O(5)	0.7659 (6)	0.9210 (5)	0.5946 (3)	0.095 (2)
O(6)	-0.0231 (3)	0.8748 (3)	0.8745 (2)	0.050(1)
N(1)	0.1795 (3)	1.0629 (2)	0.8909 (2)	0.034 (1)
N(2)	0.2495 (3)	0.9969 (2)	0.9740 (2)	0.036(1)
C(1)	0.0199 (4)	1.2242 (3)	0.7268 (2)	0.041 (1)
C(2)	-0.0630(5)	1.3164 (4)	0.6529 (2)	0.055(1)
C(3)	-0.1609 (6)	1.4584 (4)	0.6601 (3)	0.066(1)
C(4)	-0.1814 (7)	1.5135 (4)	0.7389 (3)	0.074 (2)
C(5)	-0.1008 (6)	1.4248 (3)	0.8122 (3)	0.062(1)
C(6)	0.0015 (4)	1.2804 (3)	0.8070 (2)	0.041 (1)
C(7)	0.0828 (4)	1.1960 (3)	0.8859 (2)	0.040(1)
C(8)	0.3539 (4)	0.8652 (3)	0.9650 (2)	0.034 (1)
C(9)	0.4460 (4)	0.7729 (3)	1.0428 (2)	0.037 (1)
C(10)	0.4278 (5)	0.8210 (3)	1.1252 (2)	0.048 (1)
C(11)	0.5114 (6)	0.7274 (4)	1.1968 (2)	0.060(1)
C(12)	0.6133 (6)	0.5874 (4)	1.1865 (3)	0.065 (2)
C(13)	0.6344 (6)	0.5395 (4)	1.1058 (3)	0.068 (2)
C(14)	0.5529 (5)	0.6321 (3)	1.0324 (2)	0.051 (1)
C(15)	0.3723 (4)	0.7814 (3)	0.6399 (2)	0.040(1)
C(16)	0.5250 (4)	0.8332 (3)	0.5958 (2)	0.042(1)
C(17)	0.6194 (5)	0.8053 (4)	0.5049 (2)	0.058 (1)
C(18)	0.5629 (6)	0.7301 (4)	0.4590 (2)	0.066 (2)
C(19)	0.4118 (6)	0.6799 (4)	0.5020 (3)	0.062 (2)
C(20)	0.3162 (5)	0.7048 (3)	0.5900 (2)	0.052(1)
C(21)	0.5955 (4)	0.9121 (3)	0.6407 (2)	0.044 (1)
C(22)	0.8524 (9)	0.9968 (7)	0.6320 (4)	0.096 (3)
C(23)	-0.0962 (6)	0.7768 (5)	0.8567 (3)	0.068 (2)

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1.875 (2)	Mn—O(2)	1.931 (2)
1.876 (3)	Mn—O(4)	2.234 (3)
2.269 (3)	Mn—N(1)	1.967 (3)
168.1 (1)	O(1)MnO(3)	95.6 (1)
89.6 (1)	O(1)—Mn—O(6)	95.7 (1)
90.5 (1)	O(2)MnO(3)	95.6 (1)
87.3 (1)	O(2)—Mn—O(6)	89.3 (1)
79.0(1)	O(3)—Mn—O(4)	85.2(1)
85.1 (1)	O(3)—Mn—N(1)	170.3 (1)
169.3 (1)	O(4)— $Mn$ — $N(1)$	102.4 (1)
86.9(1)		
	$\begin{array}{c} 1.875 (2) \\ 1.876 (3) \\ 2.269 (3) \\ 168.1 (1) \\ 89.6 (1) \\ 90.5 (1) \\ 87.3 (1) \\ 79.0 (1) \\ 85.1 (1) \\ 169.3 (1) \\ 86.9 (1) \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$

The structure was solved by Patterson and Fourier methods. The model was then refined by full-matrix least-squares procedures. All non-H atoms were refined using anisotropic displacement parameters. H atoms were included in the structure-factor calculations at idealized positions with fixed displacement parameters, but were not refined.

All calculations for data reduction, structure solution and refinement were performed on a MicroVAX II computer using the *SHELXTL-Plus*88 (Sheldrick, 1988) package. Data collection and cell refinement were performed using Nicolet *P*3 diffractometer software. Molecular graphics were prepared using *SHELXTL-Plus*88.

The data were collected at the National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta. Financial support received from the Department of Science and Technology, New Delhi, is gratefully acknowledged.

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## Aquachloro[bis(5-chlorosalicylidene)ethylenediaminato]manganese(III)

COLIN P. HORWITZ

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213-3890, USA

GREGORY C. DAILEY AND FOOK S. THAM

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

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### Abstract

The title compound [systematic name: aquachloro $\{5,5'$ -dichloro-2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]diphenolato-N, N', O, O'}manganese(III)], [MnCl(C<sub>16</sub>H<sub>12</sub>-Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>O)], has the Mn<sup>III</sup> center in a pseudo-octahedral environment where the four donor atoms of the Schiff base ligand define the equatorial plane [Mn—O 1.874 (3) and 1.883 (2), Mn—N 1.973 (3) and 1.986 (2) Å] with a water molecule [Mn—O 2.319 (3) Å] and a chlorine [Mn—Cl 2.572 (1) Å] occupying the axial positions.

### Comment

In general, Mn<sup>III</sup> Schiff base complexes with tetradentate ligands have metal centers that are six-coordinate in solution with the additional ligands being either anions or solvent molecules. This ligation phenomenon is observable by spectroscopic (Boucher & Day, 1977) and electrochemical means (Horwitz, Ciringh, Liu & Park, 1993). Solid-state structures of the same Mn<sup>III</sup> Schiff base complexes are found with five-coordinate (Gohdes & Armstrong, 1988; Pecoraro & Butler, 1986) and six-coordinate (Davies, Gatehouse & Murray, 1973; Matsumoto, Takemoto, Ohyosi & Okawa, 1988; Ashmawy, Beagly, McAuliffe, Parish & Pritchard, 1990) metal centers. Subtle differences in either the solvent

Lists of structure factors, anisotropic displacement parameters, Hatom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

or the anion used to crystallize the compound lead to isolation of the five- as opposed to the six-coordinate complex. However, since Mn<sup>III</sup> has a somewhat higher affinity for O- compared to N-donor ligands, the sixcoordinate complex is favored when solvents like alcohols or water are used for crystallization rather than CH<sub>3</sub>CN. Reported here is the structure of the complex  $[(5,5'-Cl-salen)Mn^{III}(H_2O)Cl]$  [5,5'-Cl-salen is bis(5chlorosalicylidene)ethylenediaminato] (I).



The metal center adopts a pseudo-octahedral geometry with the axial ligands being a H<sub>2</sub>O molecule and a chloride ion (Fig. 1). Square-pyramidal geometry was found when the analogous [(salen)Mn<sup>III</sup>Cl] compound was crystallized from CH<sub>3</sub>CN (Pecoraro & Butler, 1986). The present compound was isolated while attempting to grow crystals of the binuclear complex [(5,5'-Clsalen)Mn<sup>IV</sup>( $\mu$ -O)]<sub>2</sub> (Dailey, Horwitz & Lisek, 1992) from CH<sub>2</sub>Cl<sub>2</sub>. The chloride ion probably comes from reaction of the solvent with the dimer while the water molecule presumably comes from water present in the CH<sub>2</sub>Cl<sub>2</sub> as no precautions were taken to exclude air or water.



Fig. 1. ORTEP (Johnson, 1965) diagram of the title complex with the displacement ellipsoids set at the 50% probability level.

The Mn<sup>III</sup> centers in square-pyramidal Schiff base compounds extend well out of the square plane defined by the chelate ligand [e.g. by 0.19 Å (Pecoraro & Butler, 1986) and by 0.305 Å (Gohdes & Armstrong, 1988)]. In contrast, the metal center resides nearly within this same plane in the six-coordinate complexes. For the compound we examined, the Mn<sup>III</sup> ion is slightly [0.084(3)Å] out of the least-squares plane (-0.753x)+ 7.303y + 9.005z = 1.837) and displaced toward the chloride ligand. The Mn-O and Mn-N distances in analogous five- and six-coordinate Schiff base complexes are virtually the same. The Mn--Cl(1) distance in the title compound of 2.572(1)Å is significantly

longer than the analogous distance in [(salen)Mn<sup>III</sup>Cl] of 2.461 (1) Å. Some reasons for the Mn--Cl lengthening in  $[(5,5'-Cl-salen)Mn^{III}(H_2O)Cl]$  include: (a) the effect of a stronger steric interaction between the Schiff base ligand and the chloride ion since the metal center resides essentially in the plane of the ligand; (b) the existence of an intermolecular hydrogen bond between the water ligand and an axial chloride at the equivalent position  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$  with the intermolecular  $O(1) \cdots Cl(1)$  distance being 3.136 (4) Å [H(1a) \cdots Cl(1)] 2.30 Å and O(1)—H(1a)···Cl(1) 167°]; and (c) a more pronounced Jahn-Teller distortion as the  $d^4$  Mn<sup>III</sup> ion attains more octahedral character. There is an additional intermolecular hydrogen bond between atoms H(1b) and O(2") at the equivalent position (-x, -y, -y)-z [H(1b)...O(2'') 2.18, O(1)...O(2'') 3.015 (3) Å and  $O(1) - H(1b) \cdot \cdot \cdot O(2'') \ 169^{\circ}].$ 

### **Experimental**

The title compound was obtained from [(5,5'-Cl-salen)Mn<sup>IV</sup>- $(\mu$ -O)]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (Dailey, Horwitz & Lisek, 1992).

Crystal data

$[MnCl(C_{16}H_{12}Cl_2N_2O_2)-$	Mo $K\alpha$ radiation
(H <sub>2</sub> O)]	$\lambda = 0.71069 \text{ A}$
$M_r = 443.6$	Cell parameters from 25
Monoclinic	reflections
$P2_1/c$	$\theta = 18.92 - 24.66^{\circ}$
a = 13.428(2) Å	$\mu = 1.198 \text{ mm}^{-1}$
b = 11.780(2) Å	T = 294  K
c = 12.318(2) Å	Prism
$\beta = 115.40(1)^{\circ}$	$0.28 \times 0.18 \times 0.13$ mm
V = 1760.5 (5) Å <sup>3</sup>	Black
Z = 4	
$D_x = 1.674 \text{ Mg m}^{-3}$	
-	
Data collection	
Siemens R3m/V diffractom-	$R_{\rm int} = 0.1063$
eter	$\theta_{\rm max} = 27.5^{\circ}$
Wyckoff scans	$h = -14 \rightarrow 13$
Absorption correction:	$k = -12 \rightarrow 0$
empirical ( $\psi$ scans)	$l = 0 \rightarrow 13$
$T_{\min} = 0.736, T_{\max} =$	4 standard reflections
0.775	monitored every 60
2587 measured reflections	reflections
2313 independent reflections	intensity decay: 0.4%
1902 observed reflections	<b>5 5</b>
$[F > 4.0\sigma(F)]$	
Refinement	
Refinement on F	$(\Delta/\sigma)_{\rm max} = 0.001$
R = 0.031	$\Delta \rho_{\rm max} = 0.25 \ {\rm e} \ {\rm \AA}^{-3}$
wR = 0.042	$\Delta \rho_{\rm min} = -0.19 \ {\rm e} \ {\rm \AA}^{-3}$
S = 1.083	Atomic scattering factors
1902 reflections	from International Table
226 parameters	for X-ray Crystallograp

H atoms riding with O-H

 $w = 1/[\sigma^2(F) + 0.0007F^2]$ 

0.85 and C—H 0.96 Å

es for X-ray Crystallography (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalentisotropic displacement parameters (Å<sup>2</sup>)

### $U_{\rm eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_i^* \mathbf{a}_i \cdot \mathbf{a}_j.$

	x	у	Z	$U_{eq}$
Mn	0.0720(1)	0.2069(1)	0.0516(1)	0.041 (1)
O(1)	0.0103 (2)	0.0965 (2)	-0.1208(2)	0.068 (1)
Cl(1)	0.1356(1)	0.3568(1)	0.2197 (1)	0.053 (1)
C(1')	0.3163 (3)	0.1078 (3)	0.0979 (3)	0.046 (1)
C(2')	0.2567 (3)	0.0518 (3)	0.1531 (3)	0.045 (1)
C(3')	0.3016 (3)	-0.0469 (3)	0.2193 (3)	0.051 (1)
C(4')	0.4025 (3)	-0.0869 (3)	0.2330(3)	0.056 (1)
C(5')	0.4617 (3)	-0.0307 (3)	0.1814 (3)	0.055 (1)
C(6')	0.4197 (3)	0.0649 (3)	0.1140 (3)	0.054 (1)
N(1'a)	0.1888 (2)	0.2618 (2)	0.0079 (2)	0.042 (1)
C(1'a)	0.2797 (3)	0.2108 (3)	0.0300(3)	0.050(1)
C(2'a)	0.1621 (3)	0.3713 (3)	-0.0558 (3)	0.052 (1)
0(2')	0.1606 (2)	0.0879 (2)	0.1459 (2)	0.049 (1)
Cl(2)	0.5917(1)	-0.0805(1)	0.2039(1)	0.072 (1)
C(1'')	-0.1812 (3)	0.3008 (3)	-0.0297 (3)	0.042(1)
C(2'')	-0.1464 (3)	0.2044 (3)	0.0447 (3)	0.041 (1)
C(3'')	-0.2181 (3)	0.1564 (3)	0.0879 (3)	0.046 (1)
C(4'')	-0.3200 (3)	0.2030 (3)	0.0594 (3)	0.052(1)
C(5'')	-0.3538 (3)	0.2979 (3)	-0.0140 (3)	0.051 (1)
C(6'')	-0.2868 (3)	0.3459 (3)	-0.0591 (3)	0.049 (1)
N(1''a)	-0.0167 (2)	0.3265 (2)	-0.0624 (2)	0.042 (1)
C(1''a)	-0.1158 (3)	0.3543 (3)	-0.0834 (3)	0.046 (1)
$C(2^{\prime\prime}a)$	0.0382 (3)	0.3767 (3)	-0.1315 (3)	0.052 (1)
0(2'')	-0.0493 (2)	0.1546 (2)	0.0748 (2)	0.045 (1)
Cl(3)	-0.4846 (1)	0.3561 (1)	-0.0516(1)	0.072 (1)

## Table 2. Selected geometric parameters (Å, °)

Mn—O(1)	2.319 (3)	Mn—O(2'')	1.874 (3)
Mn - N(1'a)	1.973 (3)	N(1'a) - C(1'a)	1.280 (5)
Mn - N(1''a)	1.986(2)	N(1''a) - C(1''a)	1.285 (5)
Mn-Cl(1)	2.572(1)	N(1''a) - C(2''a)	1.468 (5)
Mn—O(2')	1.883 (2)	N(1'a) - C(2'a)	1.472 (4)
O(1)—Mn— $Cl(1)$	170.1(1)	O(1)—Mn—O(2')	91.7(1)
Cl(1)—Mn—N(1'a)	88.1(1)	N(1'a)— $Mn$ — $O(2')$	92.6(1)
Cl(1)— $Mn$ — $O(2')$	96.4 (1)	Cl(1)— $Mn$ — $N(1''a)$	88.5 (1)
O(1) - Mn - N(1''a)	83.1 (1)	O(2') - Mn - N(1''a)	173.4 (1)
N(1'a)—Mn— $N(1''a)$	83.1 (1)	Cl(1)—Mn— $O(2'')$	96.5 (1)
O(1) - Mn - O(2'')	87.9(1)	O(2') - Mn - O(2'')	91.3 (1)
N(1'a) - Mn - O(2'')	173.6(1)	O(1) Mn $N(1'a)$	87.0(1)
N(1''a) - Mn - O(2'')	92.5 (1)		

The position of the Mn atom was identified in a Patterson vector map. Direct methods of phase determination lead to an electron-density map from which all the non-H atoms were identified.

Siemens standard procedures and programs were used for all data collection operations. *SHELXTL-Plus* (Sheldrick, 1990) was used for phase determination and structure refinement.

We thank the NSF for support of this research (grant No. CHE-9200574).

Lists of structure factors, anisotropic displacement parameters, Hatom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *cis,trans*-(2,2'-Bipyridine-*N*,*N*')dibromobis(4-methylpyridine-*N*)tungsten(II)

IVAN LEBAN, JURIJ V. BRENČIČ AND BORIS ČEH

Department of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 61001 Ljubljana, Slovenia

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### Abstract

The title compound,  $[WBr_2(C_6H_7N)_2(C_{10}H_8N_2)]$ , is a neutral tungsten(II) mononuclear octahedral coordination complex. The two 4-methylpyridine molecules are in the *trans* staggered conformation with an interplanar angle of 86.5 (3)°. The bidentate bipyridine ligand is slightly twisted, the angle between separate planar pyridine moieties being 5.7 (5)°.

### Comment

Although there are numerous organometallic compounds of divalent tungsten, only a few mononuclear coordination compounds of W<sup>II</sup>, most of which are six-(Colquhoun & Williams, 1984) or seven-coordinate (Barrera, Sabat & Harman, 1991), have been structurally characterized by X-ray diffraction. WCl<sub>6</sub> and WBr<sub>5</sub> are well known starting substances for the syntheses of tungsten complexes with lower oxidation states, *i.e.* from four (Brenčič, Čeh & Šegedin, 1980) down to zero (Anderson & Richards, 1986). Using the same synthetic procedure known for obtaining mononuclear anionic complexes of W<sup>III</sup> with the formula *trans*-(BaseH)[WX<sub>4</sub>L<sub>2</sub>] [Base = pyridine, 4-methylpyridine, NH<sub>3</sub>; X = Br, Cl; L = pyridine, 4-methylpyridine (Brenčič, Čeh & Leban, 1979, 1990; Brenčič, Čeh &