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The crystal structure of aqua-chlorido-6,6'-((ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-dichlorophenolato- $\kappa^4 N, N', O, O'$)manganese(III), $C_{16}H_{12}Cl_5MnN_2O_3$

Table 1: Data collection and handling.

Crystal:	Black hexagonal
Size:	0.14 × 0.14 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.50 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	27.5°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12853, 4062, 0.059
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2963
$N(\text{param})_{\text{refined}}$:	245
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

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Abstract

$C_{16}H_{12}Cl_5MnN_2O_3$, monoclinic, $P2_1/n$ (no. 14), $a = 12.3098(5)$ Å, $b = 13.1697(5)$ Å, $c = 12.4555(6)$ Å, $\beta = 117.159(1)^\circ$, $V = 1796.60(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0591$, $wR_{\text{ref}}(F^2) = 0.1315$, $T = 150$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All commercially available reagents were used as supplied. The title compound was synthesized according to classical organic synthesis of Schiff-bases: 3,5-dichlorosalicylaldehyde 0.191 g (1.0 mmol) and ethanediamine 0.5 mL (0.5 mmol) were dissolved in a mixture containing 20 mL ethanol and 10 mL methanol. The yellow suspension was stirred at 60 °C for 30 min. Then, $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol) was successively added to the above solution and the resulting brown mixture was further stirred for another 30 min and filtered. The brown black crystals of the title compound were obtained after 1 week by slow evaporation.

Experimental details

The structure was solved with the Olex2 program [2] as an interface to the SHELXT and SHELXL programs [3, 4]. All H atoms were placed in geometrically idealized positions and refined using a riding model.

Comment

There is a growing interest in the design and synthesis of novel Schiff base complexes due to their peculiar

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Mn1	0.65459 (7)	0.36093 (6)	0.64033 (7)	0.0158 (2)
Cl5	0.67673 (12)	0.17119 (10)	0.64343 (13)	0.0249 (3)
Cl1	0.26322 (12)	0.40516 (12)	0.93134 (13)	0.0269 (3)
Cl2	0.22357 (11)	0.35239 (11)	0.48849 (12)	0.0231 (3)
Cl3	0.49306 (11)	0.32994 (11)	0.21565 (12)	0.0239 (3)
Cl4	0.93727 (12)	0.37551 (11)	0.23937 (13)	0.0233 (3)
O1	0.4891 (3)	0.3554 (3)	0.6097 (3)	0.0184 (8)
O2	0.6172 (3)	0.3702 (3)	0.4748 (3)	0.0185 (8)
O3	0.6318 (3)	0.5322 (3)	0.6480 (4)	0.0247 (9)
H3A	0.558419	0.546025	0.638826	0.037*
H3B	0.680490	0.554735	0.720406	0.037*
N1	0.7129 (4)	0.3626 (3)	0.8175 (4)	0.0172 (9)
N2	0.8313 (4)	0.3886 (3)	0.6924 (4)	0.0153 (9)
C1	0.4448 (4)	0.3714 (4)	0.6848 (5)	0.0148 (11)
C2	0.3153 (4)	0.3713 (4)	0.6409 (5)	0.0165 (11)
C3	0.2623 (4)	0.3831 (4)	0.7156 (5)	0.0190 (12)
H3	0.175890	0.381623	0.682901	0.023*
C4	0.3334 (5)	0.3971 (4)	0.8384 (5)	0.0212 (12)
C5	0.4585 (5)	0.3972 (4)	0.8860 (5)	0.0204 (12)
H5	0.507637	0.405371	0.970443	0.024*
C6	0.5137 (4)	0.3853 (4)	0.8103 (5)	0.0174 (11)
C7	0.6464 (5)	0.3778 (4)	0.8702 (5)	0.0175 (11)
H7	0.686759	0.384783	0.955511	0.021*
C8	0.8466 (4)	0.3481 (4)	0.8870 (5)	0.0200 (12)
H8A	0.867552	0.275243	0.889260	0.024*
H8B	0.875841	0.372292	0.970934	0.024*
C9	0.9051 (5)	0.4088 (5)	0.8240 (5)	0.0219 (12)
H9A	0.904312	0.482160	0.841128	0.026*
H9B	0.990803	0.387172	0.851738	0.026*
C10	0.8805 (4)	0.3981 (4)	0.6226 (5)	0.0183 (11)
H10	0.964501	0.415960	0.659111	0.022*
C11	0.8213 (5)	0.3844 (4)	0.4936 (5)	0.0179 (11)
C12	0.6918 (5)	0.3692 (4)	0.4263 (5)	0.0165 (11)
C13	0.6478 (4)	0.3536 (4)	0.3016 (5)	0.0174 (11)
C14	0.7207 (5)	0.3536 (4)	0.2456 (5)	0.0213 (12)
H14	0.686670	0.340197	0.161571	0.026*
C15	0.8461 (5)	0.3735 (4)	0.3126 (5)	0.0172 (11)
C16	0.8947 (5)	0.3874 (4)	0.4346 (5)	0.0210 (12)
H16	0.979831	0.399336	0.480190	0.025*

biological and optical properties [5, 6]. A variety of related compounds have been synthesized and investigated, in this aspect. The tetradentate Schiff-base (salen) and its analogues are of special concern as they form stable coordination environments and controllable structures [7–9]. Halogenated salen-type Schiff-base Mn(III) complexes are rare [10–12]. As a part of our current research interest on the exploration of the regulating effect of Schiff base ligands in

transition metal complexes, we report a new Mn(III) complex.

Single-crystal X-ray diffraction analyses results reveal that the asymmetric unit is formed by a mononuclear Mn(III) complex whose coordination environment is defined by N_2O_2 at the equatorial plane. The bond lengths distributions for Mn-O and Mn-N are in the range of 1.895(3) Å and 1.999(4) Å, respectively, suggesting the bond length of Mn-N is slight longer than that of Mn-O. The apical positions of the title compound are occupied by one oxygen atom O(3) from water molecule and one chlorido ligand Cl(5), with bond length of Mn(1)-O(3) and Mn(1)-Cl(5) of 2.281(4) and 2.5120(15) Å, respectively, from which we can clearly see the Jahn-Teller effect of high-spin metal center. The hexa-coordinated Mn(III) center possesses an elongated axis, furnishing a common distorted octahedral structure [13–15].

Intermolecular interaction analysis shows that monomers created offset π - π stacking. Each chlorido ligand and a water molecule of an adjacent complex form a hydrogen bond, which play an important part in linking the neighboring molecules to form supramolecular aggregates ($O3-H3 \cdots Cl5^i$: $D \cdots A = 2.3657(12)$ Å, $D-H \cdots A = 153.3(3)^\circ$, $i: 3/2-x, 1/2+y, 3/2-z$).

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