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The Reactivity of the $\{Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2\}^{2+}$ Core. The Crystal Structures of $[LMn(N_3)_3]$ and $[L'Mn(S_4)(H_2O)]$ (L = 1,4,7-Triazacyclononane, L′ = *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane)

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Introduction

Recently the synthesis and structures of some dinuclear low-molecular weight complexes of iron(III) containing the μ-oxo-di-μ-acetato-diiron(III) core have been reported [1, 2]. These complexes have proven to be useful model compounds for the diiron(III) centres in the met forms of the marine invertebrate respiratory protein hemerythrin. The reactivity of this dinuclear structural unit toward protonation (of the μ-oxo-bridge) [3] and substitution of the labile [4] μ-acetato- and μ-oxo-bridges by thiocyanate and azide ions in aqueous solution [5] at pH ~7 and 25 °C has been studied. Thus the reaction of $[L_2Fe_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2]^{2+}$, where L represents the macrocycle 1,4,7-triazacyclononane, with sodium azide or sodium thiocyanate gives rapidly the complexes $[L(X)_2Fe{-}O{-}Fe(X)_2L]$ ($X = N_3^-$, NCS^-) and at prolonged reaction times the mononuclear species $LFeX_3$ [5]. These reactions demonstrate the lability of both the μ-acetato bridges and the μ-oxo-bridge in the dinuclear starting material.

The corresponding complexes of manganese(III) have also been prepared [6], namely $[L_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2$ and $[L'_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2\cdot H_2O$ (L = 1,4,7-triazacyclononane, L′ = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane). We wish to report here the investigation of their reactivity toward azide and thiocyanate in ethanol. The rapid formation of mononuclear complexes of the type $LMnX_3$ and $L'MnX_3$ ($X = N_3^-$ and NCS^-) has been observed and the crystal structure of $[LMn(N_3)_3]$ has been determined. Thus the μ-oxo-di-μ-acetato dimanganese(III) core is also substitution labile. In contrast to their iron(III) analogues the dinuclear manganese(III) complexes are strong oxidants. The reaction of $[L'_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2]^{2+}$ with sulfide anions yielded pale yellow crystals of $[L'Mn(S_4)(H_2O)]$, a manganese(II) complex, the structure of which has also been determined by X-ray crystallography.

Experimental

Starting Materials

The ligands 1,4,7-triazacyclononane(L) and *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L′) were prepared according to procedures described in the literature [7, 8], $Mn(CH_3CO_2)_3\cdot 2H_2O$ was prepared as described in ref. 9, and $[L_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2$ as well as $[L'_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2\cdot H_2O$ as described in ref. 6.

Synthesis of $LMnX_3$ and $L'MnX_3$ Complexes ($X = N_3^-$, NCS^-)

To a solution of $[L_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2$ (or $[L'_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2](ClO_4)_2\cdot H_2O$) (0.5 g) in ethanol (30 ml) was added solid sodium azide (0.5 g) (or sodium thiocyanate) at room temperature with stirring. Small red–brown crystals of $[LMnX_3]$ or $[L'MnX_3]$ ($X = N_3^-$, NCS^-) precipitated within a few minutes. These were collected by filtration and recrystallized from hot acetonitrile. Yields: 0.3 to 0.4 g. Calc. for $C_6H_{15}N_{12}Mn$: C, 23.23; H, 4.87; N, 54.18. Found: C, 23.5; H, 5.1; N, 53.8%. Calc. for $C_9H_{15}N_6S_3Mn$: C, 30.16; H, 4.22; N, 23.45; Found: C, 30.1; H, 4.0; N, 23.3%. Calc. for $C_9H_{21}N_{12}Mn$: C, 30.68; H, 6.01; N, 47.71; Found: C, 30.4; H, 6.2; N, 47.8%. Calc. for $C_{12}H_{21}N_6S_3Mn$: C, 35.99; H, 5.29; N, 20.98; Found: C, 35.8; H, 5.4; N, 21.1%.

Synthesis of $L'Mn(S_4)(H_2O)$

A solution of $Mn(CH_3CO_2)_3\cdot 2H_2O$ (1 g) and *N,N′,-N″*-trimethyl-1,4,7-triazacyclononane (1 g) in methanol (50 ml) was stirred at room temperature for 30 min under an argon atmosphere, after which time an aqueous solution (2 ml) of $(NH_4)_2S$ (40%) was

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TABLE I. Crystal Data for [$LMn(N_3)_3$] and [$L'Mn(S_4)(H_2O)$]

	[$LMn(N_3)_3$]	[$L'Mn(S_4)(H_2O)$]
Formula	$C_6H_{15}N_{12}Mn$	$C_9H_{23}N_3OMnS_4$
Molecular weight	310.2	372.5
Crystal dimensions (mm)	0.4 x 0.3 x 0.2	0.15 x 0.2 x 0.2
Crystal system	orthorhombic	orthorhombic
Space group	(D_2^4) $P2_12_12_1$	(D_{2h}^{15}) *Pbca*
a (Å)	9.103(3)	8.321(2)
b (Å)	10.554(4)	15.128(4)
c (Å)	13.298(4)	26.37(1)
Z	4	8
V ($Å^3$)	1277.6	3318.9
Calculated density (g cm^{-3})	1.613	1.491
Instrument	AED II (Siemens)	AED II (Siemens)
Scan	ω	ω
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (graphite monochromatized)
Linear absorption coefficient (cm^{-1})	10.2	12.1
Transmission factors	0.63–0.82	0.587–0.67
2θ range (°)	2.5–60	2.5–70
Number of unique intensities ($I \geqslant 2.0\sigma(I)$)	1264	1938
Number of parameters refined	162	163
R	0.058	0.050
R_w	0.045	0.041
Goodness of fit	2.20	1.59

added. The red–brown solution immediately became pale yellow. After reducing the volume of this solution to 15 ml under reduced pressure and standing for 24 h in the refrigerator, pale yellow crystals formed, which were collected by filtration. Yield: 0.48 g. Calc. for $C_9H_{23}N_3OS_4Mn$: C, 29.02; H, 6.22; N, 11.28; S, 34.43; Found: C, 29.1; H, 6.1; N, 12.0; S, 33.9%.

X-ray Measurements and Structure Determinations

Crystals of [$LMn(N_3)_3$] (red–brown) and of [$L'Mn(S_4)(H_2O)$] (pale yellow) were grown from ethanol solution at room temperature. Data were collected with an AED II (Siemens) diffractometer with ω-scan. Crystal parameters and additional details of the data collection are given in Table I. The unit cell parameters listed in Table I were obtained by a least-squares fit to the automatically centered settings for 30 reflections, respectively. The data were corrected for Lorentz, polarisation, and anomalous dispersion effects. An empirical absorption correction was also carried out in both cases (ψ-scans). The structures were solved by standard Patterson and difference Fourier methods and were refined using anisotropic thermal parameters for all non-hydrogen atom with the exceptions of N(9) and N(12), which are N_γ-atoms of coordinated azide ligands in [$LMn(N_3)_3$] and which exhibited large thermal motions. These two nitrogen atoms were refined with an isotropic thermal parameter *U*, respectively. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 10. All hydrogen atoms were placed at calculated positions with d(C–H) = 0.96 Å and sp^3-hybridized carbon atoms and group isotropic thermal parameters. The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(I)$.*

The refinements converged with values for $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, listed in Table I. The largest peaks in final difference Fourier maps were less than 0.6 e $Å^{-3}$ in height. Final atom coordinates for [$LMn(N_3)_3$] and [$L'Mn(S_4)(H_2O)$] are given in Tables II and III, respectively; selected bond distances and angles for [$LMn(N_3)_3$] are given in Table IV and for [$L'Mn(S_4)(H_2O)$] in Table V.

Results and Discussion

The solid complexes [$LMnX_3$] and [$L'MnX_3$], where L and L′ represent the tridentate macrocycles 1,4,7-triazacyclononane and *N,N′,N″*-trimethyl-1,4,7-triazacyclononane, respectively, and X is azide or thiocyanate, were obtained by treating a solution of the respective binuclear complex [$L_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2$]$(ClO_4)_2$ and [$L'_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2$]$(ClO_4)_2 \cdot H_2O$ in ethanol with solid sodium azide or

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*Computations were carried out on an ECLIPSE Computer using the program package STRUCSY, Structure Computation system, Stoe, Darmstadt, F.R.G.

TABLE II. Fractional Atom Coordinates for [$LMn(N_3)_3$]

Atom	*x*	*y*	*z*
Mn	0.0345(1)	0.0112(1)	0.30146(8)
N(1)	0.1692(7)	0.1471(5)	0.2790(5)
N(2)	0.1526(7)	−0.1298(5)	0.2518(5)
N(3)	0.0091(6)	0.0134(7)	0.0840(5)
N(4)	−0.1381(6)	−0.1107(5)	0.3397(4)
N(5)	0.0922(6)	−0.0266(5)	0.4643(4)
N(6)	0.0848(7)	0.0004(8)	0.0138(4)
N(7)	−0.0692(6)	0.0297(6)	0.1553(4)
N(8)	−0.1050(6)	0.1441(5)	0.3722(5)
N(9)	0.3760(15)	−0.200(1)	0.317(1)
N(10)	0.273(1)	−0.1598(6)	0.2856(6)
N(11)	0.301(1)	0.1374(8)	0.2757(7)
N(12)	0.420(1)	0.129(2)	0.254(1)
C(1)	0.0309(10)	−0.1586(7)	0.4786(6)
C(2)	−0.1244(9)	−0.1679(7)	0.4390(7)
C(3)	−0.2747(7)	−0.0316(6)	0.3334(5)
C(4)	−0.2561(8)	0.0917(7)	0.3896(6)
C(5)	−0.0312	0.1813(7)	0.4686(5)
C(6)	0.022(1)	0.0690(7)	0.5277(5)

TABLE III. Fractional Atom Coordinates for [$L'Mn(S_4)$-H_2O]

Atom	*x*	*y*	*z*
Mn	0.1143(1)	0.21730(5)	0.13392(3)
S(1)	0.0975(2)	0.35330(9)	0.07585(6)
S(2)	−0.1592(2)	0.2377(1)	0.17703(6)
S(3)	−0.1326(2)	0.3947(1)	0.09179(6)
S(4)	−0.1671(2)	0.3732(1)	0.16788(7)
N(1)	0.3612(6)	0.1716(3)	0.1011(2)
N(2)	0.0420(6)	0.1140(3)	0.0720(2)
N(3)	0.1606(5)	0.0808(3)	0.1738(2)
C(1)	0.3379(8)	0.1168(4)	0.0553(2)
C(2)	0.1717(8)	0.1246(4)	0.0340(2)
C(3)	0.0387(8)	0.0227(4)	0.0936(2)
C(4)	0.0348(8)	0.0243(4)	0.1507(2)
C(5)	0.3247(7)	0.0488(4)	0.1628(2)
C(6)	0.4329(7)	0.1206(4)	0.1441(2)
C(7)	0.4642(7)	0.2500(4)	0.0887(2)
C(8)	−0.1137(7)	0.1371(4)	0.0490(2)
C(9)	0.1343(7)	0.0855(4)	0.2292(2)
O	0.2327(6)	0.3006(3)	0.1972(2)

TABLE IV. Bond Distances (Å) and Angles (°) for $LMn(N_3)_3$

Mn–N(1)	1.911(6)	N(1)–N(11)	1.207(11)
Mn–N(2)	1.951(6)	N(2)–N(10)	1.227(11)
Mn–N(4)	2.093(5)	N(3)–N(6)	1.167(10)
Mn–N(5)	2.263(5)	N(3)–N(7)	1.199(9)
Mn–N(7)	2.170(6)	N(11)–N(12)	1.125(19)
Mn–N(8)	2.113(6)	N(9)–N(10)	1.112(17)
N(5)–C(1)	1.513(9)	N(4)–C(2)	1.46(1)
N(5)–C(6)	1.46(1)	N(4)–C(3)	1.500(8)
N(8)–C(4)	1.501(9)	C(1)–C(2)	1.51(1)
N(8)–C(5)	1.50(1)	C(3)–C(4)	1.51(1)
C(5)–C(6)	1.50(1)		
N(1)–Mn–N(2)	99.5(3)	N(1)–Mn–N(7)	94.1(3)
N(2)–Mn–N(4)	91.6(3)	N(2)–Mn–N(8)	171.0(3)
N(4)–Mn–N(8)	81.3(3)	N(1)–Mn–N(8)	87.5(3)
N(1)–Mn–N(4)	168.7(2)	N(4)–Mn–N(7)	86.9(3)
N(2)–Mn–N(7)	90.3(3)	Mn–N(1)–N(11)	125.5(7)
N(7)–Mn–N(8)	94.4(3)	Mn–N(2)–N(10)	124.5(7)
N(1)–N(11)–N(12)	167.4(8)	Mn–N(7)–N(3)	115.9(5)
N(6)–N(3)–N(7)	178.9(10)	N(2)–N(10)–N(9)	172.1(11)
Mn–N(4)–C(2)	114.2(5)	C(1)–N(5)–C(6)	113.8(8)
Mn–N(4)–C(3)	105.4(3)	Mn–N(8)–C(4)	112.0(4)
C(2)–N(4)–C(3)	110.6(8)	Mn–N(8)–C(5)	106.6(4)
N(5)–C(1)–C(2)	111.1(6)	C(4)–N(8)–C(5)	112.0(8)
N(4)–C(2)–C(1)	111.6(7)	N(8)–C(5)–C(6)	112.7(7)
N(4)–C(3)–C(4)	111.1(6)	N(5)–C(6)–C(5)	112.6(7)
N(8)–C(4)–C(3)	110.1(6)		

sodium thiocyanate at room temperature. The neutral complexes precipitated as red–brown microcrystals. They are insoluble in water but may be recrystallized from hot acetonitrile or ethanol.

The reaction of red [$L_2Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2$] $^{2+}$, which formed from $Mn(CH_3CO_2)_3 \cdot 2H_2O$ and the macrocyclic ligand in methanol, with an excess of sulfide in methanol, gave a pale yellow solution, from which, after evaporation of one half of the solvent under reduced pressure, pale yellow crystals of [$L'Mn(S_4)(H_2O)$] were obtained at 0 °C. This reaction involves the reduction of the manganese(III)

TABLE V. Bond Distances (Å) and Angles (°) for $L'Mn(S_4)(H_2O)$

Mn–O	2.311(4)	S(1)–S(3)	2.058(3)
Mn–S(1)	2.569(2)	S(2)–S(4)	2.066(2)
Mn–S(2)	2.562(2)	S(3)–S(4)	2.053(3)
Mn–N(1)	2.334(5)	N(1)–C(1)	1.478(8)
Mn–N(2)	2.339(4)	N(1)–C(6)	1.496(7)
Mn–N(3)	2.349(4)	N(1)–C(7)	1.499(7)
N(2)–C(2)	1.481(8)	N(3)–C(4)	1.483(7)
N(2)–C(3)	1.495(7)	N(3)–C(5)	1.477(7)
N(2)–C(8)	1.473(7)	N(3)–C(9)	1.480(6)
C(1)–C(2)	1.497(9)		
C(3)–C(4)	1.506(8)		
C(5)–C(6)	1.494(8)		
S(1)–Mn–S(2)	96.9(1)	S(1)–Mn–N(1)	93.6(2)
S(1)–Mn–O	91.0(2)	S(2)–Mn–N(1)	169.2(1)
S(2)–Mn–O	89.6(2)	N(1)–Mn–N(2)	76.7(2)
N(2)–Mn–N(3)	76.6(2)	N(2)–Mn–O	167.9(1)
S(1)–Mn–N(2)	96.0(2)	S(1)–Mn–N(3)	168.3(1)
S(2)–Mn–N(2)	99.3(2)	S(2)–Mn–N(3)	93.0(2)
N(1)–Mn–N(3)	76.2(2)	N(1)–Mn–O	93.1(2)
N(3)–Mn–O	94.9(2)	Mn–S(1)–S(3)	99.9(1)
S(1)–S(3)–S(4)	106.4(1)	Mn–S(2)–S(4)	95.5(1)
S(2)–S(4)–S(3)	105.5(1)		

centres with concomitant formation of the S_4^{2-} anion, which then acts as a bidentate ligand.

From variable temperature magnetic susceptibility measurements between 100 and 300 K using the Faraday method of powdered samples of $[LMn(N_3)_3]$ and of $[L'Mn(S_4)(H_2O)]$ temperature independent magnetic moments of 4.96(4) μ_B and 5.82(4) μ_B were deduced, respectively, which are typical for manganese(III) (d^4, high-spin) and manganese(II) (d^5, high-spin).

Crystals of $[LMn(N_3)_3]$ consist of monomeric, neutral species; Fig. 1 shows the structure and the atom labeling scheme. Table IV summarizes important bond distances and angles. The macrocyclic ligand 1,4,7-triazacyclononane occupies one face of a distorted octahedral polyhedron, which is completed by three facially coordinated azido ligands. The Mn–N distances of the MnN_6 core vary from 1.91 Å to 2.26 Å. The high-spin manganese(III) complex (d^4) displays the expected static Jahn–Teller distortion. A tetragonal elongation of the MnN_6 polyhedron is clearly seen: there are two long axial Mn–N distances; namely Mn–N(5) and Mn–N(7) of 2.263(5) Å and 2.170(6) Å of one of the coordinated amine nitrogen atoms and of one azide nitrogen, respectively, and four shorter equatorial Mn–N distances of 1.911(6), 1.951(6), 2.093(5) and 2.113(6) Å, the former two of which are manganese–azido and the latter two are manganese–amine distances. Thus the three Mn–N distances of the coordinated macrocycle are not equivalent demonstrating again the stereochemical flexibility of this nine-membered ring.

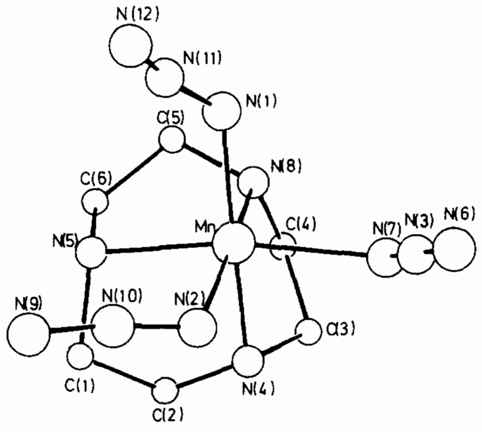

Fig. 1. The molecule $[LMn(N_3)_3]$ showing the atom numbering.

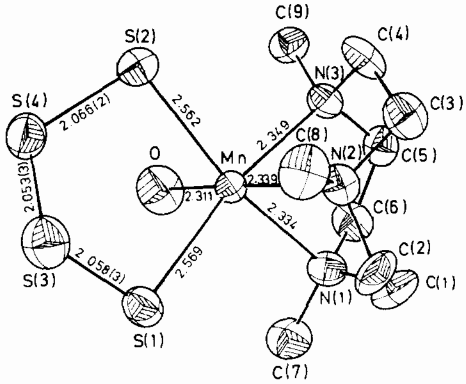

Fig. 2. The molecule $[L'Mn(S_4)(H_2O)]$ showing the atom numbering.

The N–Mn–N bond angles of the tridentate amine are significantly smaller than 90° (~86°) superimposing a trigonal distortion of the MnN_6 polyhedron over the tetragonal Jahn–Teller distortion. The three five-membered chelate rings $\overline{Mn-N-C-C-N}$ are not planar; they adopt ($\delta\delta\delta$) conformation in the crystal investigated. Since $[LMn(N_3)_3]$ crystallizes in the space group $P2_12_12_1$, only one enantiomer is present; crystals of $LMn(N_3)_3$ resolve spontaneously on crystallization.

The manganese(II) ion in $[L'Mn(S_4)(H_2O)]$ is surrounded by three nitrogen atoms of the macrocycle *N,N′,N″*-trimethyl1,4,7-triazacyclononane, two sulfur atoms of a bidentate S_4 ligand and one oxygen atom of a coordinated water molecule resulting in a distorted octahedral geometry. Figure 2 shows the neutral molecule and the atom labeling scheme. The three Mn–N bond distances of the coordinated amine are within experimental error equivalent (av. 2.341 Å) and significantly longer than those in the corresponding $[LMn(N_3)_3]$ complex. This is in accord with

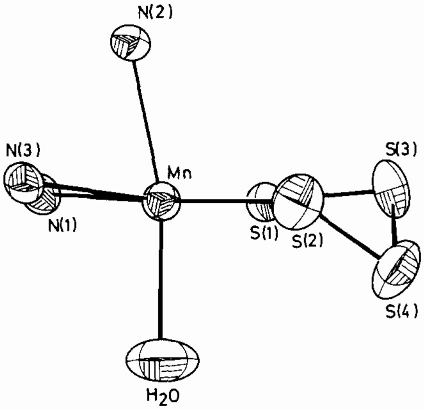

Fig. 3. View of the MnN_3S_4O core of $[L'Mn(S_4)(H_2O)]$ illustrating the puckering of the Mn–S–S–S–S ring.

the observation that the former contains a high-spin manganese(II) centre whereas the latter has a high-spin manganese(III) centre. The five-membered Mn–S–S–S–S ring formed by coordination of a bidentate S_4 group is strongly puckered, which is nicely illustrated in Fig. 3, it adopts either λ- or δ-conformation, both of which are present in the centrosymmetric space group *Pbca*. The three five-membered chelate rings formed by coordination of the cyclic amine also adopt either (λλλ)- or (δδδ)-conformations.

The Mn–S bonds are quite weak (the av. Mn–S distance is 2.565 Å); they are only slightly smaller than the sum of the ionic radii of manganese(II) (coordination number 6, high-spin) and the sulfide ion (2.67 Å) indicating little covalent character of the Mn–S bonds. The S–S bonds are normal sulfur–sulfur single bonds, but they display small, barely significant, differences. The two outer S–S bonds of the metallocycle are longer (S(1)–S(3): 2.058(3) Å and S(2)–S(4): 2.066(2) Å), whereas the central S(3)–S(4) bond length is relatively shorter 2.053(3) Å; and resemble in this respect the situation found in $(\eta_5\text{-Cp})_2W(S_4)$ [11] and in $[(C_2H_5)_4N]_2[Ni(S_4)_2]$ [12, 13].

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