

Amine and Imine Nitrogen Atoms of a New Schiff Base Type Ligand Simultaneously Coordinated to a Dinuclear Mn₂O₂ Core

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The dinuclear Mn(IV) complex [Mn(C-X-salpn)(μ-O)]₂·Me₂CO (H₂salpn=*N,N'*-bis(salicylidene)-1,3-diaminopropane and X = CH₂C(=O)CH₃) crystallizes in the monoclinic space group *C*2/*c* with *a* = 27.388(6), *b* = 10.388(2), *c* = 19.797(4) Å, β = 133.11(3)°, *V* = 4111(1) Å³ and *Z* = 4. It contains a new Schiff base type ligand, which is related to salpn by the addition of acetone to one of the two C=N moieties. Main feature of the centrosymmetric structure is a planar Mn₂O₂ four-membered ring. The coordination environment of the manganese atoms is roughly octahedral comprising two phenolic oxygen atoms as well as two amine and two imine nitrogen atoms of the ligand. The Mn···Mn distance is 2.740(8) Å and the Mn-O-Mn bridging angle amounts to 97.2(1)°.

Key words: Dinuclear Mn(IV) Complex, Salpn Type Schiff Base, Crystal Structure

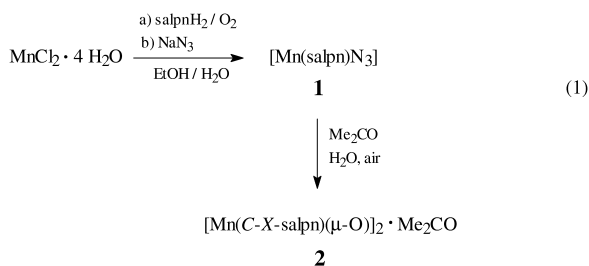
Introduction

The preparation and characterization of oxo bridged manganese complexes have been extensively studied after the discovery of several biomolecules containing di- or tetranuclear Mn units in the photosystem II [1 – 3]. These bis(μ-oxo)dimanganese complexes exhibit various catalytic activities [4 – 6]. Also it is well known that many metals including Mn play an important role in the activation of dinitrogen through the formation of nitrido complexes, which are generally suggested as key intermediates in the inorganic nitrogen cycle [7]. In the course of our investigations of the terminal nitrido functionality of both oligomeric and monomeric forms of [MnN(salpn)] (salpnH₂: *N,N'*-bis(salicylidene)-1,3-diaminopropane), we unexpectedly isolated the dinuclear Mn(IV) complex [Mn(C-X-salpn)(μ-O)]₂·Me₂CO (**2**) containing the new salpn related ligand **3**. Here we report on the results of a single crystal X-ray structure investigation of **2**.

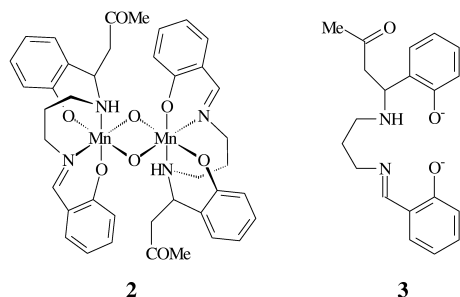
Results and Discussion

The synthesis of five-coordinated manganese(III) complexes has been reported by many researchers [8,9]. Here we describe an alternative route to such compounds. The new Mn(III) azido complex **1** with

the tetradentate Schiff base salpn is obtained in high yield in one step starting from MnCl₂, which is reacted in ethanol/water in the presence of air first with the ligand salpnH₂ and subsequently with two equivalents of NaN₃ (eq. (1)).



The Mn(III) azido complex **1** on photolysis is expected to give the corresponding Mn(V) nitrido compound [Mn(salpn)N]. **1** is isolated as a brown solid and characterized by elemental analysis as well as UV and IR spectroscopy. The complex is almost insoluble in methylene chloride and acetone. However, in an attempt to dissolve **1** in acetone in the presence of air a small quantity of deep red crystals formed in the course of several days. According to the result of a single crystal X-ray structure determination the red crystals were identified as the dinuclear complex



[Mn(C-X-salpn)(μ -O)]₂·Me₂CO (**2**) containing the new ligand **3**.

The molecular structure of complex **2** in the crystal is shown in Fig. 1, selected structural parameters are given in Table 1. Main feature of the structure of **2** is a planar four-membered Mn₂O₂ ring. The center of this ring is situated on a crystallographically imposed center of inversion so that half of the molecule is symmetry generated. The Mn–O distances within the ring (1.835(4) and 1.819(2) Å) are within the limits of accuracy almost equal. The Mn···Mn distance amounts to 2.740(8) Å. The bond angle at the metal center of 82.85(6)° and at the bridging oxygen atom of 97.15(6)° as well as the distances within the Mn₂O₂ ring compare well to those found for analogous dinuclear Mn(IV)-complexes with related salpn ligands [10–12]. In contrast, longer Mn–O bond distances (2.089–2.094 Å) are observed in bis(hydroxo) bridged Mn(III) complexes [13]. The coordination environment around the manganese atoms is roughly octahedral. Like salpn, **3** coordinates to the metal atoms by the two phenolic oxygen atoms and by the imine and amine nitrogen atoms. As observed for di- μ -oxo dimanganese complexes with bidentate Schiff bases [10], coordination of **3** is such that one phenolic oxygen atom and the imine nitrogen atom are situated *trans* to the bridging oxo groups. The distances Mn(1)–O(1) (1.912(2) Å) and Mn(1)–O(2) (1.909(5) Å) are practically equal, regardless of the *trans* bonded atom. The same applies also to the manganese nitrogen distances to the imine Mn(1)–N(1) 2.053(4) Å and amine Mn(1)–N(2) 2.072(2) Å nitrogen atoms within the limits of accuracy. There are intramolecular hydrogen bonds between the amino nitrogen atoms N(2) and N(2') and the corresponding phenolic oxygen atoms O(1') and O(1), coordinated to the other metal center (Table 1).

The dinuclear complex **2** is a rare example of a compound in which the ligand coordinates by an imino *and*

Table 1. Selected interatomic distances (Å) and angles (°) for [Mn(C-X-salpn)(μ -O)]₂·Me₂CO (**2**).

Mn(1)–O(4)	1.819(2)	Mn(1)–O(4')	1.835(4)
Mn(1)–O(1)	1.912(2)	Mn(1)–O(2)	1.909(5)
Mn(1)–N(2)	2.072(2)	Mn(1)–N(1)	2.053(4)
Mn(1)–Mn(1')	2.74(1)	O(1')–H(72)	1.98(3)
N(2)–O(1')	2.79(1)	Mn(1)–O(4)–Mn(1')	97.15(6)
O(4)–Mn(1)–O(4')	82.85(6)	O(1)–Mn(1)–O(4)	91.48(6)
O(1)–Mn(1)–O(4')	93.03(6)	O(1)–Mn(1)–O(2)	88.26(6)
O(1)–Mn(1)–N(2)	178.15(7)	O(1)–Mn(1)–N(1)	87.09(6)
O(4)–Mn(1)–O(2)	178.50(6)	O(4')–Mn(1)–O(2)	97.88(6)
O(2)–Mn(1)–N(2)	89.91(7)	O(2)–Mn(1)–N(1)	87.66(6)
N(2)–Mn(1)–O(4)	88.79(7)	N(2)–Mn(1)–O(4')	89.10(7)
N(2)–Mn(1)–N(1)	92.50(7)	N(1)–Mn(1)–O(4)	91.65(6)

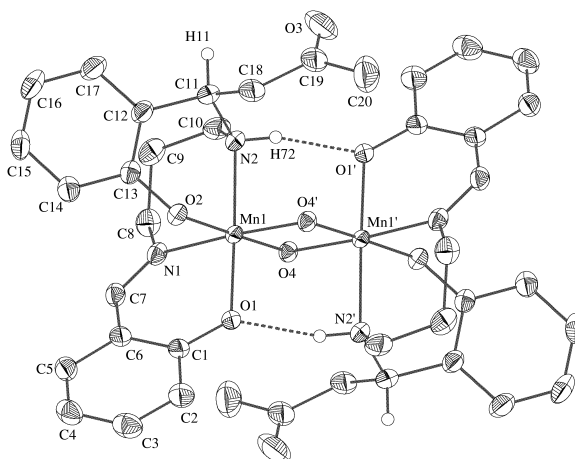


Fig. 1. A view of the molecular structure of [Mn(C-X-salpn)(μ -O)]₂·Me₂CO (**2**) in the crystal. Displacement ellipsoids are shown at the 50% probability level. H atoms, except those at the C–N bond to the amino nitrogen atom, and the acetone molecule have been omitted for clarity.

an amino group simultaneously to the same metal. Its formation from **1** implies changes at the metal as well as at the ligand. It might start with the hydrolysis of the azide ligand in the monomeric manganese(III) azido complex **1** to give the corresponding manganese(III) hydroxo species, which on oxidation will dimerize to give the four-membered Mn₂O₂ ring. The new ligand **3** results obviously from the addition of one acetone molecule to one of the two C=N moieties of the salpn ligand.

Experimental Section

Preparation of [Mn(salpn)(N₃)] (**1**)

SalpnH₂ (147 mg, 0.52 mmol) was dissolved in 20 ml of ethanol. Under mild heating, MnCl₂·4H₂O (94 mg,

Table 2. Selected crystallographic data for $[\text{Mn}(\text{C-X-salpn})(\mu\text{-O})_2]\cdot\text{Me}_2\text{CO}$ (**2**).

Formula	$\text{C}_{43}\text{H}_{50}\text{N}_4\text{O}_9\text{Mn}_2$
$f_w(\text{g}\cdot\text{mol}^{-1})$	876.76
Space group	$C2/c$ (No. 15)
	$a = 19.797(2) \text{ \AA}$
	$b = 10.3884(5) \text{ \AA}$
	$c = 20.023(2) \text{ \AA}$
	$\beta = 93.09(1)^\circ$
Vol [\AA^3]	4111.9(6)
Z	4
$D_{\text{calc}}(\text{g}/\text{cm}^3)$	1.416
$\mu[\text{cm}^{-1}]$	0.675
$F(000)$	1832
Index ranges	$-26 \leq h \leq 25$
	$-13 \leq k \leq 12$
	$-24 \leq l \leq 26$
Reflections collected	4911
Independent reflections	3508 [$R(\text{int}) = 0.0754$]
Data/restraints/parameters	4911/0/359
Goodness-of-fit on F^2	0.921
R Indices for all data	$R = 0.0648$, $wR2 = 0.0933$
Final R Indices [$I > 2\sigma(I)$]	$R = 0.0395$, $wR2 = 0.0867$
Largest diff. Peak and hole	0.520, $-0.300 \text{ e}\cdot\text{\AA}^{-3}$

0.47 mmol) was added to this solution and stirred for 1 h, followed by the addition of NaN_3 (0.62 g, 0.95 mmol) in 2 ml of water. The reaction was continued for another 3 h. The brown precipitate was filtered from the solution, and the solid was washed with ethanol three times and dried in a vacuum. Yield: 85%. UV/vis (CH_3CN): λ_{max} ($\log \epsilon$) = 372 (3.97), 274 (sh), 228 (2.13) nm. – IR (film): $\nu = 2032, 1614, 1542, 1445, 1304, 906, 804, 756, 616 \text{ cm}^{-1}$. – $\text{C}_{17}\text{H}_{16}\text{N}_5\text{O}_2\text{Mn}$

(377.28): calcd. C 54.12, H 4.27, N 18.56; found C 53.81, H 4.23, N 18.42.

Formation and X-ray structure determination of $[\text{Mn}(\text{C-X-salpn})(\mu\text{-O})_2]\cdot\text{Me}_2\text{CO}$ (**2**)

From a suspension of **1** in acetone in the presence of air a small number of deep red crystals of **2**, suitable for single crystal X-ray structure determination, formed in the course of two weeks. X-ray data collection was carried out on a STOE IPDS area-detector diffractometer using a single crystal with dimensions $0.32 \times 0.18 \times 0.13 \text{ mm}$ with graphite monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Details for data collection and structure refinement are summarized in Table 2. Cell constants were determined on the basis of 5000 reflections. Data reduction was achieved using the STOE IPDS Software [14]. The structure was solved and refined using the SIR97 program package [15]. All H atoms of the complex were found in the difference Fourier map and refined isotropically. The acetone molecule is statistically disordered over two positions. Its methyl protons were not considered in the refinement, which accounts for the relatively high residual electron density in the difference Fourier map and the $wR2$ value of 0.0933. Atomic coordinates, bond lengths, angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center as supplementary material [16].

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