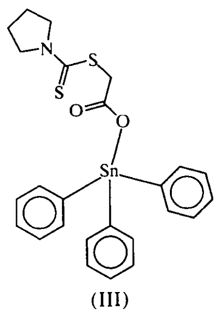
Triphenyltin alkanoates adopt linear carboxylate-bridged polymeric structures that usually propagate by twofold screw-axial translations; these polymers display a repeat distance of 5.2 Å, this distance being generally insensitive to the nature of the substituent on the carboxylate anion (Ng *et al.*, 1988). Triphenyltin *N*,*N*-dimethylthiocarbamoylthioacetate, which crystallizes with two symmetry-independent molecules in the unit cell, propagates by a twofold screw axis, but its repeat distance of 4.3 Å represents an anomaly (Ng & Kumar Das, 1995). The shorter repeat distance implies a more helical conformation of the polymeric chain. The repeat distance contrasts with a length of 4.9 Å for trimethyltin *N*,*N*-dimethylthiocarbamoylthioacetate, whose two symmetry-independent molecules propagate by mere translations, so that the architecture approaches a zigzag arrangement (Ng & Kumar Das, 1996). The rigidities of the polymeric backbone in the two carboxylates can be distinguished by the slope of the variable-temperature Sn^{119m} Mössbauer plot (Ng & Kumar Das, 1991).



(I)



(II)



(III)