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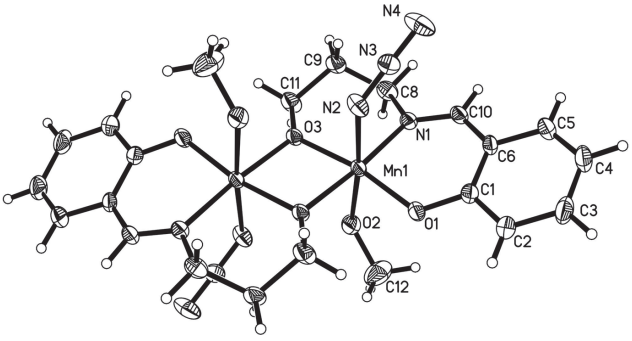
Crystal structure of diazido-dimethanolato-bis(μ$_2$-2-(((3-oxidopropyl)imino)methyl)phenolato-κ^4*O*:*O*,*O*′,N)dimanganese(III), $C_{22}H_{28}Mn_2N_8O_6$



DOI 10.1515/ncrs-2017-0049
Received February 20, 2017; accepted July 4, 2017; available online July 21, 2017

Abstract

$C_{22}H_{28}Mn_2N_8O_6$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2827(15)$ Å, $b = 8.6433(17)$ Å, $c = 11.410(2)$ Å, $\alpha = 98.58(3)°$, $\beta = 96.15(3)°$, $\gamma = 107.67(3)°$, $V = 667.8(2)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0414$, $wR_{ref}(F^2) = 0.0972$, $T = 293(2)$ K.

CCDC no.: 1534484

Table 1: Data collection and handling.

Crystal:	Dark-green pillar
Size:	0.35 × 0.18 × 0.15 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	9.9 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS RAPID IP, φ and ω
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6593, 3041, 0.047
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2482
$N(param)_{refined}$:	172
Programs:	SHELX [1], Rigaku programs [2]

The title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Salicylaldehyde (0.122 g, 1.0 mmol), tris(hydroxymethyl) aminomethane (0.121 g, 1.0 mmol) and triethylamine (0.101 g, 1.0 mmol) were dissolved in methanol (25 mL), forming a yellow solution. $Mn(NO_3)_2{\cdot}6H_2O$ (0.144 g, 0.5 mmol) and sodium azide (0.076 g, 1 mmol) were successively added to the solution with stirring. The resulting dark brown suspension was heated at 65 °C for 3 h and the color slowly changed to browne. After filtration, the brown filtrate was sealed in a beaker and kept undisturbed at room temperature. The dark-green needle-shaped crystals were isolated after one week (Yield: 75% based on Mn).

Experimental details

H atoms were generated geometrically and refined as riding atoms with C—H = 0.93 Å and U_{iso}(H) = 1.2 times U_{eq}(C) for H atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2 times U_{eq}(C) for methylene H atoms.

Comment

Design and synthesis of polynuclear transition metal aggregates have attracted great interest not only because of

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Mn1	−0.00166(5)	0.91026(4)	0.87763(3)	0.03005(16)
O3	−0.1103(3)	1.0652(2)	0.95540(15)	0.0329(4)
O2	−0.2781(3)	0.7163(2)	0.91414(17)	0.0460(5)
O1	0.0933(3)	0.7421(2)	0.82476(15)	0.0435(4)
N1	−0.1351(3)	0.8998(3)	0.71247(18)	0.0339(4)
N2	0.2557(3)	1.1140(3)	0.85423(19)	0.0446(6)
N3	0.2749(3)	1.1586(3)	0.7617(2)	0.0406(5)
C10	−0.0749(4)	0.8426(3)	0.6183(2)	0.0392(6)
H10A	−0.1307	0.8551	0.5446	0.047*
C9	−0.2508(4)	1.1358(4)	0.7785(2)	0.0443(6)
H9A	−0.1212	1.2065	0.7731	0.053*
H9B	−0.3438	1.1882	0.7516	0.053*
C1	0.1434(4)	0.7099(3)	0.7168(2)	0.0372(5)
C11	−0.2614(4)	1.1202(4)	0.9075(2)	0.0479(7)
H11A	−0.2505	1.2267	0.9546	0.057*
H11B	−0.3870	1.0424	0.9126	0.057*
C8	−0.2938(4)	0.9702(4)	0.6967(2)	0.0442(6)
H8A	−0.4126	0.8935	0.7125	0.053*
H8B	−0.3162	0.9831	0.6140	0.053*
C5	0.1300(5)	0.7225(4)	0.5069(2)	0.0518(7)
H5A	0.0815	0.7553	0.4395	0.062*
C2	0.2687(4)	0.6169(3)	0.7056(3)	0.0464(6)
H2B	0.3142	0.5793	0.7715	0.056*
N4	0.2960(5)	1.2001(4)	0.6714(3)	0.0702(9)
C6	0.0692(4)	0.7620(3)	0.6168(2)	0.0387(6)
C12	−0.2869(7)	0.5494(4)	0.9100(4)	0.0817(13)
H12A	−0.4115	0.4870	0.9267	0.123*
H12B	−0.1852	0.5449	0.9690	0.123*
H12C	−0.2699	0.5034	0.8316	0.123*
C4	0.2579(6)	0.6376(4)	0.4969(3)	0.0602(9)
H4A	0.3010	0.6173	0.4241	0.072*
C3	0.3252(5)	0.5805(4)	0.5953(3)	0.0564(8)
H3A	0.4083	0.5178	0.5870	0.068*

their potential application in biology, catalysis and material science but also owing to their intriguing variety of architectures and topologies [3, 4]. In this field, the manganese Schiff base complex is a fruitful subclass of transition metal compounds, which have been paid much attention on their bioinorganic and physical aspects such as to imitate the oxygen evolution center (OEC) in photosystem (PSII) and single-molecule magnets (SMMs) [5, 6]. A number of manganese clusters with extraordinary topologies have been reported [7, 8]. However, related research involving azide is rather rare [9]. Hence, we selected azide and single-arm Schiff base ligand salicylideneamino-3-hydroxypropane as starting material, and isolated a new complex $[Mn_2(C_{20}H_{20}N_2O_4)(N_3)_2(CH_3OH)_2]$.

The crystal structure of title compound consists of a discrete binuclear cluster. The Mn(III) ions are six-coordinated: equatorial sites are defined by three oxygen atoms and one nitrogen atom from the Schiff base ligand, the axial sites are occupied by one oxygen atom of methanolato ligand and one nitrogen atom from azide. The bond lengths of Mn—O(N) are in the range of 1.8417(19)–2.319(2) Å. The bond angles around Mn(III) ions range from 78.76 to 174.53°. All the bond lengths are within normal ranges. In addition, the benzoimidazol rings in adjacent molecules are almost parallel. The average interplanar distance is 3.771(2) Å, which suggests π−π interactions.

Acknowledgements: This work was supported by Science and Technology Bureau of Kunming projects (No. 2015-05-A-H-02-3105; 2015-05-B-H-02-3003), Fund for Less Developed Regions of the National Natural Science Foundation of China (No. 611660071, 1564023), Agricultural plastic film and products research and development of Plateau area (No. DH1606).

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