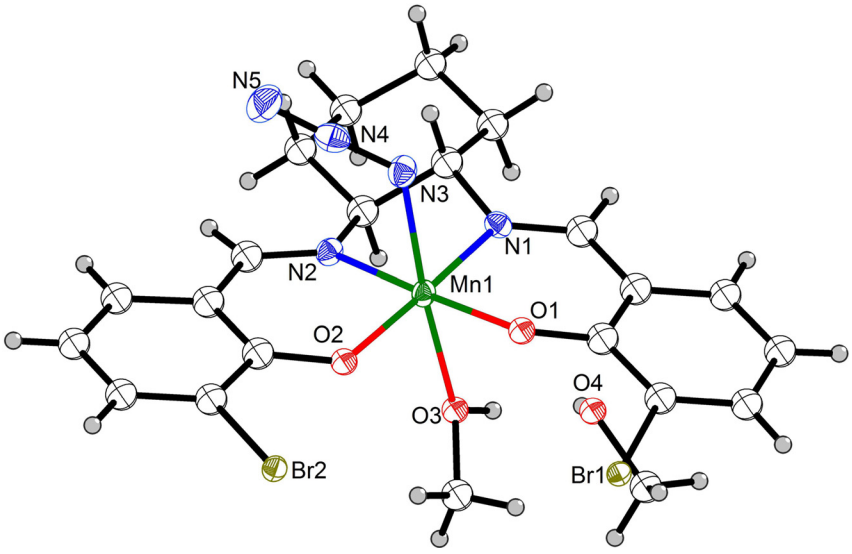
Dian Liu* and Xun Ma

The crystal structure of (azido)-κ^{1}N-6,6′-((cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3-bromophenolato-κ^4*N*,*N*,*O*,*O*)-(methanol)-manganese(III)–methanol(1/1), $C_{22}H_{26}Br_2MnN_5O_4$



https://doi.org/10.1515/ncrs-2021-0014
Received January 11, 2021; accepted January 28, 2021;
published online March 8, 2021

Abstract

$C_{22}H_{26}Br_2MnN_5O_4$, monoclinic, $P2_1/n$ (no. 14), a = 8.0106(4) Å, b = 14.5925(7) Å, c = 21.0425(11) Å, β = 100.330(2)°, V = 2419.9(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0372, $wR_{ref}(F^2)$ = 0.0766, T = 296.15 K.

CCDC no.: 2054933

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.

***Corresponding author: Dian Liu**, School of Medicine, Kunming University, Yunnan, Kunming 65200, P. R. China,
E-mail: liuliu2021666@163.com. https://orcid.org/0000-0001-5472-2832
Xun Ma, Department of Chemical Science and Technology, Kunming University, Yunnan, Kunming 65200, P. R. China

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.20 × 0.18 × 0.16 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.89 mm^{-1}
Diffractometer, scan mode:	D8/Apex-II, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	21493, 5556, 0.055
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4352
$N(param)_{refined}$:	313
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

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-bromosalicylaldehyde 0.191 g (1.0 mmol) and 1,2-cyclohexanediamine 0.5 mL (0.5 mmol) were dissolved in a mixture containing 20 ml ethanol and 10 ml methanol, the yellow suspension was

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.41310 (4)	0.84706 (2)	0.21718 (2)	0.02729 (9)
Br2	0.74380 (4)	0.55152 (2)	0.32091 (2)	0.03056 (9)
Mn3	0.49315 (5)	0.77543 (3)	0.44203 (2)	0.01596 (10)
O1	0.4796 (2)	0.84161 (12)	0.36432 (9)	0.0194 (4)
O2	0.5781 (2)	0.66865 (12)	0.40928 (9)	0.0217 (4)
O3	0.2181 (2)	0.73190 (13)	0.40079 (10)	0.0238 (5)
H3	0.1283 (17)	0.7630 (16)	0.4025 (12)	0.036*
N1	0.3863 (3)	0.87739 (14)	0.48311 (11)	0.0172 (5)
N2	0.4849 (3)	0.71447 (14)	0.52611 (11)	0.0179 (5)
N3	0.7503 (3)	0.83041 (15)	0.48626 (12)	0.0223 (5)
N4	0.8403 (3)	0.78879 (16)	0.52744 (13)	0.0245 (6)
N5	0.9298 (4)	0.74964 (19)	0.56802 (15)	0.0415 (8)
C1	0.3682 (3)	0.90619 (17)	0.34289 (13)	0.0168 (6)
C2	0.3251 (3)	0.92362 (18)	0.27604 (14)	0.0196 (6)
C3	0.2188 (4)	0.99425 (19)	0.25212 (15)	0.0261 (7)
H3A	0.192111	1.003497	0.207727	0.031*
C4	0.1505 (4)	1.05203 (19)	0.29323 (15)	0.0259 (7)
H4	0.083137	1.101517	0.276848	0.031*
C5	0.1839 (4)	1.03505 (18)	0.35813 (15)	0.0237 (7)
H5	0.136425	1.072628	0.385839	0.028*
C6	0.2891 (3)	0.96157 (17)	0.38388 (14)	0.0177 (6)
C7	0.3101 (3)	0.94617 (17)	0.45260 (14)	0.0195 (6)
H7	0.264581	0.989738	0.476886	0.023*
C8	0.4063 (4)	0.86666 (18)	0.55387 (14)	0.0200 (6)
H8	0.524054	0.881911	0.572467	0.024*
C9	0.2926 (4)	0.92551 (19)	0.58740 (15)	0.0257 (7)
H9A	0.174664	0.913250	0.569331	0.031*
H9B	0.314905	0.989772	0.580586	0.031*
C10	0.3259 (4)	0.9045 (2)	0.65947 (15)	0.0308 (7)
H10A	0.440363	0.923366	0.678088	0.037*
H10B	0.247869	0.939681	0.680167	0.037*
C11	0.3047 (4)	0.8031 (2)	0.67283 (15)	0.0296 (7)
H11A	0.187198	0.785620	0.658435	0.036*
H11B	0.333061	0.792095	0.718970	0.036*
C12	0.4186 (4)	0.7440 (2)	0.63819 (14)	0.0250 (7)
H12A	0.536804	0.757189	0.655261	0.030*
H12B	0.398334	0.679689	0.645557	0.030*
C13	0.3808 (4)	0.76419 (18)	0.56618 (14)	0.0217 (6)
H13	0.261422	0.749251	0.550087	0.026*
C14	0.5662 (3)	0.64043 (18)	0.54576 (14)	0.0213 (6)
H14	0.566078	0.622705	0.588207	0.026*
C15	0.6563 (3)	0.58311 (17)	0.50838 (14)	0.0183 (6)
C16	0.7397 (3)	0.50573 (18)	0.53875 (15)	0.0234 (7)
H16	0.739827	0.495999	0.582430	0.028*
C17	0.8206 (3)	0.44450 (18)	0.50565 (16)	0.0251 (7)
H17	0.874928	0.393748	0.526713	0.030*
C18	0.8215 (3)	0.45830 (17)	0.44053 (16)	0.0237 (7)
H18	0.876774	0.416994	0.417780	0.028*
C19	0.7399 (3)	0.53350 (17)	0.40959 (14)	0.0191 (6)
C20	0.6549 (3)	0.59871 (17)	0.44198 (14)	0.0193 (6)
C21	0.1924 (4)	0.6862 (2)	0.33929 (16)	0.0333 (8)
H21A	0.166885	0.730669	0.305329	0.050*
H21B	0.099518	0.643937	0.336733	0.050*
H21C	0.293456	0.653397	0.334749	0.050*
O4	−0.0441 (3)	0.84744 (16)	0.39200 (11)	0.0349 (5)
H4A	−0.108939	0.839127	0.417514	0.052*
C22	−0.1386 (4)	0.8504 (2)	0.32790 (16)	0.0345 (8)
H22A	−0.062813	0.860662	0.298067	0.052*
H22B	−0.219881	0.899297	0.324388	0.052*
H22C	−0.196719	0.793212	0.318037	0.052*

then stirred at 60 °C for 30 min. Then, $MnCl_2{\cdot}4H_2O$ (0.099 g, 0.5 mmol) and NaN_3 (0.035 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 one 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, with O–H = 0.84 Å (phenolic hydroxyl), 0.95 Å (benzene), and with U_{iso}(H) = 1.2 U_{eq}(C) for H atoms on phenolic hydroxyl and benzene.

Comment

There is a growing interest in the design and synthesis of novel Schiff base complexes due to their peculiar biological and optical properties [5, 6]. A variety of related compounds have been synthesized and investigated. In this aspect, tetradentate Schiff-bases (salen) and its analogues are of special concern as they provide a stable coordination environment and controllable structures [7–9]. The literatures about azide containg salen type Schiff-base complexes is still at an early stage [10, 11]. As a part of our current research interest on the regulating effect of Schiff base ligands on transition metal complexes, we report herein a new Mn(III)-complex.

The asymmetric unit is formed by a mononuclear Mn(III) ion with the coordination environment defined by N_2O_2 at the equatorial plane. The bond lengths distributions for Mn–O and Mn–N are in the range of 1.992(2) Å and 1.88(2) Å, respectively, suggesting the bond length of Mn–N is slightly longer than that of Mn–O. The apical positions of the title compound are occupied by one oxygen atom O(3) from methanol and the azido ligand (Mn–O: 2.3073(19) Å; Mn–N: 2.251(2) Å). We can clearly see the Jahn–Teller effect of high-spin d^4 metal center, furnishing a commonly distorted

octahedral structure. Bond angles around Mn(III) centers were found to be similar to previous analogous [12–14].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This work was supported by Fund for Less Developed Regions of the National Natural Science Foundation of China (No. 31760257, 21761017); Joint Basic Research Program (partial) of Yunnan Local Undergraduate Universities (2017FH001–002). The reserve academic and technical leaders of Yunnan Province (2019HB098).
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND*. Visual Crystal Structure Information System. Ver. 4.0; Crystal Impact: Bonn, Germany, 2015.
5. Zhang D., Zhang H., Chen K. Three chiral Schiff-base-manganese(III)- based complexes: synthesis, structures and magnetic properties. *J. Chem. Res.* 2015, *39*, 346–350.
6. Wu Q., Pu Q., Wu Y., Shi H., He Y., Li J., Fan Q. POM-assisted synthesis of the first cyclohexanediamine-based Salen-type Mn III -dimer complexes. *J. Coord. Chem.* 2015, *68*, 1010–1020.
7. Darensbourg D. J., Frantz E. B. X–Ray crystal structures of five-coordinate (salen)MnN_3 derivatives and their binding abilities towards epoxides: chemistry relevant to the epoxide–CO_2 copolymerization process. *Dalton Trans.* 2008, 5031–5036; https://doi.org/10.1039/b806364h.
8. Kurahashi T., Hada M., Fujii H. Critical role of external axial ligands in chirality amplification of *trans*-cyclohexane-1,2-diamine in Salen complexes. *J. Am. Chem. Soc.* 2009, *131*, 12394–12405.
9. Kurahashi T., Fujii H. Chiral distortion in a Mn^{IV}(salen)$(N_3)_2$ derived from Jacobsen's catalyst as a possible conformation model for its enantioselective reactions. *Inorg. Chem.* 2008, *47*, 7556–7567.
10. Bhargavi G., Rajasekharan M. V., Costes J. P. Synthesis, crystal structure and magnetic properties of [Mn((1*R*,2*R*)–Salcy)N_3/NCS] complexes: solvent dependent crystallization of monomers, chains and dimers. *ChemistrySelect* 2017, *2*, 7975–7982.
11. Kachi–Terajima C., Ishii R., Tojo Y., Fukuda M., Kitagawa Y., Asaoka M., Miyasaka H. Ferromagnetic exchange coupling in a family of Mn^{III} Salen-type Schiff-base out-of-plane dimers. *J. Phys. Chem. C* 2017, *121*, 12454–12468.
12. Nastase S., Tuna F., Maxim C., Muryn C. A., Avarvari N., Winpenny R. E. P., Andruh M. Supramolecular dimers and chains resulting from second # coordination sphere interactions. *Cryst. Growth Des.* 2007, *7*, 1825–1831.
13. Bhargavi G., Rajasekharan M. V., Costes J. P., Tuchagues J. P. Synthesis, crystal structure and magnetic properties of dimeric Mn^{III} Schiff base complexes including pseudohalide ligands: ferromagnetic interactions through phenoxo bridges and single molecule magnetism. *Polyhedron* 2009, *28*, 1253–1260.
14. Mondal I., Ghosh K., Chattopadhyay S. Synthesis and structural characterization of three manganese(III) complexes with N_2O_2 donor tetradentate Schiff base ligands: exploration of their catalase mimicking activity. *Inorg. Chim. Acta* 2019, *494*, 123–131.