

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)

Table 2. Selected geometric parameters (Å, °)

Mn—O(1)	1.875 (2)	Mn—O(2)	1.931 (2)
Mn—O(3)	1.876 (3)	Mn—O(4)	2.234 (3)
Mn—O(6)	2.269 (3)	Mn—N(1)	1.967 (3)
O(1)—Mn—O(2)	168.1 (1)	O(1)—Mn—O(3)	95.6 (1)
O(1)—Mn—O(4)	89.6 (1)	O(1)—Mn—O(6)	95.7 (1)
O(1)—Mn—N(1)	90.5 (1)	O(2)—Mn—O(3)	95.6 (1)
O(2)—Mn—O(4)	87.3 (1)	O(2)—Mn—O(6)	89.3 (1)
O(2)—Mn—N(1)	79.0 (1)	O(3)—Mn—O(4)	85.2 (1)
O(3)—Mn—O(6)	85.1 (1)	O(3)—Mn—N(1)	170.3 (1)
O(4)—Mn—O(6)	169.3 (1)	O(4)—Mn—N(1)	102.4 (1)
O(6)—Mn—N(1)	86.9 (1)		

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-Plus88* (Sheldrick, 1988) package. Data collection and cell refinement were performed using Nicolet P3 diffractometer software. Molecular graphics were prepared using *SHELXTL-Plus88*.

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.

Lists of structure factors, anisotropic displacement parameters, H-atom 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.

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

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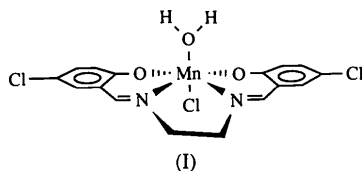
Abstract

The title compound [systematic name: aquachloro{5,5'-dichloro-2,2'-[1,2-ethanediy]bis(nitrimethylidene)}diphenolato-*N,N',O,O'*}manganese(III)], [MnCl(C₁₆H₁₂Cl₂N₂O₂)(H₂O)], has the Mn^{III} 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^{III} 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^{III} 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

or the anion used to crystallize the compound lead to isolation of the five- as opposed to the six-coordinate complex. However, since Mn^{III} has a somewhat higher affinity for O- compared to N-donor ligands, the six-coordinate complex is favored when solvents like alcohols or water are used for crystallization rather than CH₃CN. Reported here is the structure of the complex [(5,5'-Cl-salen)Mn^{III}(H₂O)Cl] [5,5'-Cl-salen is bis(5-chlorosalicylidene)ethylenediaminato] (I).



The metal center adopts a pseudo-octahedral geometry with the axial ligands being a H₂O molecule and a chloride ion (Fig. 1). Square-pyramidal geometry was found when the analogous [(salen)Mn^{III}Cl] compound was crystallized from CH₃CN (Pecoraro & Butler, 1986). The present compound was isolated while attempting to grow crystals of the binuclear complex [(5,5'-Cl-salen)Mn^{IV}(μ-O)]₂ (Dailey, Horwitz & Lisek, 1992) from CH₂Cl₂. The chloride ion probably comes from reaction of the solvent with the dimer while the water molecule presumably comes from water present in the CH₂Cl₂ as no precautions were taken to exclude air or water.

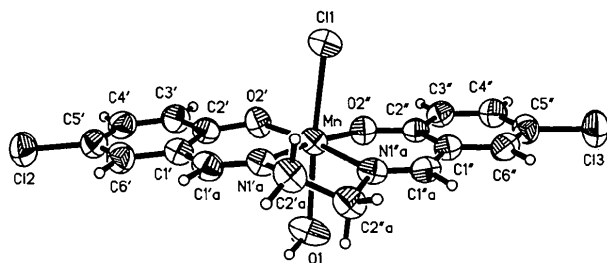


Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	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)
O(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''a)	0.0382 (3)	0.3767 (3)	-0.1315 (3)	0.052 (1)
O(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 (\AA , $^\circ$)

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.

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Lists of structure factors, anisotropic displacement parameters, H-atom 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)

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Abstract

The title compound, $[\text{WBr}_2(\text{C}_6\text{H}_7\text{N})_2(\text{C}_{10}\text{H}_8\text{N}_2)]$, 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 $86.5(3)^\circ$. The bidentate bipyridine ligand is slightly twisted, the angle between separate planar pyridine moieties being $5.7(5)^\circ$.

Comment

Although there are numerous organometallic compounds of divalent tungsten, only a few mononuclear coordination compounds of W^{II} , most of which are six- (Colquhoun & Williams, 1984) or seven-coordinate (Barrera, Sabat & Harman, 1991), have been structurally characterized by X-ray diffraction. WCl_6 and WBr_5 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^{III} with the formula *trans*-(BaseH)[WX_4L_2] [Base = pyridine, 4-methylpyridine, NH_3 ; X = Br, Cl; L = pyridine, 4-methylpyridine (Brenčič, Čeh & Leban, 1979, 1990; Brenčič, Čeh &