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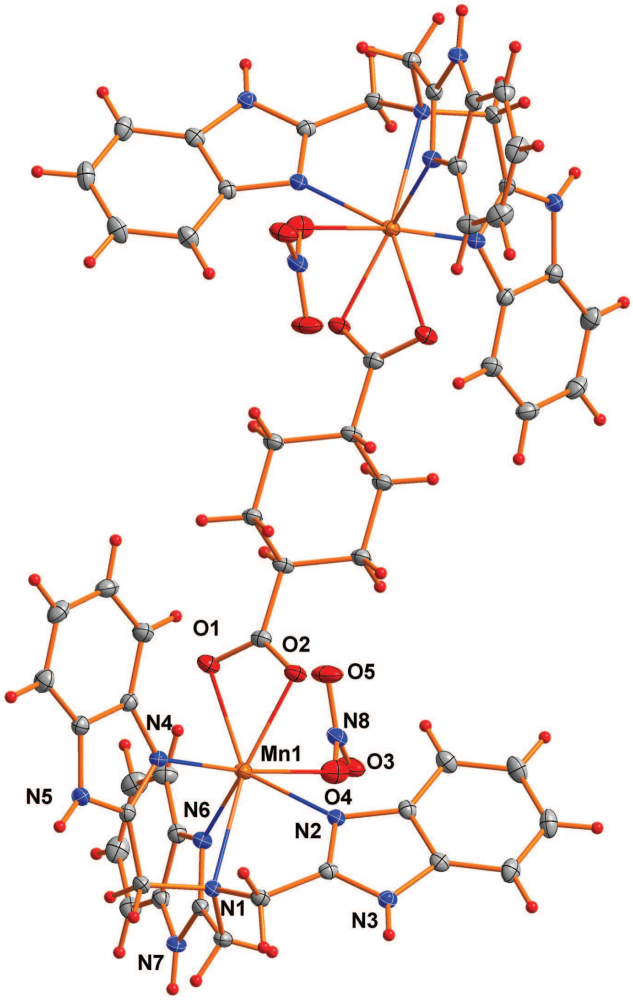
Crystal structure of dinitrato-κ*O*-bis(tris((1*H*-benzo[*d*]imidazol-2-yl)methyl)amine-κ^4*N*,*N*′,*N*″,*N*‴)-(μ$_2$-cyclohexane-1,4-dicarboxylato-κ^4*O*,*O*′:*O*″,*O*‴)dimanganese(II) – methanol – water (1/6/2), $C_{62}H_{80}Mn_2N_{16}O_{18}$



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Abstract

$C_{62}H_{80}Mn_2N_{16}O_{18}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.3232(10)$ Å, $b = 12.879(2)$ Å, $c = 13.035(2)$ Å, $\alpha = 84.854(17)°$, $\beta = 69.317(16)°$, $\gamma = 73.929(13)°$, $V = 1708.8(4)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0320$, $wR_{ref}(F^2) = 0.0860$, $T = 113$ K.

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The title complex 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.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.18 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	4.5 cm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, φ and ω
$2\theta_{max}$, completeness:	55.0°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	21912, 7697, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6684
$N(param)_{refined}$:	463
Programs:	Rigaku [1], SHELX [2]

Source of material

Tris(2-benzimidazolylmethyl)amine (*ntb*) was prepared according to the literature [3]. To a stirred methanol solution (20 mL) containing manganese(II) nitrate hexahydrate (0.057 g, 0.2 mmol) and *ntb* (0.08 g, 0.2 mmol), a methanol solution (10 mL) of 1,4-cyclohexanedicarboxylic acid (*1,4-chdc*, 0.017 g, 0.1 mmol) and triethylamine (0.022 g, 0.2 mmol) was added dropwise. After stirring for 2 hours, the

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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	0.21115(2)	0.694694(16)	0.256283(16)	0.01324(6)
O1	0.05032(10)	0.87599(8)	0.27014(8)	0.0198(2)
O2	0.16460(10)	0.78056(8)	0.11962(8)	0.0183(2)
N1	0.37957(11)	0.55528(9)	0.32723(9)	0.0144(2)
N2	0.30654(11)	0.54827(9)	0.14608(9)	0.0146(2)
N3	0.44956(11)	0.38684(9)	0.09640(9)	0.0156(2)
H3	0.5211(12)	0.3339(11)	0.0949(14)	0.019*
N4	0.36001(11)	0.76995(9)	0.26991(9)	0.0154(2)
N5	0.53332(12)	0.77207(10)	0.31315(10)	0.0173(2)
H5	0.6009(13)	0.7453(13)	0.3345(14)	0.021*
N6	0.11428(11)	0.64874(9)	0.42388(9)	0.0158(2)
N7	0.09927(12)	0.53849(10)	0.56724(10)	0.0173(2)
H7	0.1232(16)	0.4817(10)	0.6054(13)	0.021*
C1	0.47872(13)	0.49409(11)	0.23124(11)	0.0156(3)
H1A	0.5244	0.4236	0.2541	0.019*
H1B	0.5442	0.5347	0.1928	0.019*
C2	0.41079(13)	0.47708(11)	0.15718(11)	0.0144(3)
C3	0.27590(13)	0.50067(11)	0.06935(11)	0.0152(3)
C4	0.17654(14)	0.53760(12)	0.02454(12)	0.0195(3)
H4	0.1168	0.6070	0.0426	0.023*
C5	0.16878(15)	0.46865(14)	−0.04741(12)	0.0238(3)
H5A	0.1032	0.4924	−0.0802	0.029*
C6	0.25472(15)	0.36491(13)	−0.07330(12)	0.0237(3)
H6	0.2439	0.3194	−0.1209	0.028*
C7	0.35479(14)	0.32779(12)	−0.03080(12)	0.0205(3)
H7B	0.4138	0.2580	−0.0485	0.025*
C8	0.36446(13)	0.39825(11)	0.03944(11)	0.0160(3)
C9	0.43506(14)	0.61566(11)	0.38008(12)	0.0172(3)
H9C	0.5232	0.5727	0.3780	0.021*
H9D	0.3786	0.6310	0.4577	0.021*
C10	0.44363(13)	0.71921(11)	0.31950(11)	0.0154(3)
C11	0.39856(13)	0.86402(11)	0.22803(11)	0.0157(3)
C12	0.34815(15)	0.94645(11)	0.16619(12)	0.0199(3)
H12	0.2743	0.9461	0.1477	0.024*
C13	0.40969(15)	1.02870(12)	0.13282(13)	0.0226(3)
H13	0.3772	1.0859	0.0905	0.027*
C14	0.51893(15)	1.02999(12)	0.15970(13)	0.0237(3)
H14	0.5586	1.0880	0.1352	0.028*
C15	0.56991(15)	0.94889(12)	0.22087(13)	0.0225(3)
H15	0.6437	0.9496	0.2393	0.027*
C16	0.50786(14)	0.86559(11)	0.25439(12)	0.0173(3)
C17	0.30344(13)	0.48782(11)	0.40446(11)	0.0158(3)
H17A	0.3483	0.4530	0.4564	0.019*
H17B	0.2943	0.4306	0.3642	0.019*
C18	0.17171(14)	0.55918(11)	0.46528(11)	0.0153(3)
C19	−0.00552(14)	0.68930(11)	0.50692(11)	0.0167(3)
C20	−0.10481(14)	0.78350(12)	0.51140(13)	0.0214(3)
H20	−0.1011	0.8298	0.4500	0.026*
C21	−0.20906(15)	0.80657(13)	0.60937(14)	0.0253(3)
H21	−0.2772	0.8709	0.6156	0.030*
C22	−0.21651(15)	0.73731(13)	0.69977(13)	0.0247(3)
H22	−0.2896	0.7561	0.7655	0.030*
C23	−0.12055(15)	0.64278(12)	0.69562(12)	0.0215(3)
H23	−0.1259	0.5955	0.7564	0.026*
C24	−0.01524(14)	0.62051(11)	0.59729(12)	0.0172(3)
C25	0.07500(13)	0.86226(11)	0.16962(11)	0.0156(3)
C26	0.00474(13)	0.94399(11)	0.10449(11)	0.0158(3)
H26	−0.0816	0.9844	0.1565	0.019*
C27	−0.02012(14)	0.89042(11)	0.01658(12)	0.0174(3)
H27A	−0.0768	0.8417	0.0522	0.021*
H27B	0.0641	0.8461	−0.0328	0.021*
C28	0.08584(14)	1.02552(11)	0.05105(12)	0.0169(3)
H28A	0.0967	1.0628	0.1090	0.020*
H28B	0.1739	0.9861	0.0029	0.020*
O3	0.76893(11)	0.64776(9)	0.34751(10)	0.0282(3)
O4	0.97589(11)	0.63672(9)	0.26736(9)	0.0291(3)
O5	0.82973(12)	0.78146(9)	0.25057(11)	0.0341(3)
N8	0.85978(13)	0.69016(10)	0.28720(10)	0.0216(3)
O6	0.85550(15)	0.05328(11)	0.36219(11)	0.0465(4)
H6A	0.9216	0.0008	0.3388	0.070*
C29	0.8445(2)	0.08450(15)	0.46705(16)	0.0405(5)
H29A	0.9256	0.1008	0.4630	0.061*
H29B	0.8291	0.0255	0.5187	0.061*
H29C	0.7711	0.1489	0.4922	0.061*
O7	0.44194(14)	0.71153(11)	0.58787(12)	0.0421(3)
H7A	0.3693	0.7215	0.6389	0.063*
C30	0.4965(2)	0.7970(2)	0.5864(2)	0.0546(6)
H30A	0.4451	0.8631	0.5630	0.082*
H30B	0.5868	0.7799	0.5350	0.082*
H30C	0.4958	0.8079	0.6600	0.082*
O8	0.20492(13)	0.77757(10)	0.75540(10)	0.0336(3)
H8	0.1839	0.8352	0.7228	0.050*
C31	0.1151(3)	0.71489(19)	0.7676(2)	0.0552(6)
H31A	0.0550	0.7200	0.8437	0.083*
H31B	0.1633	0.6392	0.7491	0.083*
H31C	0.0651	0.7424	0.7185	0.083*
O9	0.67037(10)	0.23401(9)	0.09111(9)	0.0207(2)
H9A	0.7072(15)	0.2303(14)	0.1400(10)	0.025*
H9B	0.7257(14)	0.2288(14)	0.0257(7)	0.025*

filtrate of the resulting solution was allowed to stand at room temperature for several weeks to give light brown crystals, in a yield of 58%.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms. H atoms of water molecule were initially found in the difference Fourier map and were refined with restraint O···H distance of 0.86 Å. The U_{iso} values of the hydrogen atoms were set to 1.2 U_{eq}(C).

Discussion

Superoxide dismutases (SODs) can catalyze the conversion of superoxide to hydrogen peroxide and dioxygen *via* redox active metals [3, 4]. Mn-SOD is found in eukaryotic cell,

prokaryotic cell and stroma of mitochondria. It has been proven by X-ray crystallography that the manganese in the Mn-SODs from Bacillus stearothermophilus [5], Thermus thermophilus [6] and humans [7] is five-coordinated in a trigonal-bipyramidal geometry with a N_3O_2 coordination sphere and is ligated by three histidine residues, one aspartic acid residue and a water molecule [8].

The tetradentate tripodal ligand, tris(2-benzimidazolylmethyl) amine (*ntb*), similar to the histidine imidazole in coordination aspects of Mn-SOD, shows great potential to mimic the properties of SODs. In order to model the active site structure of Mn-SOD, a novel manganese(II) complex $[Mn_2(ntb)_2(chdc)]2(NO_3)_2 \cdot 6CH_3OH \cdot 2H_2O$ was synthesized and characterized. The two Mn atoms are bridged by 1,4-cyclohexanedicarboxylate in an asymmetrically bidetate mode (Mn-O: 2.16/2.51 Å). The distance between two Mn(II) metal centers is 11.030 Å. Each Mn is primarily five-coordinated with four nitrogen atoms from ligand of *ntb* and one the stronger coordinated oxygen atom from 1,4-cyclohexanedicarboxylate ligand. The O4 atom of the nitrate counter anion/anionic ligand shows a Mn-O distance of 2.91 Å. This is most probably to be seen as a coordination, as otherwise a large hole is present in the coordination sphere of the Mn(II) metal center (*cf*. the figure). The further discussion is focused on the five strong coordinated ligand atoms. The trigonal plane is occupied by three ligating nitrogen atoms of the benzimidazolyle groups with Mn1 being 0.0771 Å out of the plane. The bond distances are 2.2469(12) Å for Mn1-N2, 2.2269(12) Å for Mn1-N4 and 2.1819(13) Å for Mn1-N6. The angles of the trigonal plane are 104.21(5)° for N(6)-Mn(1)-N(4), 110.47(5)° for N6-Mn1-N(2) and 111.02(4)° for N4-Mn1-N2, respectively. The axial positions are occupied by one nitrogen atom N(1) from *ntb* and one carboxylate oxygen atom O2 of 1,4-cyclohexanedicarboxylate ligand with bond length of 2.6016(13) Å for Mn1-N1 and 2.1590(11) Å for Mn1-O2. The bond angle of O2-Mn1-N1 is 148.4(4)°. The bond length between Mn1 and the tertiary amine N1 atom is significantly longer (about 0.383 Å) than Mn-N(benzimidazole) (average 2.219 Å). This significant elongation has also been observed in other manganese complexes of tripodal tetradentate ligands with benzimidazolylmethyl group [3]. This complex can be regarded as the model complex of the active site structure of Mn-SOD.

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