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Trichloro(4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′)manganese(III) Acetonitrile Solvate (1/1)

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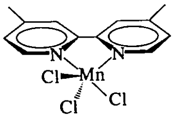
Abstract

The structure of the title compound, [MnCl$_3$(C$_{12}$H$_{12}$N$_2$)].CH$_3$CN, consists of monomeric manganese(III) species with distorted trigonal bipyramidal geometry; Mn—N$_{ax}$ 2.035 (1), Mn—N$_{eq}$ 2.096 (1), Mn—Cl$_{ax}$ 2.2187 (5), and Mn—Cl$_{eq}$ 2.2587 (5) and 2.3117 (5) Å. The Mn complexes stack as pairs in columns along the *a* axis, separated by columns of acetonitrile. Spacing between the Mn^{III} atoms is not uniform and alternating distances of 6.704 (1) ($-x$, $-y$, $-z$) and 7.713 (1) Å ($1-x$, $-y$, $-z$) are observed.

Comment

Recently, physicists have been interested in studying the magnetic properties of integer-spin (S) linear-chain Heisenberg antiferromagnets in comparison with those of non-integer-spin systems. These studies led to evidence of an energy gap in $S = 1$ linear-chain systems (Katsumata *et al.*, 1989; Katsumata, 1995; Ajiro *et al.*, 1989). The $S = 2$ linear-chain Heisenberg antiferromagnet (2,2′-bipyridine)trichloromanganese(III) (Perlepes *et al.*, 1991) has been studied and the experimental results show evidence of an energy gap at low temperatures (Granroth *et al.*, 1996). An attempt to synthesize the 4,4′-dimethyl derivative of (2,2′-bipyridine)trichloromanganese(III), *i.e.* (1), was successful and its crystal structure was determined and is presented here.



(1)

Complex (1) is monomeric and contains an Mn^{III} ion in a five-coordinate environment. Mn^{III} complexes are generally octahedral but (1) has the Mn atom in a distorted trigonal-bipyramidal coordination arrangement where the bidentate ligand occupies one axial and one equatorial position. The equatorial angles deviate significantly from the ideal value of 120° but their sum is 358.56 (4)°, while the axial angle deviates from the ideal 180° in order to accommodate the bidentate ligand. The geometry requirement of the bidentate ligand is manifested in a large deviation of the angle N1—Mn—N12 [77.95 (6)°] from the ideal value. The rest of the axial–equatorial angles are close to 90°, with the exception of Cl2—Mn—Cl3 [97.28 (2)°]. The Mn—N distances are slightly longer than their counterparts in manganese(III)–porphyrin complexes, which lie in the range 1.963–2.072 Å (Balch *et al.*, 1994; Arasasingham *et al.*, 1987; Tulinsky & Chen, 1977; Day *et al.*, 1974). The two axial bonds to N1 and Cl2 are shorter than similar bonds in the equatorial plane. The Mn^{III} ion is a d^4 system with the $d_{x^2-y^2}$ orbital containing one electron while d_{z^2} is empty. Shortening of the axial bonds along the **z** direction is observed as a result of lower electronic shielding, similar to a Jahn–Teller effect.

The Mn complexes pack as pairs in columns along the *a* axis, with the aromatic ring planes parallel to each other due to inversion symmetry. The separation between adjacent complexes is not uniform: the distance between the aromatic ring planes within a pair is 3.528 (1) Å ($-x$, $-y$, $-z$) and the distance between pairs is 3.630 (1) Å ($1-x$, $-y$, $-z$). Larger separations are observed between the Mn atoms: distances within and between pairs are 6.704 (1) ($-x$, $-y$, $-z$) and 7.713 (1) Å ($1-x$, $-y$, $-z$), respectively. A similar packing motif is observed for the solvent molecules: pairs of acetonitrile molecules (related by inversion symmetry) are arranged in columns along the *a* axis and fill voids in the crystal lattice.

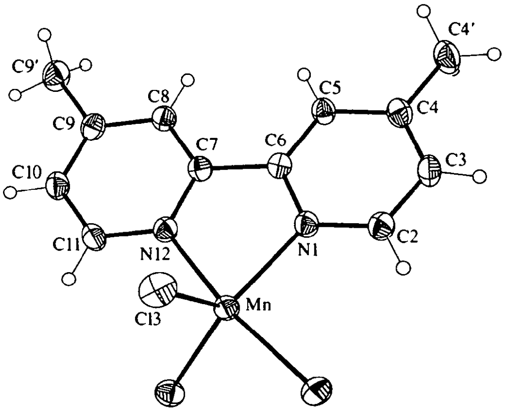


Fig. 1. The molecular structure of complex (1), with 50% probability ellipsoids, showing the atom-numbering scheme.

Experimental

The title compound was prepared using the method outlined by Perlepes *et al.* (1991), except that 4,4′-dimethyl-2,2′-bipyridine was used instead of 2,2′-bipyridine. Dark-blue needles were obtained by slow evaporation from the reaction solution.

Crystal data

$[MnCl_3(C_{12}H_{12}N_2)].C_2H_3N$
$M_r = 386.58$
Monoclinic
$P2_1/n$
$a = 7.4118\,(1)$ Å
$b = 16.7280\,(3)$ Å
$c = 13.5168\,(1)$ Å
$\beta = 90.748\,(1)°$
$V = 1675.73\,(4)$ Å^3
$Z = 4$
$D_x = 1.532$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8132 reflections
$\theta = 2.0$–$27.5°$
$\mu = 1.261$ mm^{-1}
$T = 173\,(2)$ K
Needle
$0.25 \times 0.19 \times 0.19$ mm
Dark blue

Data collection

Siemens SMART platform diffractometer
ω scans
Absorption correction: empirical from ψ scans (*SHELXTL5*; Sheldrick, 1995)
$T_{min} = 0.703$, $T_{max} = 0.787$
11 406 measured reflections

3840 independent reflections
3476 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.50°$
$h = -9 \rightarrow 8$
$k = -13 \rightarrow 22$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.081$
$S = 1.07$
3822 reflections
197 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 1.0062P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.01$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXTL5* (Sheldrick, 1995)
Extinction coefficient: 0.0034 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn—N1	2.096 (1)	Mn—Cl2	2.2187 (5)
Mn—N12	2.035 (1)	Mn—Cl3	2.3117 (5)
Mn—Cl1	2.2587 (5)		
N1—Mn—N12	77.95 (6)	N12—Mn—Cl2	168.86 (4)
N1—Mn—Cl1	137.16 (4)	N12—Mn—Cl3	91.65 (4)
N1—Mn—Cl2	92.63 (4)	Cl1—Mn—Cl2	92.65 (2)
N1—Mn—Cl3	110.55 (4)	Cl1—Mn—Cl3	110.85 (2)
N12—Mn—Cl1	90.36 (4)	Cl2—Mn—Cl3	97.28 (2)

A hemisphere of frames, 0.3° in ω, was collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. Intensity decay was <1%. ψ-Scan empirical absorption corrections were applied based on the entire data set. Full data-collection details are in the archived CIF and are also reported elsewhere (Abboud *et al.*, 1997). The H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.96 and 0.93 Å were used for methyl and sp^2 C atoms, respectively. H-atom displacement parameters were set at $1.2U_{eq}$ of the parent C atom or $1.5U_{eq}$ for methyl H atoms.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART* and *SAINT* (Siemens, 1995). Data reduction: *SHELXTL5* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL5*. Program(s) used to refine structure: *SHELXTL5*. Molecular graphics: *SHELXTL5*. Software used to prepare material for publication: *SHELXTL5*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1372). Services for accessing these data are described at the back of the journal.

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Tricarbonyl(η^5-cyclopentadienyl)(trimethylphosphine-*P*)molybdenum(II) Tetrafluoroborate

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Abstract

The title compound, $[Mo(C_5H_5)(C_3H_9P)(CO)_3]BF_4$, forms by a ligand-redistribution reaction from $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PMe_3)FBF_3]$, which is produced at low temperature by protonation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}$