

Dinuclear manganese complexes containing 1,4-dimethyl-1,4,7-triazacyclononane ligands as well as carboxylato and oxo bridges

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Abstract

The reaction of 1,4-dimethyl-1,4,7-triazacyclononane (L-Me₂) with MnCl₂ · 4H₂O in acetonitrile gives, in the presence of sodium formate, hydrogen peroxide, triethylamine and KPF₆, the dinuclear Mn(III)–Mn(IV) complex cation [(L-Me₂)₂Mn₂(O)₂(OOCH)]²⁺ (**1**) which crystallises as the hexafluorophosphate salt. The analogous reaction with sodium benzoate, however, yields the dinuclear Mn(III)–Mn(III) complex cation [(L-Me₂)₂Mn₂(O)(OOCCH₃)₂]²⁺ (**2**), isolated also as the hexafluorophosphate salt. In the case of sodium acetate, both cations, the Mn(III)–Mn(IV) complex [(L-Me₂)₂Mn₂(O)₂(OOCCH₃)]²⁺ (**3**) and the known Mn(III)–Mn(III) complex [(L-Me₂)₂Mn₂(O)(OOCCH₃)₂]²⁺ (**4**) are available, depending upon the molar ratio. The single-crystal X-ray structure analyses show for the green crystals of [**1**][PF₆]_{1.5}[Cl]_{0.5} · 1.5 H₂O and [**3**][PF₆]₂ · (CH₃)₂CO, a Mn–Mn distance of 2.620(2) and 2.628(4) Å, respectively, while for the red-violet crystal of [**4**][PF₆]₂, a Mn–Mn distance of 3.1416(8) Å is observed. All four compounds show catalytic activity for the oxidation of isopropanol with hydrogen peroxide in water and in acetonitrile to give acetone in the presence of oxalic or ascorbic acid as co-catalysts.

Keywords: 1,4-Dimethyl-1,4,7-triazacyclononane ligand; Oxidation; Hydrogen peroxide; Manganese

1. Introduction

Manganese complexes containing macrocyclic ligands with three nitrogen-donor atoms have found much interest as model complexes for biologically active systems [1]. In particular, the coordination chemistry of 1,4,7-triazacyclononane and its derivatives has been pioneered by K. Wieghardt in the 1980s. Thus, 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L-Me₃) were found to react with manganese(III) acetate to give the dinuclear manganese(III) complexes [L₂Mn₂(O)(OOCCH₃)₂]²⁺ and [(L-Me₃)₂Mn₂(O)(OOCCH₃)₂]²⁺ [2], the latter one

reacts in basic media under aerobic conditions to give the manganese(IV) tri-μ-oxo complex [(L-Me₃)₂Mn₂(O)₃]²⁺ [3], while the analogous reaction of the first one leads to the tetranuclear manganese(IV) complex [L₄Mn₄O₆]⁴⁺ [3–5]. A full series of dinuclear Mn(II)–Mn(II), Mn(III)–Mn(III) and Mn(III)–Mn(IV) di-μ-acetato complexes, containing 1,4,7-trimethyl-1,4,7-triazacyclononane [(L-Me₃)₂Mn₂(OH)(OOCCH₃)₂]⁺, [(L-Me₃)₂Mn₂(O)(OOCCH₃)₂]²⁺ and [(L-Me₃)₂Mn₂(O)(OOCCH₃)₂]³⁺ has been described by Wieghardt as model complexes for the active centre of photosystem II [6]. Dinuclear Mn(II)–Mn(III) bis-acetato complexes with 1,4,7-triazacyclononane derived ligand have been reported by Hendrickson et al. [7].

After the discovery of the catalytic activity of these and other Mn(III) and Mn(IV) complexes containing 1,4,7-triazacyclononane derived ligands for low-temperature

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bleaching [8], the catalytic oxidation potential of this type of complexes has been demonstrated for the oxidation of phenols [9] and sulfides [10], as well as for the *cis*-hydroxylation [11] and for the epoxidation [12,13] of olefins with hydrogen peroxide (see Scheme 1).

In 1998, G.B. Shul'pin discovered that the presence of acetic or other carboxylic acids strongly increases the catalytic oxidation potential of the dinuclear manganese(IV) complex $[(L-Me_3)_2Mn_2(O)_3]^{2+}$ (Wiegardt's complex) [14,15], so that even alkanes, including ethane and methane could be oxidised with hydrogen peroxide in acetonitrile [16,17] or water [18]. The importance of a carboxylate buffer for this catalyst was also demonstrated a few years later for the oxidation of benzylic groups [19]. The role of the carboxylic acid seems to consist in converting $[(L-Me_3)_2Mn_2(O)_3]^{2+}$ into $[(L-Me_3)_2Mn_2(O)_2(OH)]^+$, which then reacts with H_2O_2 to form highly active dinuclear Mn(III)–Mn(IV) and even Mn(IV)–Mn(V) species [20,21].

Whereas the methyl substituents in L-Me₃ can be replaced by other alkyl groups without much change in the coordination chemistry [22], replacing only one of the three methyl groups for hydrogen inhibits the formation of the Mn₂(O)₃ core [23]. Thus, with the ligand 1,4-dimethyl-1,4,7-triazacyclononane (L-Me₂) only the Mn(III)–Mn(III) complex $[(L-Me_2)_2Mn_2(O)(OOCCH_3)_2]^{2+}$ is known [23], the mixed-valence Mn(III)–Mn(IV) complex $[(L-Me_2)_2Mn_2(O)_2(OOCCH_3)]^{2+}$ has been postulated without being isolated and characterised [23].

Herein we report a straight-forward synthesis for dinuclear Mn(III)–Mn(III) and Mn(III)–Mn(IV) complexes containing L-Me₂ ligands as well as carboxylato- and oxo- bridges, including the isolation and X-ray characterisation of the postulated [23] complex $[(L-Me_2)_2Mn_2(O)_2(OOCCH_3)]^{2+}$ as the hexafluorophosphate. The single-crystal structure analysis of the hexafluorophosphate of the known complex $[(L-Me_2)_2Mn_2(O)(OOCCH_3)_2]^{2+}$ is also reported [23]. The catalytic oxidation properties of these complexes are discussed.

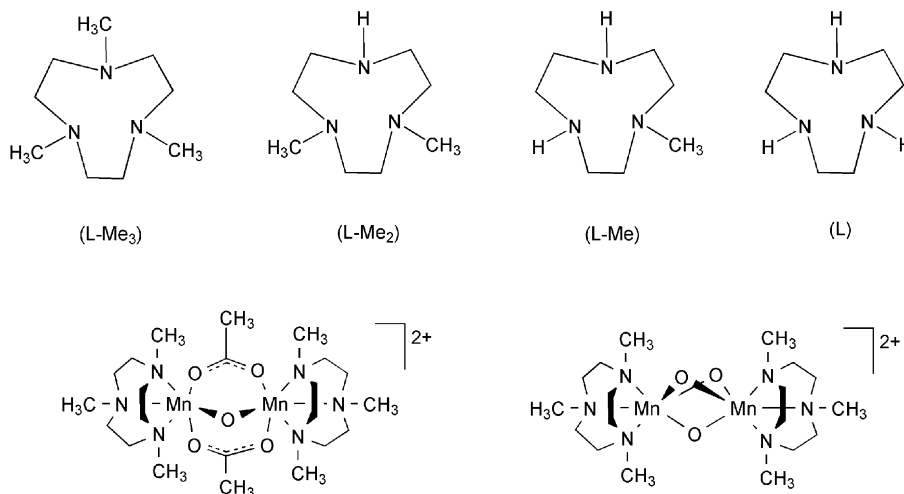
2. Experimental

2.1. General remarks

All reactions were carried out by standard Schlenk techniques under nitrogen atmosphere. Organic solvents were degassed and saturated with nitrogen prior to use. Infrared spectra were recorded using a Perkin–Elmer Spectrum One spectrophotometer. Micro analyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). The starting compound 1,4-dimethyl-1,4,7-triazacyclononane (L-Me₂) was prepared according to the published method [24]. Manganese(II) chloride dihydrate, sodium formate monohydrate, sodium acetate trihydrate, sodium benzoate, potassium hexafluorophosphate, *p*-toluenesulfonic acid monohydrate, hydrogen peroxide (30 wt% solution in water) and triethylamine were purchased from Acros, Aldrich or Fluka and were used without further purification.

2.2. General synthetic procedure

In a 50 ml Schlenk tube, a mixture of L-Me₂ (157.3 mg, 1.00 mmol) and *p*-toluenesulfonic acid monohydrate (190.2 mg, 1.00 mmol) was dissolved in 15 mL of acetonitrile. To this clear light-yellow solution, solid MnCl₂ · 4 H₂O (198 mg, 1.00 mmol) was added under vigorous stirring. The mixture was treated with ultrasound (10–15 min) and then stirred for half an hour. Then, KPF₆ (276 mg, 1.50 mmol) and the corresponding sodium carboxylate (**1**: HCOONa · H₂O, 129 mg, 1.50 mmol; **2**: C₆H₅COONa, 216 mg, 1.50 mmol; **3**: CH₃COONa · 3 H₂O, 68 mg, 0.50 mmol; **4**: CH₃COONa · 3 H₂O, 204 mg, 1.50 mmol) were added to the slurry. After stirring at 45 °C for 20 min, the suspension was cooled to 0 °C, before 5 mL of an acetonitrile solution of H₂O₂ (102 μL, 1.0 mmol) and of triethylamine (278 μL, 2.0 mmol) was added. Then the green-brown suspension was stirred at



Scheme 1. Triazacyclononane ligands and dinuclear manganese complexes containing the trimethyl derivative.

20 °C for 2 h. After filtration through celite and washing with 2 ml of acetone, the volume of the filtrate was reduced to 3 mL in vacuo, and 3 mL of water was added. The dark solution was again concentrated in vacuo without heating, until a solid precipitated. The product was filtered off, washed with ethanol, ether and dried under vacuum. Single crystals suitable for X-ray analysis were grown from an acetone solution into which the ether was allowed to slowly diffuse within 48 h.

[(L-Me)₂Mn₂(O)₂(OOCH)]PF₆]₂ ([1]PF₆]₂): Yield 45%. IR (KBr pellets) ν (cm⁻¹): 3667(m), 3593(m), 3322(m), 2947(m), 2877(m), 1617(m), 1586(s), 1458(s), 1392(m), 1326(s), 1003(m), 843 (vs), 690(s), 558(s). *Anal.* Calc. for C₁₇H₃₉F₁₂Mn₂N₆O₄P₂ · H₂O: C, 25.23; H, 5.11; N, 10.38. Found: C, 25.29; H, 5.14; N, 10.31%.

[(L-Me)₂Mn₂(O)(OOCCH₃)₂]PF₆]₂ ([2]PF₆]₂): Yield 75%. IR (KBr pellets) ν (cm⁻¹): 3435(m), 3335(m), 2991(m), 2925(m), 1610(s), 1599(s), 1558(s), 1463(s), 1398(vs), 1181(s), 1034(m), 1011(m), 840(vs), 723(s), 697(s), 558(s). *Anal.* Calc. for C₃₀H₄₈F₁₂Mn₂N₆O₅P₂ · H₂O · (CH₃)₂CO: C, 37.80; H, 5.38; N, 8.01. Found: C, 37.80; H, 5.40; N, 8.10%.

[(L-Me)₂Mn₂(O)₂(OOCCH₃)]PF₆]₂ ([3]PF₆]₂): Yield 50%. IR (KBr pellets) ν (cm⁻¹): 3384(m), 3334(m), 2996(m), 2949(m), 1579(s), 1463(s), 1392(s), 1342(m), 1104(m), 1033(s), 1003(s), 944(m), 839(vs), 740(m), 686(s), 613(s), 558(s). *Anal.* Calc. for C₁₈H₄₁F₁₂Mn₂N₆O₄P₂ · (CH₃)₂CO: C, 29.21; H, 5.49; N, 9.73. Found: C, 29.25; H, 5.46; N, 9.69%.

[(L-Me)₂Mn₂(O)(OOCCH₃)₂]PF₆]₂ ([4]PF₆]₂): Yield 55%. IR (KBr pellets) ν (cm⁻¹): 3436(m), 3332(s), 2984(m), 2947(m), 2917(m), 1578(s), 1459(s), 1420(s), 1091(m), 1058(m), 1024(m), 1004(m), 958(m), 839(vs),

713(m), 694(m), 558(s). *Anal.* Calc. for C₂₀H₄₄F₁₂Mn₂N₆O₅P₂: C, 28.31; H, 5.23; N, 9.91. Found: C, 28.29; H, 5.25; N, 9.82%.

2.3. X-ray crystallographic study

Single-crystals of [1]PF₆]_{1.5}[Cl]_{0.5} · 1.5H₂O, [3]PF₆]₂ · (CH₃)₂CO and [4]PF₆]₂ were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo K α graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment varying from 0.7° to 2.0°, $D_{\max} - D_{\min} = 12.45 - 0.81$ Å. The structures were solved by direct methods using the program SHELXS-97 [25]. The refinement and all further calculations were carried out using SHELXL-97 [26]. In all compounds the hydrogen atoms have been included in calculated positions and treated as riding atoms using the SHELXL default parameters. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2 . In [1]PF₆]_{1.5}[Cl]_{0.5} · 1.5H₂O, the chloride anion was disordered over two positions and the partial occupancy factor was fixed at 50:50. Moreover, all attempts to refine the disordered solvent molecules failed, therefore the SQUEEZE instruction in PLATON03 [27] was used to calculate the potential solvent accessible area in the unit cell; 300 Å³ were calculated containing 30 electrons which have been attributed to three H₂O molecules (3 × 10) per unit cell. Similarly, in [3]PF₆]₂ · (CH₃)₂CO, three fluorine atoms of the hexafluorophosphate anion were found to be disordered over two positions and their partial occupancy factor was fixed at 50:50. Crystallographic details are summarised in Table 1. Figs. 1–3 were drawn with ORTEP [28] and Figs. 4–6 with MERCURY [29].

Table 1

Crystallographic and selected experimental data for [1]PF₆]_{1.5}[Cl]_{0.5} · 1.5H₂O, [3]PF₆]₂ · (CH₃)₂CO and [4]PF₆]₂

	[1]PF ₆] _{1.5} [Cl] _{0.5} · 1.5H ₂ O	[3]PF ₆] ₂ · (CH ₃) ₂ CO	[4]PF ₆] ₂
Chemical formula	C ₁₇ H ₄₂ Cl _{0.5} F ₉ Mn ₂ N ₆ O _{5.5} P _{1.5}	C ₂₁ H ₄₇ F ₁₂ Mn ₂ N ₆ O ₅ P ₂	C ₂₀ H ₄₄ F ₁₂ Mn ₂ N ₆ O ₅ P ₂
Formula weight	763.63	863.47	848.43
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>C mmm</i>	<i>C 2/m</i>	<i>P 2₁/n</i>
Crystal colour and shape	green plate	green plate	red rod
Crystal size	0.5 × 0.5 × 0.2	0.4 × 0.3 × 0.1	0.5 × 0.2 × 0.2
<i>a</i> (Å)	13.259(3)	33.968(5)	14.3384(10)
<i>b</i> (Å)	29.657(6)	11.9980(12)	16.6439(16)
<i>c</i> (Å)	8.593(2)	19.298(2)	15.2611(11)
<i>B</i> (°)	90	118.225(10)	115.683(7)
<i>V</i> (Å ³)	3379.0(13)	6929.7(14)	3282.2(5)
<i>Z</i>	4	8	4
<i>T</i> (K)	173(2)	173(2)	173(2)
<i>D</i> _{calc} (g cm ⁻³)	1.501	1.655	1.717
μ (mm ⁻¹)	0.944	0.927	0.977
Scan range (°)	2.28 < θ < 25.90	2.15 < 2θ < 25.75	1.92 < 2θ < 26.02
Unique reflections	1872	7127	6202
Reflections used [$I > 2\sigma(I)$]	1270	1829	4214
<i>R</i> _{int}	0.0640	0.2389	0.0653
Final <i>R</i> indices [$I > 2\sigma(I)$]	0.0712, <i>wR</i> ₂ 0.2200	0.0825, <i>wR</i> ₂ 0.1829	0.0538, <i>wR</i> ₂ 0.1333
<i>R</i> indices (all data)	0.0984, <i>wR</i> ₂ 0.2375	0.2714, <i>wR</i> ₂ 0.2400	0.0819, <i>wR</i> ₂ 0.1441
Goodness-of-fit	1.120	0.737	1.014
Max, Min $\Delta\rho/e$ (Å ⁻³)	0.841, -0.637	0.893, -0.956	1.463, -0.750

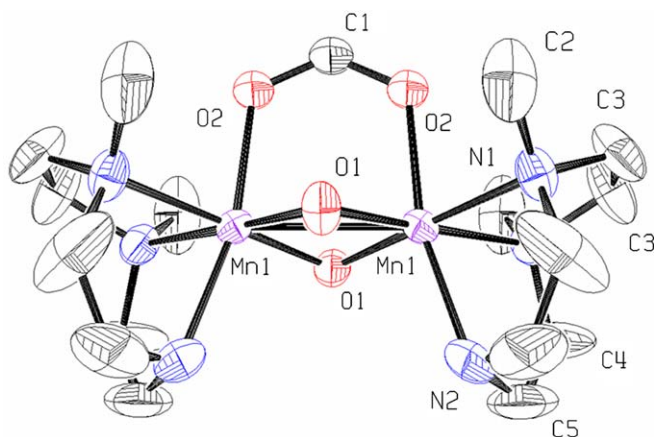


Fig. 1. Ortep drawing of cation **1** in $[1][PF_6]_{1.5}[Cl]_{0.5} \cdot 1.5H_2O$ at the 35% probability level. Hydrogen atoms, solvent molecules, chloride and hexafluorophosphate anions are omitted for clarity.

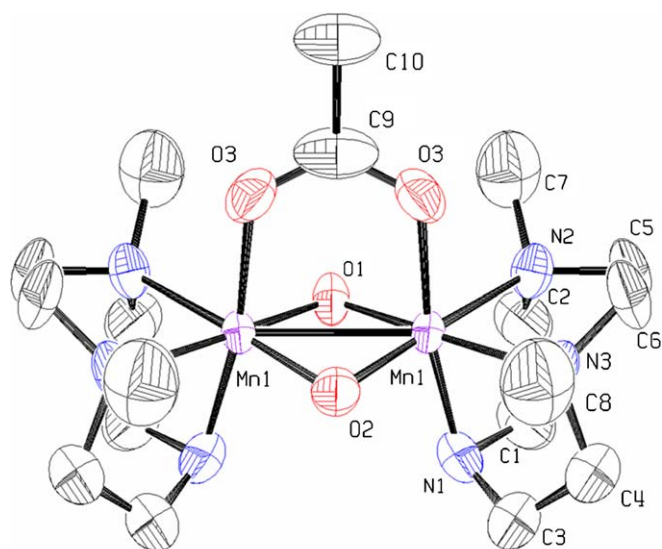


Fig. 2. Ortep drawing of one crystallographically independent cation **3** in $[3][PF_6]_2 \cdot (CH_3)_2CO$ at the 50% probability level. Hydrogen atoms, solvent molecules and hexafluorophosphate anions are omitted for clarity.

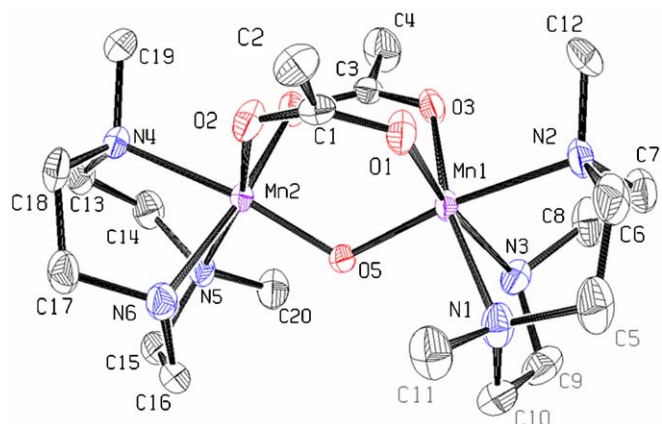


Fig. 3. Ortep drawing of cation **4** in $[4][PF_6]_2$ at the 50% probability level. Hydrogen atoms and hexafluorophosphate anions are omitted for clarity.

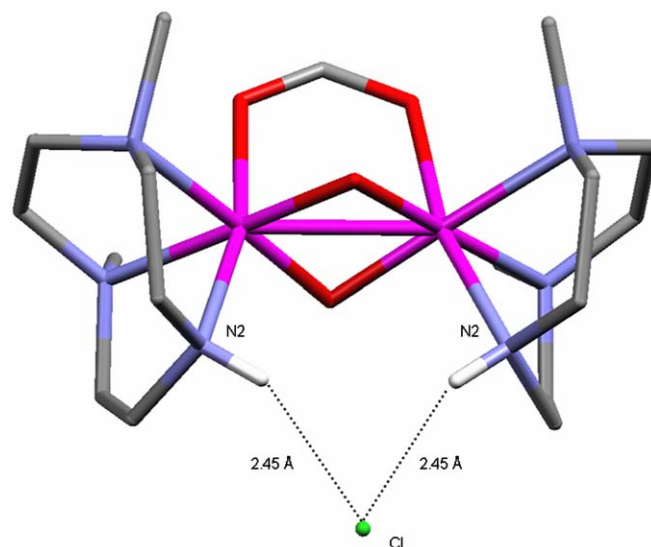


Fig. 4. Capped sticks representation of cation **1** in $[1][PF_6]_{1.5}[Cl]_{0.5} \cdot 1.5H_2O$, showing the intermolecular interactions with the chloride anion.

2.4. Catalytic runs

The oxidation of isopropanol was carried out in air in thermostated cylindrical pyrex vessels with vigorous stirring at 20.0 °C. The total volume of the reaction solution was 10 mL. In a typical experiment, 512 μ L of hydrogen peroxide (30% aqueous solution, 0.50 M) was added to a solution containing the catalyst (1.0×10^{-4} M), ascorbic acid (0.01 M) or oxalic acid/disodium oxalate (0.01/0.01 M) and isopropanol (153 μ L, 0.20 M) in water or acetonitrile. Blank experiments were carried out without a catalyst or co-catalyst.

The samples of the reaction solution were analysed by GC (chromatograph DANI-86.10; fused silica capillary column 25 m \times 0.32 mm \times 0.25 μ m, CP-WAX52CB, integrator SP-4400, helium as carrier gas) using acetonitrile (0.190 M) as internal standard. The flame ionisation detector response factors were obtained after calibration experiments, using a standard substrate mixture.

3. Results and discussion

The classical synthesis of the manganese(III)–manganese(III) complexes $[L_2Mn_2(O)(OOCCH_3)_2]^{2+}$ and $[(L-Me_3)_2Mn_2(O)(OOCCH_3)_2]^{2+}$ from manganese(III) acetate and L or L-Me₃ in moist ethanol reported by K. Wiegardt et al. [2] fails in the case of L-Me₂; the analogous complex $[(L-Me_2)_2Mn_2(O)(OOCCH_3)_2]^{2+}$ was synthesised by J. Koek et al. [23] by adding one equivalent of a strong acid to the acetonitrile solution of the triazamacrocycle prior to coordination. Presumably the monoprotonation of L-Me₂ preorganises the conformation of the macrocycle suitable for complexation.

We extended this idea to the synthesis of (L-Me₂)₂Mn₂ complexes containing various carboxylato bridges in the

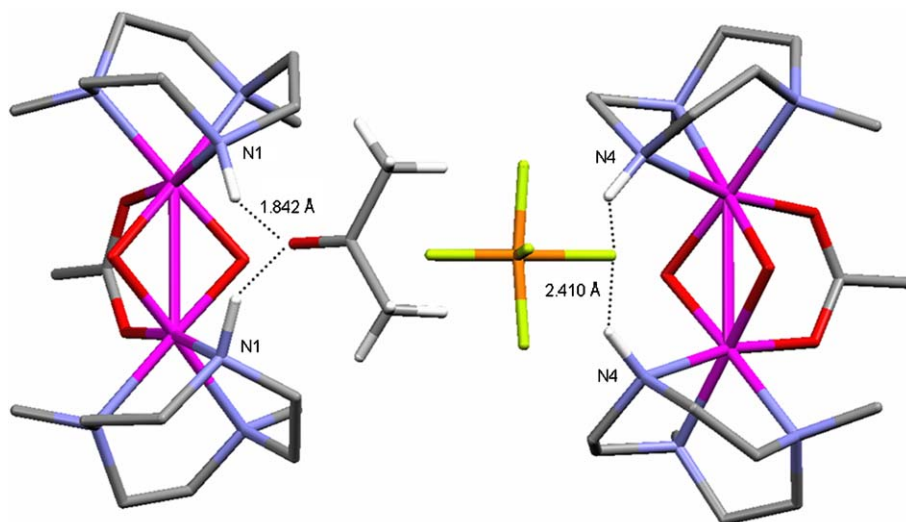


Fig. 5. Capped sticks representation of cation **3** in $[3][\text{PF}_6]_2 \cdot (\text{CH}_3)_2\text{CO}$, showing the intermolecular interactions with an acetone molecule and a hexafluorophosphate anion.

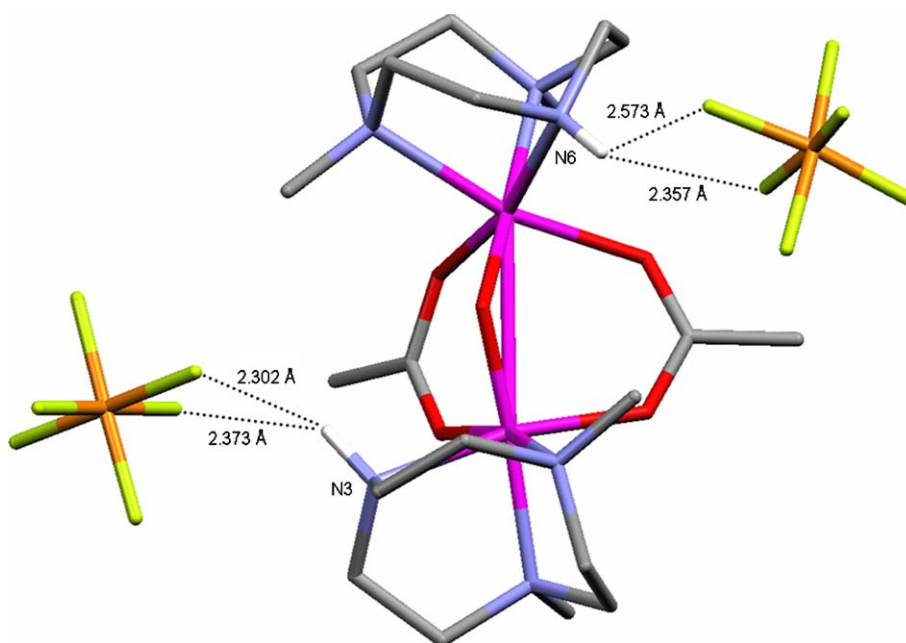
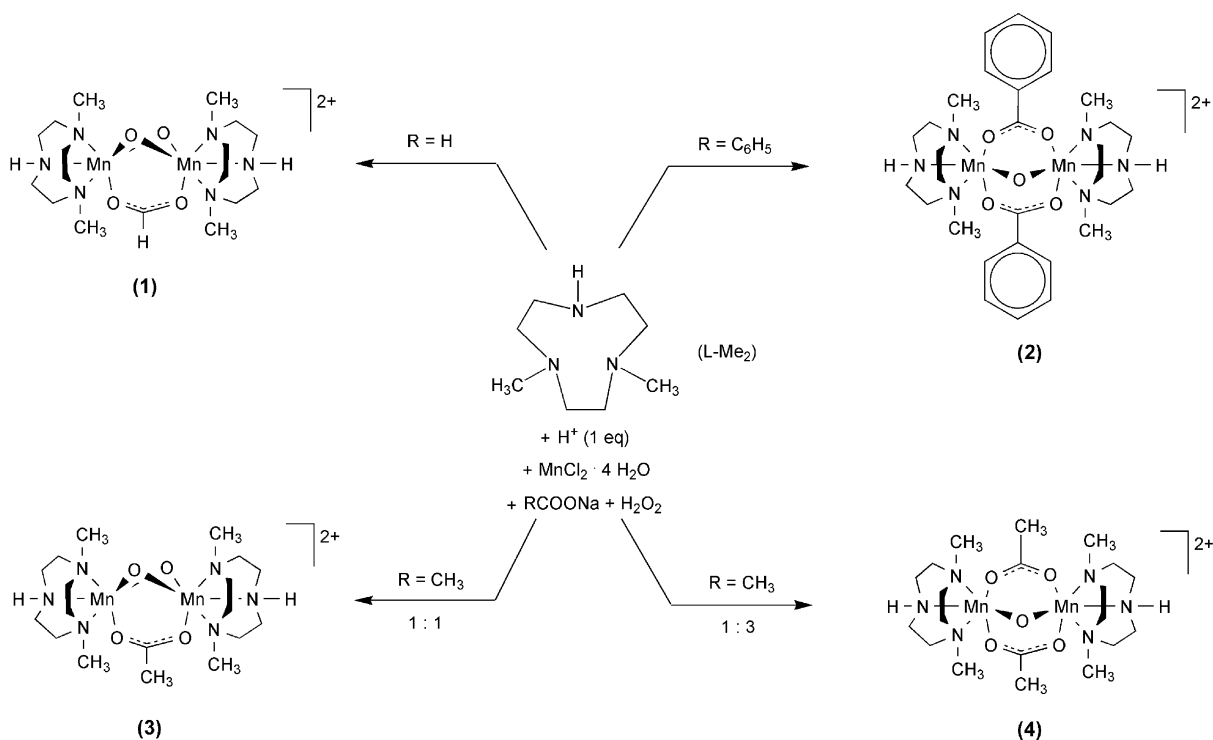


Fig. 6. Capped sticks representation of cation **4** in $[4][\text{PF}_6]_2$, showing the intermolecular interactions with the hexafluorophosphate anions.

presence of $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ as strong acid and hydrogen peroxide as oxidant, see Scheme 2. We found that the nature of the dinuclear complexes formed depends on the nature of the carboxylate used: with formate, the Mn(III)–Mn(IV) complex $[(\text{L-Me}_2)_2\text{Mn}_2(\text{O})_2(\text{OOCH})]^{2+}$ (**1**) is obtained, while benzoate gives the Mn(III)–Mn(III) complex $[(\text{L-Me}_2)_2\text{Mn}_2(\text{O})(\text{OOCCH}_3)_2]^{2+}$ (**2**). With acetate, both cations of the green Mn(III)–Mn(IV) complex $[(\text{L-Me}_2)_2\text{Mn}_2(\text{O})_2(\text{OOCCH}_3)]^{2+}$ (**3**) and the violet-brown [23] Mn(III)–Mn(III) complex $[(\text{L-Me}_2)_2\text{Mn}_2(\text{O})(\text{OOCCH}_3)_2]^{2+}$ (**4**) are accessible, depending on the molar ratio of sodium acetate to manganese(II) chloride tetrahydrate.

All complexes **1–4** are paramagnetic and could be isolated as the hexafluorophosphate salts, which are well soluble in acetone and acetonitrile, but sparingly soluble in ethanol, isopropanol and water.

Green X-ray quality crystals of $[1][\text{PF}_6]_{1.5}[\text{Cl}]_{0.5} \cdot 1.5\text{H}_2\text{O}$ and $[3][\text{PF}_6]_2 \cdot (\text{CH}_3)_2\text{CO}$ were obtained by slow diffusion of ether into an acetone solution containing **1** and **3**, respectively. In $[3][\text{PF}_6]_2 \cdot (\text{CH}_3)_2\text{CO}$, there are two crystallographically independent Mn(III)–Mn(IV) cations of **3** per unit cell. The molecular structure of **1** and **3** is shown in Figs. 1 and 2, respectively. Similarly, red-violet crystals of $[4][\text{PF}_6]_2$ are obtained by slow diffusion of ether into



Scheme 2. Reaction of 1,4-dimethyl-1,4,7-triazacyclononane (L-Me₂) with manganese(II) chloride tetrahydrate in the presence of hydrogen peroxide and the corresponding sodium carboxylate.

an acetone solution containing **4**. The molecular structure of **4** is presented in Fig. 3. Selected bond lengths and angles of complexes [**1**][PF₆]_{1.5}[Cl]_{0.5} · 1.5H₂O, [**3**][PF₆]₂ · (CH₃)₂CO and [**4**][PF₆]₂ are listed in Table 2.

The molecular structures of the green Mn(III)–Mn(IV) dioxo complexes [(L-Me₂)₂Mn₂(O)₂(OOCH)]²⁺ (**1**) and

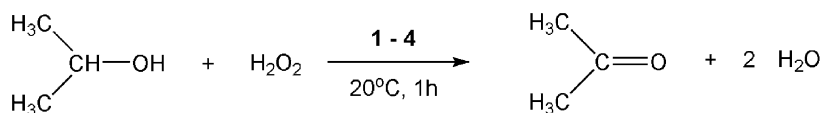
[(L-Me₂)₂Mn₂(O)₂(OOCCH₃)]²⁺ (**3**), show a metal–metal distance of 2.620(2) and 2.628(4) Å, respectively. These distances compare well to the isoelectronic Mn(III)–Mn(IV) cations [L₂Mn₂(O)₂(OOCCH₃)]²⁺ (2.588(2) Å) [30] and [(dtne-Me₄)₂Mn₂(O)₂(OOCCH₃)]²⁺ (2.574(2) Å, dtne-Me₄ = 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane) [31]. In contrast, the red-violet Mn(III)–Mn(III) complex [(L-Me₂)₂Mn₂(O)(OOCCH₃)₂]²⁺ (**4**) possesses a longer metal–metal distance: The molecular structure of **4** reveals a distance of 3.1416(8) Å, comparable to those observed in the analogous Mn(III)–Mn(III) complexes [L₂Mn₂(O)(OOCCH₃)₂]²⁺ (3.096(2) Å) [32], [L(L-Me₃)Mn₂(O)(OOCCH₃)₂]²⁺ (3.121(2) Å) [33] and [(L-Me₃)₂Mn₂(O)(OOC(CH₃)₃)₂]²⁺ (3.193(1) Å) [34].

Interestingly, all complexes show intermolecular interactions with solvent molecules or anions, owing to the presence of an N–H moiety within the ligand L-Me₂. Therefore, in [**1**][PF₆]_{1.5}[Cl]_{0.5} · 1.5 H₂O, the hydrogen atoms of the two N–H amino groups interact strongly with a chloride anion, see Fig. 4. The distances between the nitrogen atoms and the chloride anion are 3.230(7) Å with N–H···Cl angles of 157.0°.

In [**3**][PF₆]₂ · (CH₃)₂CO where two crystallographically independent molecules of **3** are present per unit cell, two different intermolecular interactions are observed, see Fig. 5. One cation of **3** interacts with a hexafluorophosphate anion, whereas the second cation forms hydrogen bonds with an acetone molecule. In the intermolecular hydrogen bonded system involving the acetone molecule, the N···O distance is 2.78(1) Å with an N–H···O angle

Table 2
Selected bond lengths (Å) and angles (°) for [**1**][PF₆]_{1.5}[Cl]_{0.5} · 1.5H₂O, [**3**][PF₆]₂ · (CH₃)₂CO and [**4**][PF₆]₂

	[1][PF ₆] _{1.5} [Cl] _{0.5}	[3][PF ₆] ₂	[4][PF ₆] ₂
<i>Interatomic distances</i>			
Mn–Mn	2.620(2)	2.628(4)	3.1416(8)
Mn–Mn		2.599(4)	
Mn–O (oxo)	1.814(3)	1.797(7)	1.796(3)
Mn–O (oxo)		1.781(7)	1.799(2)
Mn–O (oxo)		1.814(7)	
Mn–O (oxo)		1.836(8)	
Mn–O (carboxylato)	2.115(4)	2.082(8)	2.008(3)
Mn–O (carboxylato)		2.064(8)	2.074(3)
Mn–O (carboxylato)			2.022(3)
Mn–O (carboxylato)			2.123(3)
Mn–N (H)	2.083(8)	2.16(1)	2.141(3)
Mn–N (H)		2.150(8)	2.144(4)
Mn–N (Me)	2.115(4)	2.11(1)	2.107(3)
Mn–N (Me)		2.11(1)	2.236(3)
Mn–N (Me)		2.11(1)	2.246(4)
Mn–N (Me)		2.12(1)	2.118(3)
<i>Angles</i>			
Mn–O–Mn (oxo)	92.5(2)	92.6(5)	121.8(2)
Mn–O–Mn (oxo)		92.8(5)	
O–C–O (carboxylato)	128.6(9)	123(2)	124.1(4)
O–C–O (carboxylato)		125(2)	124.9(4)



Scheme 3. Catalytic oxidation of isopropanol with hydrogen peroxide.

of 144.9° , whereas with the fluorine atoms of the hexafluorophosphate, the N...F distances are 3.05(1) and 3.20(1) Å with angles of 166.6° and 133.2° , respectively.

Finally, in $[\mathbf{4}][\text{PF}_6]_2$, the amino protons of the N–H moieties interact independently with the two hexafluorophosphate anions, see Fig. 6. The distances between the nitrogen and fluorine atoms are 3.022(6) and 3.242(6) Å (for N3) and 3.234(9) and 3.134(9) Å (for N6) with N–H...F angles ranging from 127.2° to 146.1° .

We tested the catalytic potential of the complexes **1–4** for the oxidation of isopropanol with hydrogen peroxide to give acetone, see Scheme 3. The oxidation reaction was carried out in aqueous solution or in acetonitrile in the presence of ascorbic or oxalic acid as co-catalysts at 20°C . The results are shown in Figs. 7 and 8.

The highest activity was observed for complex **2** in water in the presence of oxalate buffer, the TON (catalyst turnover number, mol of products per mol of catalyst) being 124 after 1 h at 20°C , which is not as high as that of $[(\text{L-Me}_3)_2\text{Mn}_2(\text{O})_3]^{2+}$, for which a TON of 848 was observed under the same conditions [18]. However, while $[(\text{L-Me}_3)_2\text{Mn}_2(\text{O})_3]^{2+}$ in combination with carboxylic (typically acetic) acid as co-catalyst is more active in acetonitrile [16] than in water [18], the complexes **1–4** are more active in aqueous solution (Fig. 8).

The role of the co-catalyst (ascorbic or oxalic acid) is not clear, it may serve as a reducing agent and/or as a carboxylato ligand. The beneficial effect of ascorbic acid as co-catalyst has been observed in the oxidation of 2-pentanol to give 2-pentanone, catalysed by mixture of

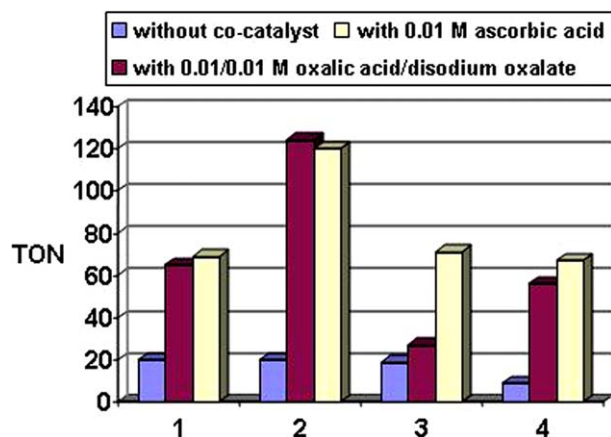


Fig. 7. Oxidation of isopropanol in water, catalysed by the complexes **1–4** in the absence/presence of ascorbic or oxalic acid as co-catalysts (20°C , 1 h, 1.0×10^{-4} M complex **1–4**, 0.20 M isopropanol, 0.50 M H_2O_2 , TON – catalyst turnover number).

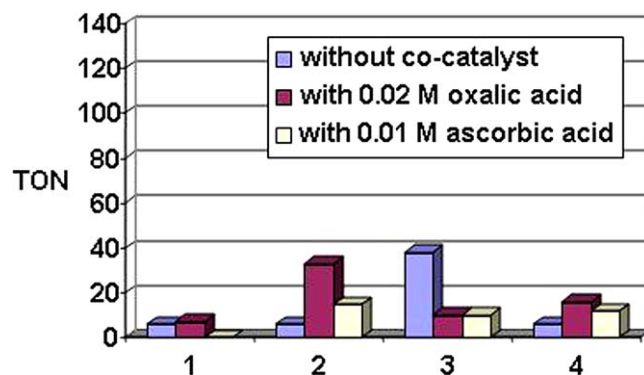


Fig. 8. Oxidation of isopropanol in acetonitrile, catalysed by the complexes **1–4** in the absence/presence of ascorbic or oxalic acid as co-catalysts (20°C , 1 h, 1.0×10^{-4} M complex **1–4**, 0.20 M isopropanol, 0.50 M H_2O_2 , TON – catalyst turnover number).

$\text{Mn}(\text{OOCCH}_3)_2 \cdot 4 \text{H}_2\text{O}$ and L-Me₃ in moist acetonitrile [35].

4. Supplementary materials

CCDC-286897 $[\mathbf{1}][\text{PF}_6]_{1.5}[\text{Cl}]_{0.5} \cdot 1.5\text{H}_2\text{O}$, 286898 $[\mathbf{3}][\text{PF}_6]_2 \cdot (\text{CH}_3)_2\text{CO}$, and 286899 $[\mathbf{4}][\text{PF}_6]_2$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting, The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033.

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