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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$
H-atom completeness 91%
R factor = 0.091
wR factor = 0.290
Data-to-parameter ratio = 8.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

(SP-4-1)-Bis{aqua[(1R,2R)-N,N'-bis(salicylidene)-
cyclohexane-1,2-diyl diamine- $\kappa^4\text{O},\text{N},\text{N}',\text{O}'$]man-
ganese(III)}-di- μ -cyano- $\kappa^4\text{N}:\text{C}$ -[dicyanonickel(II)]

The title compound, $[\text{Mn}_2\text{Ni}(\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2)_2(\text{CN})_4(\text{H}_2\text{O})_2]$, is the first chiral trinuclear complex having an $\text{Mn}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}-\text{CN}-\text{Mn}^{\text{III}}$ unit. A pair of the *trans* sites of $[\text{Ni}(\text{CN})_4]^{2-}$ links two Mn^{III} units. The Mn^{III} ion has a pseudo-octahedral coordination geometry with the four donor atoms of the tetradentate chiral Schiff base forming the equatorial plane, and with a bridging cyanide and an aqua ligand at the axial positions.

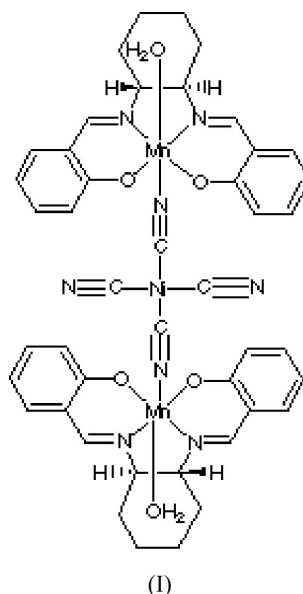
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Comment

In recent years, photofunctional and magnetic complexes have been studied widely (Sato, 2003; Sato *et al.*, 2003). One of the important goals is to discover photofunctional molecular magnets such as Prussian blue analogues (Sato *et al.*, 1996), which exhibit photo-induced electron transfer. Furthermore, cyanide-bridged heterometallic assemblies containing Schiff base Mn^{III} complexes ($^5\text{B}_{1g}$ ground state) have been developed by using $[\text{Ni}(\text{CN})_4]^{2-}$ (Yuan *et al.*, 2002), $[\text{Fe}(\text{CN})_6]^{3-}$ (Miyasaka *et al.*, 2003), and $[\text{Mo}(\text{CN})_8]^{3-}$ or $[\text{W}(\text{CN})_8]^{4-}$ (Przychodzen *et al.*, 2004) precursors. Some trinuclear $\text{Mn}^{\text{III}}-\text{NC}-\text{Cr}^{\text{III}}-\text{CN}-\text{Mn}^{\text{III}}$ or $\text{Mn}^{\text{III}}-\text{NC}-\text{Fe}^{\text{III}}-\text{CN}-\text{Mn}^{\text{III}}$ clusters exhibit characteristics of single-molecule magnets (Choi *et al.*, 2004).



Electronic properties due to individual units and crystal structures of the resulting assemblies are important for the design of cyanide-bridged heterometallic complexes. For example, Mn^{III} complexes are employed as catalysts for Kochi–Jacobsen–Katsuki enantioselective oxidation (Koren-dovych & Rybak-Akimova, 2004; Martínez *et al.*, 2002; Reger

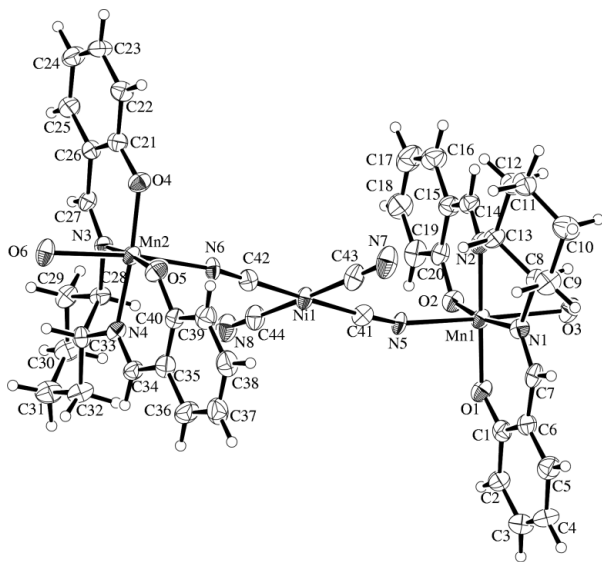


Figure 1
The structure of molecule 1, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

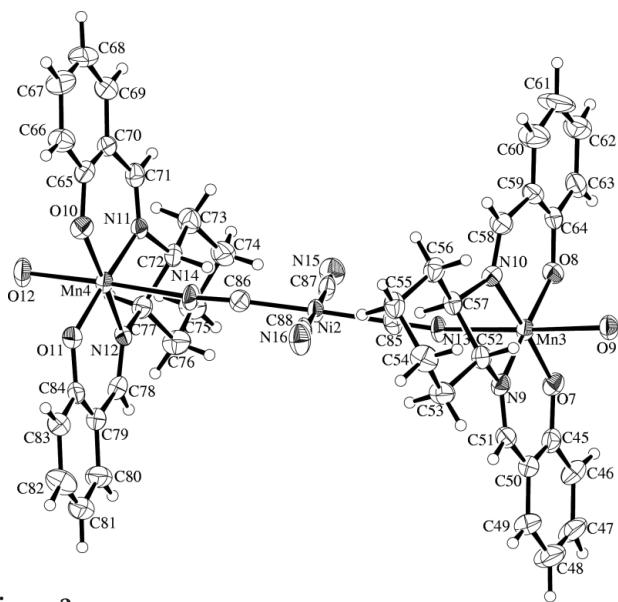


Figure 2
The structure of molecule 2, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

& Janda, 2000) and metalloprotein models for photosystem II (Ashmawy *et al.*, 1985; Aurangzeb *et al.*, 1994; Bermejo *et al.*, 1996). On the other hand, $[\text{Ni}(\text{CN})_4]^{2-}$ is known as a building block for various types of cyanide-bridged complexes (Muga *et al.*, 2004; Shen *et al.*, 2004; Maji *et al.*, 2001; Černák & Abboud, 2002; Černák *et al.*, 1990; Park & Iwamoto, 1992, 1993). For Mn^{III} complexes with O_h symmetry, the 5D ground state may split into $^5T_{2g}$ and 5E_g terms, and Jahn–Teller distortion removes the orbital degeneracy of the 5E_g ground state to give an orbital singlet lowest in energy, either the $^5A_{1g}$ or $^5B_{1g}$. Axial elongation results in a $^5B_{1g}$ ground state with negative D (Kennedy & Murray, 1985). The planar $[\text{Ni}(\text{CN})_4]^{2-}$ unit with D_{4h} symmetry exhibits prominent low-energy charge-transfer transitions, $A_{1g} \rightarrow A_{2u} [a_{1g}(d_{z^2}) \rightarrow$

$a_{2u}(p_x, \pi^*)]$ and $A_{1g} \rightarrow E_u [e_g(d_{xz}, d_{yz}) \rightarrow a_{2u}(p_x, \pi^*)]$, when the planar units are subjected to external perturbation or structural strain (Mantz & Musselman, 2002). We report here the crystal structure of the title compound, (I), which is the first chiral trinuclear $\text{Mn}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}-\text{CN}-\text{Mn}^{\text{III}}$ cluster.

In (I), there are two independent complex molecules in the asymmetric unit, molecules 1 (Ni1 complex, Fig. 1) and 2 (Ni2 complex, Fig. 2). Each molecular structure consists of one $[\text{Ni}(\text{CN})_4]^{2-}$ unit and two $[\text{Mn}\{(1R,2R)\text{-salchxn}\}(\text{H}_2\text{O})]$ units [salchxn is N,N' -bis(salicylidene)cyclohexane-1,2-diyl-diamine], forming an $\text{Mn}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}-\text{CN}-\text{Mn}^{\text{III}}$ trinuclear cluster. Terminal water ligands prevent it from forming infinite one-dimensional cyanide-bridged chains. The Mn^{III} ions adopt an elongated octahedral coordination geometry with displacement of Mn1 from the O1/N1/N2/O2 least-squares plane towards the axial cyanide ligand of 0.061 (5) Å, Mn2 from O4/N3/N4/O5 of 0.036 (5) Å, Mn3 from O7/N9/N10/O8 of 0.048 (5) Å, and Mn4 from O10/N11/N12/O11 of 0.049 (5) Å. Both elongated axial sites of the Mn^{III} ion, namely strong π -bonding cyanide and water having lone pairs, due to Jahn–Teller distortion are consistent with common high-spin Mn^{III} Schiff base complexes with $^5B_{1g}$ ground state. Because of the tetradentate Schiff base ligands, the overall molecular shapes are almost planar for the Mn1 and Mn3 units, or slightly stepped for the Mn2 and Mn4 units. The angles between least-squares planes of the aromatic rings are 5.6 (3), 4.3 (3), 4.9 (4) and 5.0 (3)° for the Mn1 (C1–C6 and C15–C20), Mn2 (C21–C26 and C35–C40), Mn3 (C45–C50 and C59–C64), and Mn4 (C65–C70 and C79–C84) units, respectively. The angles between the O1/N1/N2/O2 least-squares plane and N1/C7/C6/C1/O1 or N2/C14/C15/C20/O2 are 3.0 (3) and 5.9 (4)° in the Mn1 unit, between O4/N3/N4/O5 and N3/C27/C26/C21/O4 or N4/C34/C35/C40/O5 are 15.0 (3) and 14.7 (4)° in Mn2, between O7/N9/N10/O8 and N9/C51/C50/C45/O7 or N10/C58/C59/C64/O8 are 2.9 (3) and 10.2 (4)° in Mn3, and between O10/N11/N12/O11 and N11/C71/C70/C65/O10 or N12/C78/C79/C84/O11 are 10.9 (4) and 7.7 (4)° in Mn4, respectively. Besides these, no remarkable geometrical parameters for the related chiral Mn(salchxn) complexes (Nishikori *et al.*, 1999; Lenoble *et al.*, 1998; Nishikori *et al.*, 2000; Pospisil *et al.*, 1996) are found in (I).

On the other hand, only two of the four cyanides of $[\text{Ni}(\text{CN})_4]^{2-}$ units are involved in bridges, in other words, two cyanides do not form two-dimensional networks. Each cyanide linkage is slightly bent to form wave-like clusters, which may be attributed to bulky ligands and chirality derived from the Mn(salchxn) structural units. The structural features suggest that these trinuclear $\text{Mn}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}-\text{CN}-\text{Mn}^{\text{III}}$ clusters exhibit potentially interesting electronic functions. The dihedral angles between the least-squares planes of C41/C43/C42/C44 (Ni1) and O1/N1/N2/O2 (Mn1) or O4/N3/N4/O5 (Mn2) are 72.7 (3) and 86.1 (3)°, and between those of C85/C87/C86/C88 (Ni2) and O7/N9/N10/O8 (Mn3) or O10/N11/N12/O11 (Mn4) are 75.3 (3) and 85.8 (4)°, respectively. The axial water ligands are expected to form one-dimensional hydrogen-bonded chains along the molecular long axis, namely the crystallographic c axis. Geometrically, the following inter-

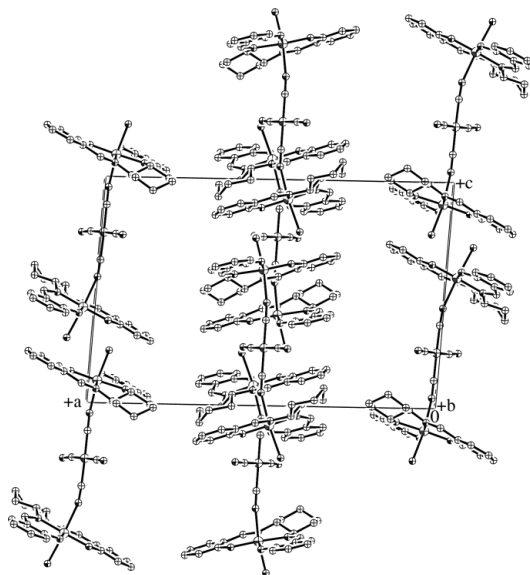


Figure 3
The molecular packing diagram of (I), viewed down the *b* axis. H atoms have been omitted for clarity.

molecular hydrogen bonds are expected: $O3 \cdots O4^i = 2.92$ (1) Å, $O3 \cdots O5^i = 3.33$ (1) Å, $O6 \cdots O1^{ii} = 2.82$ (1) Å, $O6 \cdots O2^{ii} = 3.22$ (1) Å, $O9 \cdots O10^i = 2.95$ (1) Å, $O9 \cdots O11^i = 3.24$ (1) Å, $O12 \cdots O7^{ii} = 3.00$ (1) Å and $O12 \cdots O8^{ii} = 3.15$ (1) Å [symmetry codes: (i) *x*, *y*, *z* - 1; (ii) *x*, *y*, *z* + 1].

Experimental

Under an N_2 atmosphere at 298 K, treatment of $[Et_4N]ClO_4$ (1.380 g, 6.01 mmol) and $K_2[Ni(CN)_4]$ (0.736 g, 3.05 mmol) in methanol (100 ml) for 72 h gave rise to $[Et_4N]_2[Ni(CN)_4]$, a precursor. To a solution of salicylaldehyde (0.065 g, 0.53 mmol) and (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (0.029 g, 0.25 mmol) in methanol (30 ml), $Mn(CH_3CO_2)_3 \cdot 2H_2O$ (0.069 g, 0.26 mmol), $NaClO_4 \cdot H_2O$ (0.064 g, 0.45 mmol) and $[Et_4N]_2[Ni(CN)_4]$ were added and stirred for 24 h at 298 K. Brown prismatic crystals suitable for X-ray crystallography were obtained from the resulting brown solution [yield 90%; m.p. 600 K (decomposition)]. IR (KBr, cm^{-1}): 1617 (imine), 2135 (cyanide).

Crystal data

$[Mn_2Ni(C_{20}H_{20}N_2O_2)_2(CN)_4 \cdot (H_2O)_2]$	$D_x = 1.290$ Mg m^{-3}
$M_r = 949.44$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 23.260$ (2) Å	$\theta = 10.4$ – 12.6°
$b = 13.872$ (2) Å	$\mu = 0.94$ mm^{-1}
$c = 15.182$ (3) Å	$T = 298$ (2) K
$\beta = 93.79$ (4)°	Prism, brown
$V = 4888$ (2) Å ³	$0.60 \times 0.60 \times 0.20$ mm
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.086$
ω - 2θ scans	$\theta_{max} = 27.6^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 30$
$T_{min} = 0.530$, $T_{max} = 0.828$	$k = 0 \rightarrow 18$
12714 measured reflections	$l = -19 \rightarrow 19$
11688 independent reflections	3 standard reflections
8645 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 6.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.290$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 2.49$ e Å ⁻³
8645 reflections	$\Delta\rho_{min} = -0.71$ e Å ⁻³
1004 parameters	Absolute structure: Flack (1983), no Friedel pairs
H-atom parameters constrained	Flack parameter = 0.01 (3)

Table 1

Selected geometric parameters (Å, °).

Ni1—C43	1.859 (15)	Mn2—N3	1.977 (10)
Ni1—C42	1.860 (11)	Mn2—N4	1.991 (9)
Ni1—C41	1.869 (12)	Mn2—O6	2.295 (8)
Ni1—C44	1.900 (15)	Mn2—N6	2.298 (8)
Ni2—C86	1.854 (12)	Mn3—O7	1.859 (8)
Ni2—C87	1.853 (14)	Mn3—O8	1.879 (9)
Ni2—C88	1.860 (14)	Mn3—N9	1.988 (10)
Ni2—C85	1.888 (12)	Mn3—N10	1.987 (9)
Mn1—O2	1.863 (9)	Mn3—N13	2.302 (8)
Mn1—O1	1.876 (8)	Mn3—O9	2.381 (8)
Mn1—N1	1.965 (10)	Mn4—O11	1.852 (9)
Mn1—N2	2.001 (10)	Mn4—O10	1.888 (9)
Mn1—N5	2.285 (8)	Mn4—N11	1.976 (10)
Mn1—O3	2.406 (9)	Mn4—N12	1.991 (9)
Mn2—O5	1.857 (9)	Mn4—N14	2.276 (8)
Mn2—O4	1.882 (8)	Mn4—O12	2.302 (9)
C41—Ni1—C42	178.0 (5)	O6—Mn2—N3	87.1 (3)
C41—Ni1—C43	85.7 (5)	O6—Mn2—N4	84.7 (4)
C41—Ni1—C44	93.1 (5)	O6—Mn2—N6	170.2 (3)
C42—Ni1—C43	92.3 (5)	N3—Mn2—N4	82.5 (4)
C42—Ni1—C44	88.9 (5)	N3—Mn2—N6	86.6 (4)
C43—Ni1—C44	177.7 (6)	N4—Mn2—N6	87.1 (4)
C85—Ni2—C86	178.0 (6)	O7—Mn3—O8	91.4 (4)
C85—Ni2—C87	93.1 (5)	O7—Mn3—O9	91.8 (3)
C85—Ni2—C88	87.4 (5)	O7—Mn3—N9	93.4 (4)
C86—Ni2—C87	88.8 (5)	O7—Mn3—N10	175.8 (4)
C86—Ni2—C88	90.8 (5)	O7—Mn3—N13	94.2 (4)
C87—Ni2—C88	177.6 (6)	O8—Mn3—O9	89.7 (3)
O1—Mn1—O2	91.5 (4)	O8—Mn3—N9	172.2 (4)
O1—Mn1—O3	89.6 (3)	O8—Mn3—N10	92.8 (4)
O1—Mn1—N1	93.8 (4)	O8—Mn3—N13	93.7 (4)
O1—Mn1—N2	176.6 (4)	O9—Mn3—N9	84.0 (4)
O1—Mn1—N5	93.7 (3)	O9—Mn3—N10	88.8 (4)
O2—Mn1—O3	91.0 (4)	O9—Mn3—N13	173.0 (4)
O2—Mn1—N1	170.2 (4)	N9—Mn3—N10	82.5 (4)
O2—Mn1—N2	91.9 (4)	N9—Mn3—N13	92.1 (4)
O2—Mn1—N5	93.7 (4)	N10—Mn3—N13	85.0 (4)
O3—Mn1—N1	80.8 (4)	O10—Mn4—O11	90.7 (4)
O3—Mn1—N2	90.9 (4)	O10—Mn4—O12	91.4 (4)
O3—Mn1—N5	174.2 (3)	O10—Mn4—N11	94.0 (4)
N1—Mn1—N2	83.0 (4)	O10—Mn4—N12	173.8 (4)
N1—Mn1—N5	94.2 (4)	O10—Mn4—N14	96.7 (4)
N2—Mn1—N5	85.5 (4)	O11—Mn4—O12	90.8 (4)
O4—Mn2—O5	92.1 (4)	O11—Mn4—N11	175.3 (4)
O4—Mn2—O6	91.4 (4)	O11—Mn4—N12	92.6 (4)
O4—Mn2—N3	93.4 (4)	O11—Mn4—N14	92.9 (4)
O4—Mn2—N4	174.4 (4)	O12—Mn4—N11	88.4 (4)
O4—Mn2—N6	96.5 (4)	O12—Mn4—N12	83.4 (4)
O5—Mn2—O6	92.3 (4)	O12—Mn4—N14	171.0 (4)
O5—Mn2—N3	174.5 (4)	N11—Mn4—N12	82.7 (4)
O5—Mn2—N4	92.0 (4)	N11—Mn4—N14	87.2 (4)
O5—Mn2—N6	93.3 (4)	N12—Mn4—N14	88.3 (4)

H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and included in the final cycles of refinement using riding-model constraints. H atoms of the aqua ligands were not included, since they could not be observed in difference Fourier maps, nor located uniquely by considering hydrogen-bonding features. The benzene rings (C1—C6, C15—C20,

C21–C26, C35–C40, C45–C50, C59–C64, C65–C70 and C79–C84) were treated as rigid groups. The maximum residual density is located 2.80 Å from H13. There remains a large void space in the crystal. Location of solvent water molecules was unsuccessful in the refinement. A void space or flexible region in the crystal structure is also suggested by the remarkable dependence of the IR spectra (cyanide bands) on the temperature, *viz.* 2135 cm⁻¹ at 300 K and 2141 cm⁻¹ at 9 K.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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