DALTON

Improved syntheses, structures, spectral and electrochemical properties of $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]^{2+}$ and $[Mn^{IV}_2(\mu\text{-}O)_3L_2]^{2+}$ complexes. Two homologous series derived from eight *N*-substituted 1,4,7-triazacyclononanes †

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A series of eight *N*-substituted 1,4,7-triazacyclononanes L has been prepared having combinations of hydrogen, methyl, ethyl or propyl substituents on the three nitrogens. From the monoprotonated macrocycles dinuclear manganese complexes $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$ (X = ClO_4 or PF_6) were prepared under anhydrous conditions in high yield. A relationship between the absorption bands and the electrochemical properties of the complexes containing variously methyl-substituted L has been observed. From the Me_xEt_{3-x}- and Pr^i_3-substituted macrocycles triple oxygen-bridged dinuclear manganese complexes $[Mn^{IV}_2(\mu\text{-}O)_3L_2]^{2+}$ were prepared starting from L, a manganese(II) salt and counter ion, subsequently treated with alkaline hydrogen peroxide. The yields of this reaction depend on the sizes of substituents at N on the macrocycle. The crystal structure of $[Mn^{IV}_2(\mu\text{-}O)_3L_2][PF_6]_2\cdot 0.5KPF_6$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) has been determined. This revealed the core to be almost identical to that of known triethyl analogue, with the methyl groups of the ethyl substituents pointing outwards to minimize steric interaction. The Mn–Mn distance of 2.295 Å is likewise exceptionally short and the value for the Mn–O–Mn bond angle of 77.9° is also very low. The NMR and UV/VIS absorption spectra and electrochemical measurements indicate very similar structures for these triple oxygen-bridged dinuclear manganese complexes.

Manganese complexes of 1,4,7-triazacyclononane (tacn, L^1) and its 1,4,7-trimethyl analogue (L^4) have been described as models for biologically active systems,[1] such as the polynuclear manganese cluster in the 'oxygen evolving centre' of the water oxidation catalyst, photosystem II.[2a–g] Many unusual and interesting manganese complexes with L^1 and L^4 have been described.[3a–j,4] Undoubtedly, the nine-membered ring causes the formation of very stable compounds.[5] A number of these compounds are stable towards strong acids or bases, whilst similar compounds with other ligands exhibit acid- or base-catalysed ligand dissociation or formation of metal (hydr)-oxides.[5] Furthermore, tacn-type compounds are redox-active and due to their flexibility are also able to co-ordinate metal centres in many oxidation states.

Our recent interest in manganese complexes with this type of ligand[6a] and described in patent applications (potential catalytic bleach activating agents)[6b] prompted us to develop generic synthetic routes for preparing new tacn derivatives having different alkyl substituents on the three nitrogens and synthesize their manganese co-ordination complexes in an efficient way. In this paper we describe the preparation of manganese complexes of eight homologous ligands. Compounds L^5–L^8 have not been reported before, while manganese complexes have only been described for L^1 and L^4.[4] As will be shown, a relationship has been found between the substituent pattern on the ring and the co-ordination properties. Moreover, the electronic absorption spectra and electrochemical properties of the dinuclear Mn^{III}_2 complexes obtained have been related to the substituent pattern on the ligand.

† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

Results and Discussion

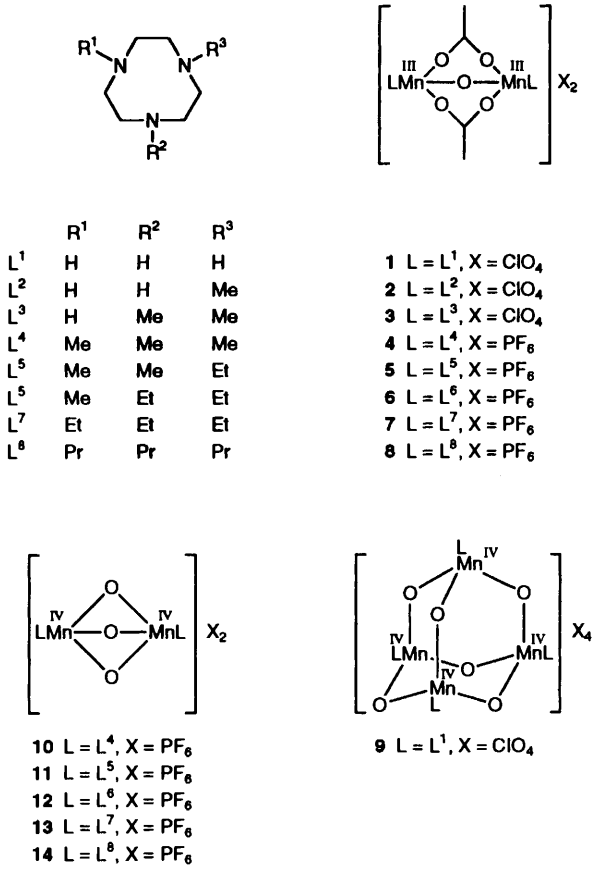
Synthesis of the macrocycles

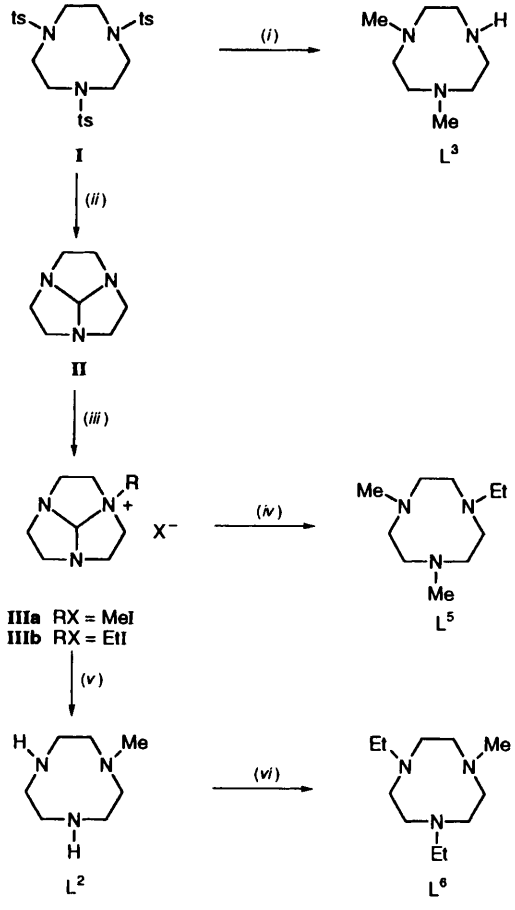
In the series L^1–L^8, the hydrogens on the nitrogens of tacn are successively replaced; first hydrogen for a methyl group and next by an ethyl group. In order to extend our study on the influence of alkyl size of the substituents of N on the reactivity, L^8 was also included. The triisopropyl derivative was reported by Wieghardt and co-workers[7] to be reactive only under extreme conditions and was therefore not included.

The symmetrical compounds L^7 and L^8 were prepared by reductive alkylation of L^1 in acetic and propionic acid respectively using sodium tetrahydroborate as the reducing agent.[8] The preparation of asymmetrically *N*-alkylated tacn compounds is shown in Scheme 1. The partial detosylation of 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane **I**[9] using mild conditions gave the 1-*p*-tolylsulfonyl derivative[10] which could be converted by Eschweiler–Clarke methylation[11] and subsequent more vigorous detosylation to L^3. Derivatization of the triorthoamide **II**,[12–14] obtained from L^1 and dimethylaminoformaldehyde dimethyl acetal, with methyl or ethyl iodide gave the salts **IIIa** and **IIIb**. Hydrolysis and deformylation of **IIIa** gave L^2 which was ethylated giving L^6 using the same method as described in the Experimental section for L^7. Direct Eschweiler–Clarke methylation of the salt **IIIb** gave L^5 without the need for a separate hydrolysis step.

Preparation of the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$ complexes

The synthesis of dinuclear $Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2$ complexes from L^1 and L^4 described by Wieghardt *et al.*[4] was found to





Scheme 1 ts = *p*-tolylsulfonyl (tosyl). (*i*) HBr–$MeCO_2H$ (mild), HCHO–HCO_2H, H_2SO_4; (*ii*) HBr–$MeCO_2H$, KOH, distil, NMe_2-$CH(OMe)_2$; (*iii*) RX; (*iv*) HCHO, HCO_2H (for **IIIb**); (*v*) HCl, NaOH (for **IIIa**); (*vi*) $MeCO_2H$, $NaBH_4$

give a low yield for L^4 (30%) and was hardly reproducible for L^1 due to the water-substitution lability of the complexes obtained. With acetonitrile as solvent and L^4, a non-aqueous route was developed and optimized. Starting with the 3HX salt of the macrocycle, a high conversion extent was observed (method A). It was found that the addition of only 1 equivalent of a strong acid (sulfuric, hydrochloric, or toluene-*p*-sulfonic acid) to the free macrocycle prior to complexation was required for both high selectivity and high yield (method B). Monoprotonation of the macrocycle probably preorganizes its conformation[15] leading to a selective complexation in high yield.

In Table 1 the yields obtained with L^1–L^8 using the optimized procedures A and B are given. All the complexes were analysed by infrared, absorption (Table 5), and positive-ion FAB mass spectrometry, and some of them by elemental analysis (Table 2). The $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$ complexes were easily prepared from L^1–L^6 in good yields. Compound L^7, having three *N*-ethyl groups, was found to be far less reactive; even after 2 d of reaction only 10% conversion into the desired complex was found. In the case of L^8, having three *N*-propyl groups, only a small conversion was observed using absorption spectroscopy, but even after 3 d no product could be isolated. A similar observation has recently been reported by Wieghardt and co-workers[7] for the co-ordination of 1,4,7-triisopropyl-1,4,7-triazacyclononane (refluxing xylene with the hexacarbonyls of Cr, Mo or W). This low reactivity is explained by the kinetic stability of the monoprotonated macrocycle caused by shielding of the large substituents. This is probably also the case with three ethyl, and even more pronounced with three propyl, groups on the macrocycle. It should be noted that the $Mn^{III}_2(\mu\text{-}O)(O_2CMe)_2$ core is already present in the $Mn^{III}(O_2CMe)_3$ used {as $[Mn_3(\mu\text{-}O)(\mu\text{-}O_2CMe)_6][O_2CMe]$[16]} and the bulkier macrocycles react more slowly with this core because sterically their substituents must be correctly orientated during coupling.

Oxidation of the $Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2$ complexes

As described by Wieghardt *et al.*[4] the $[Mn^{IV}_2(\mu\text{-}O)_3L^4_2]X_2$ complex can be obtained by oxidation of $[Mn^{III}_2(\mu\text{-}O)(O_2CMe)_2L^4_2]X_2$ with dioxygen in the presence of triethylamine (method C). A more powerful synthetic route to these complexes was developed by a direct reaction of the macrocycles and manganese(II) salts and subsequent oxidation by alkaline peroxide, method D. First the macrocycle and manganese(II) chloride are allowed to react in aqueous ethanol in the presence of hexafluorophosphate. An intermediate, probably a mono- or di-nuclear $Mn^{II}L$ complex, is formed. Subsequent cooling and careful addition of a stoichiometric amount of alkaline hydrogen peroxide, followed by neutralization and filtration, gives the complexes. This procedure was optimized for L^4 and also used for L^5–L^8. The yields are presented in Table 1. Again L^7 (triethyl) and even more pronounced L^8 (tripropyl) gave low conversions and yields. For L^1 another complex was obtained. Wieghardt also described the formation of a tetranuclear complex **9** both from **1** and also directly from L^1 and manganese salts, under somewhat different conditions.[3i,4] In the case of **2** and **3** other species were formed. The absorption spectra of the solutions obtained were similar to that of the well described $[Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)L^1_2]X_2$ complex[4] suggesting similar structures. The presence of only one *N*-methyl group on the tacn ring prevents formation of the tetranuclear system **9** (exhibited by L^1). Moreover replacing only one methyl group for hydrogen, going from L^4 to L^3, inhibits formation of the $Mn^{IV}_2(\mu\text{-}O)_3$ core. Clearly the oxidation reaction is strongly modified by the gradual replacement of hydrogens for methyl groups on the nitrogens of tacn. Evidence in support of the structures were provided by

Table 1 Method and yields for the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]$ complexes from the reaction of manganese(III) acetate and their oxidation products, together with their yields using the alkaline oxidation method D

Ligand	Product	Yield (%) (method)	Structure obtained after oxidation	Product	Yield (%)
L^1	**1**	73 (A)	$Mn^{IV}_4(\mu\text{-}O)_6L_4$	**9**	n.d.
L^2	**2**	69 (B)	$Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)L_2$?		
L^3	**3**	38 (A)	$Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)L_2$?		
L^4	**4**	92 (B)	$Mn^{IV}_2(\mu\text{-}O)_3L_2$	**10**	84
L^5	**5**	48 (B)	$Mn^{IV}_2(\mu\text{-}O)_3L_2$	**11**	81
L^6	**6**	51 (B)	$Mn^{IV}_2(\mu\text{-}O)_3L_2$	**12**	64
L^7	**7**	5 (A)	$Mn^{IV}_2(\mu\text{-}O)_3L_2$	**13**	7
L^8	**8**	< 1 (A/B)	$Mn^{IV}_2(\mu\text{-}O)_3L_2$	**14**	1

n.d. = Not determined.

Table 2 Elemental analysis data (%) for some of the prepared complexes (calculated values in parentheses)

Complex	C	H	N	O	F	K	Mn	P or Cl
1	23.61	4.40	10.2				12.9	
	(23.35)	(4.40)	(10.2)				(13.3)	
2	29.95	5.55	11.3	27.6			14.85	9.70
	(29.65)	(5.50)	(11.5)	(28.5)			(15.05)	(9.70)
3	31.7	5.95	11.15				14.35	9.35
	(31.7)	(5.85)	(11.1)				(14.5)	(9.35)
4	28.85	5.60	9.35		26.75		7.35	
	(29.55)	(5.65)	(9.40)		(25.5)		(6.90)	
7	34.65	5.35	8.70		23.45		12.0	6.45
	(35.0)	(6.30)	(8.75)		(23.75)		(11.45)	(6.45)
10	27.25	5.00	10.75		28.55			7.75
	(27.35)	(5.35)	(10.65)		(28.85)			(7.85)
11	24.35	4.85	8.50	4.70	33.6	n.d.	11.3	9.55
	(24.45)	(4.75)	(8.55)	(4.90)	(34.75)	(2.00)	(11.15)	(9.45)
12	25.7	5.05	8.30	5.50	32.6	3.35	10.9	8.70
	(25.4)	(4.95)	(8.10)	(5.40)	(32.9)	(3.75)	(10.55)	(8.95)
13	30.15	5.80	8.75	5.75	28.7	1.85	11.3	7.90
	(29.55)	(5.70)	(8.60)	(5.75)	(29.2)	(2.00)	(11.25)	(7.95)

n.d. = Present but not determined.

Table 3 Final coordinates of the non-hydrogen atoms of complex **13**

Atom	*x*	*y*	*z*
Mn(1)	0.171 83(6)	0.751 58(13)	0.051 92(5)
O(1)	0.247 4(5)	0.666 2(3)	0.014 1(2)
O(2)	0.25	0.75	0.127 9(3)
N(1)	0.078 4(6)	0.849 8(6)	0.098 3(4)
N(2)	0.078 7(6)	0.661 5(7)	0.092 5(5)
N(3)	0.080 0(4)	0.756 5(8)	−0.035 4(3)
C(1)	0.043 5(8)	0.799 9(10)	0.160 3(6)
C(2)	0.009 3(8)	0.710 6(9)	0.136 0(7)
C(3)	0.030 5(9)	0.620 4(7)	0.028 0(7)
C(4)	0.010 3(8)	0.692 6(8)	−0.024 7(6)
C(5)	0.040 2(8)	0.857 4(6)	−0.030 5(5)
C(6)	0.018 4(11)	0.878 7(11)	0.041 6(7)
C(11)	0.135 9(10)	0.927 2(8)	0.128 9(7)
C(12)	0.082 8(10)	0.990 9(11)	0.175 9(8)
C(21)	0.124 4(9)	0.584 0(8)	0.129 6(6)
C(22)	0.060 9(12)	0.511 5(9)	0.161 8(6)
C(31)	0.129 7(5)	0.744 8(8)	−0.102 9(4)
C(32)	0.073 1(8)	0.753 1(13)	−0.171 2(5)
K(1)	0.25	0.25	0.75
P(1)	0.056 04(13)	0.250 1(3)	0.632 82(11)
F(11)	0.081 1(5)	0.188 2(6)	0.700 2(4)
F(12)	0.116 3(12)	0.322 4(6)	0.659 8(9)
F(13)	0.034 6(7)	0.311 1(6)	0.566 9(4)
F(14)	0.099(9)	0.169 0(7)	0.596 3(7)
F(15)	0.144 8(7)	0.218 6(14)	0.602 7(6)
F(16)	−0.036 3(7)	0.269 2(13)	0.665 2(6)

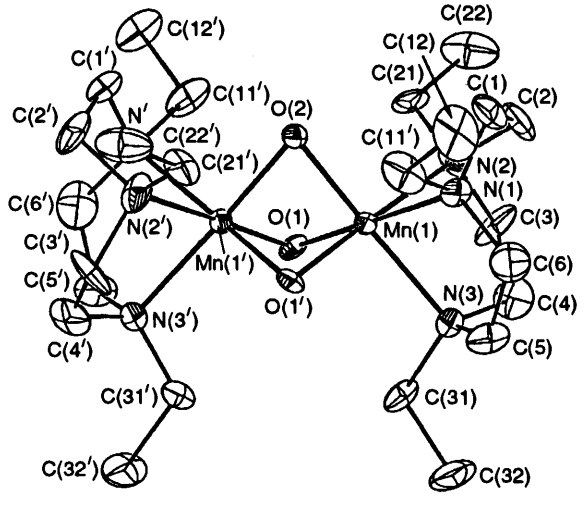


Fig. 1 An ORTEP plot drawn at the 30% probability level for the dinuclear cation of complex **13**

infrared, absorption, negative-ion FAB^- (some also positive-ion FAB), NMR spectroscopy, elemental analyses (Table 2), and in the case of **13** also by an X-ray analysis. Crystallization of **11** and **12** was found to be less easy, which is probably related to a combination of the lack of symmetry and the occurrence of possible rotamers of the non-symmetrical ligands co-ordinated to the manganese ions. Also elemental analysis (Table 2) indicated that various amounts of hexafluorophosphate and water can be present.

Crystal structure of complex 13

The molecular structure of complex **13** has been confirmed by single-crystal X-ray analysis. Fractional coordinates are given in Table 3, relevant bond distances and angles in Table 4. An ORTEP[17] drawing of the dication is shown in Fig. 1, together with the atom labelling used.

Table 4 Selected bond distances (Å) and angles (°) for complex **13**

Mn(1)–O(1)	1.817(6)	C(1)–C(2)	1.475(19)
Mn(1)–O(2)	1.825(4)	C(3)–C(4)	1.476(16)
Mn(1)–N(1)	2.170(9)	C(5)–C(6)	1.419(16)
Mn(1)–N(2)	2.047(10)	C(11)–C(12)	1.50(2)
Mn(1)–N(3)	2.117(6)	C(21)–C(22)	1.537(19)
Mn(1)–Mn(1′)	2.2952(13)	C(31)–C(32)	1.527(13)
Mn(1)–O(1′)	1.833(6)	K(1)–F(11)	2.799(8)
N(1)–C(1)	1.463(15)	K(1)–F(12)	2.796(16)
N(1)–C(6)	1.441(17)	P(1)–F(11)	1.595(8)
N(1)–C(11)	1.526(16)	P(1)–F(12)	1.471(14)
N(2)–C(2)	1.489(16)	P(1)–F(13)	1.554(9)
N(2)–C(3)	1.522(16)	P(1)–F(14)	1.530(12)
N(2)–C(21)	1.491(15)	P(1)–F(15)	1.492(12)
N(3)–C(4)	1.402(15)	P(1)–F(16)	1.510(11)
N(3)–C(5)	1.595(14)		
N(3)–C(31)	1.467(7)		
O(1)–Mn(1)–O(2)	84.82(19)	O(1′)–Mn(1)–O(2)	84.34(19)
O(1)–Mn(1)–N(1)	178.0(3)	N(1)–Mn(1)–N(2)	81.9(4)
O(1)–Mn(1)–N(2)	96.1(3)	N(1)–Mn(1)–N(3)	83.2(3)
O(1)–Mn(1)–N(3)	96.5(3)	O(1′)–Mn(1)–N(1)	97.2(3)
O(1)–Mn(1)–O(1′)	84.8(2)	N(2)–Mn(1)–N(3)	83.2(4)
O(2)–Mn(1)–N(1)	95.5(2)	O(1′)–Mn(1)–N(2)	178.4(3)
O(2)–Mn(1)–N(2)	97.1(3)	O(1′)–Mn(1)–N(3)	95.3(3)
O(2)–Mn(1)–N(3)	178.6(3)	Mn(1)–O(1)–Mn(1′)	77.93(18)
		Mn(1)–O(2)–Mn(1′)	77.9(2)

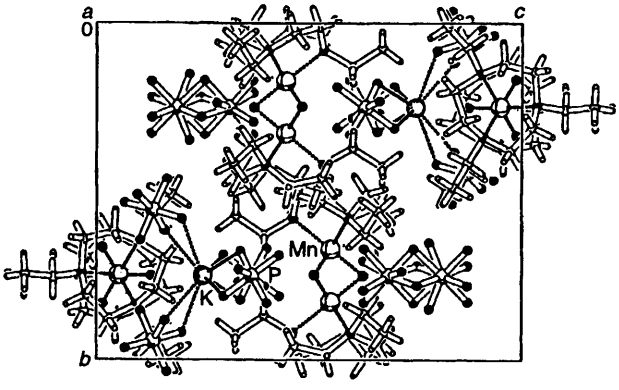


Fig. 2 Projection of the unit-cell contents of complex **13** down the *a* axis

Fig. 1 shows that the cation is very similar to that of compound **10**.[4] The Mn · · · Mn and Mn–N distances are very similar to those in the (L^4) analogue,[4] in agreement with the NMR and electronic spectra, and electrochemical properties (see below). All other distances and angles are as expected. The ethyl groups are pointed outwards, thereby minimizing the steric interaction between the two bulky groups. Extra KPF_6 cocrystallizes with the manganese complex. The structural analysis reveals that, per $[Mn_2O_3L_2]^{2+}$ dication, two PF_6 anions and half a $K(PF_6)_4$ anion are present. Part of the PF_6 groups are disordered over a $\bar{4}$ site. The unit cell contains four dications and its structure is shown in Fig. 2. The anionic $[K(PF_6)_4]^{3-}$ unit is not disordered and contains K^+ coordinated by 12 F^- ions with K–F distances of around 2.8 Å. Similar distances have been reported for a KPF_6 polymeric chain in potassium triethylenetetramine palladium(II) tris(hexafluorophosphate).[18]

NMR spectroscopy of the $Mn^{IV}_2(\mu\text{-}O)_3L_2$ complexes

Proton NMR spectra of the dinuclear $Mn^{IV}(\mu\text{-}O)_3Mn^{IV}$ complexes were measured in order to obtain further structural data, especially from the asymmetric ligands. It has been noted by Wieghardt *et al.*[4] that the two manganese ions in **10** are very strongly coupled, yielding a $S = 0$ ground state. The NMR spectrum in CD_3CN of this complex supports this observation,

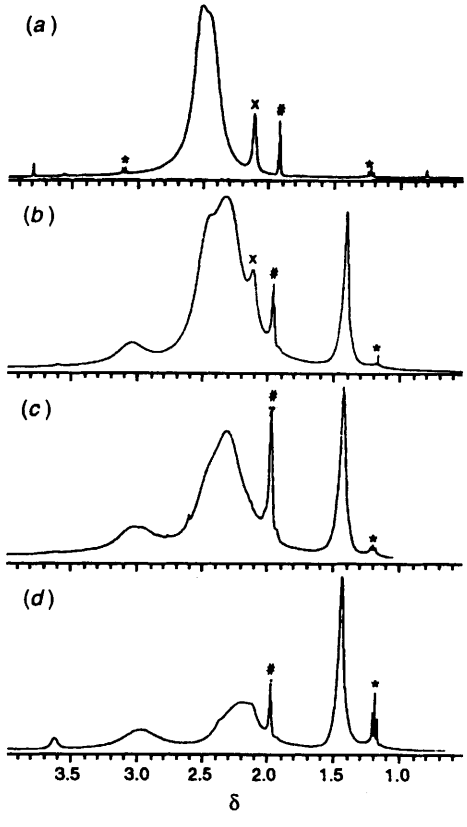


Fig. 3 The 360 MHz ^1H NMR spectra of complexes **10** (*a*), **11** (*b*), **12** (*c*) and **13** (*d*) in CD_3CN. Signals marked with * are from residual ethanol, # from CHD_2CN and × from water

as shown in Fig. 3(*a*). Two signals at δ 2.27 and 2.45 have been observed at 348 K. By synthesizing the complex with deuteriated methyl groups the signal at δ 2.45 disappears. This shows that the signal around δ 2.27 is caused by the methylene protons of the nine-membered ring. It is noted that, although the signals are in the range for diamagnetic compounds, they are significantly broadened. It is unlikely that paramagnetic impurities cause this broadening, as different batches of this compound yielded exactly the same spectra. Therefore it is

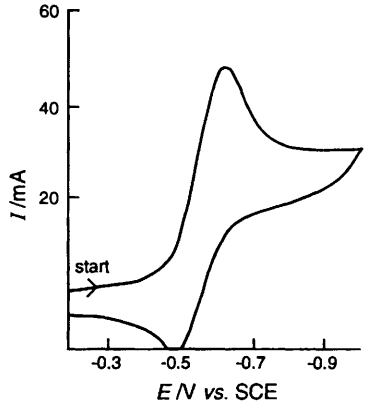


Fig. 4 Cyclic voltammogram of complex **13** in MeCN solution containing 0.1 mol dm^{-3} NBu_4ClO_4

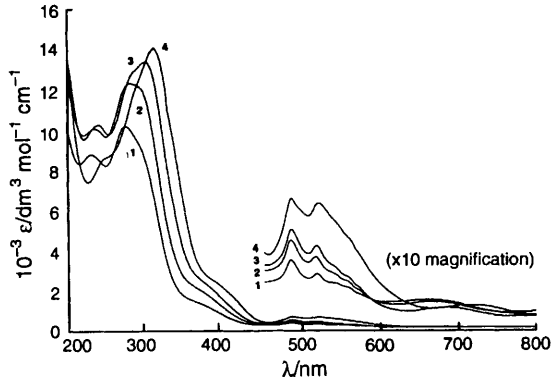


Fig. 5 Absorption spectra of the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]$ complexes **1–4** in acetonitrile

more likely that temperature-independent paramagnetism causes the broadening.

The NMR spectra of complexes **11–13** are also shown in Fig. 3 and corresponding data are presented in Table 5. Assignment was straightforward, as the methylene groups of the triazacyclononane ligand are always observed between δ 2.20 and 2.34. The methyl groups for the complexes with L^4–L^6 are found around δ 2.47, the ethyl groups for complexes **11–13** at δ 1.41 (CH_3) and *ca.* δ 3.0 (CH_2).

It should be noted that no indications for the presence of different geometrical isomers were found, as the signals of the protons of **14** and **12**, *i.e.* the complexes containing asymmetric ligands, do not suggest a broadening or a splitting. However, the signals are already quite broad and the differences in chemical shifts for the isomers may be too small to observe a splitting.

Electrochemical properties

The redox properties of the manganese complexes are presented in Table 6. The dinuclear $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]^{2+}$ complexes exhibit two oxidation processes. The first has been assigned to a $Mn^{III}Mn^{III} \longrightarrow Mn^{III}Mn^{IV}$ couple around 0.6–1.0 V *vs.* saturated calomel electrode (SCE) and the second to a $Mn^{III}Mn^{IV} \longrightarrow Mn^{IV}Mn^{IV}$ process at 1.2–1.5 V. The redox potentials observed for **1** and **4** are in agreement with literature values.[3] Both waves are reversible. The reduction wave ($Mn^{III}Mn^{III} \longrightarrow Mn^{III}Mn^{II}$) of these complexes is irreversible, in agreement with previous observations by Wieghardt *et al.*[4]

In the complexes **1–4** (ligands L^1–L^4) a systematic shift to more positive values for the $Mn^{III}Mn^{III} \longrightarrow Mn^{III}Mn^{IV}$ and $Mn^{III}Mn^{IV} \longrightarrow Mn^{IV}Mn^{IV}$ oxidation waves is observed with increasing number of methyl groups, in agreement with the metal-centred orbitals being increasingly stabilized. This indicates that the ligands become weaker donors as more

Table 5 Proton NMR data for the $[Mn_2(\mu\text{-}O)_3L_2]X_2$ complexes with L = L^4 **10**, L^5 **11**, L^6 **12** and L^7 **13** measured in CD_3CN at 323 K

Compound	NCH_2CH_2N	NCH_3	NCH_2CH_3
10	2.31	2.49	—
11	2.34	2.47	3.05, 1.41
12	2.29	2.46	3.01, 1.41
13	2.20	—	2.98, 1.42

methyl groups are introduced on the tacn ring. Furthermore, solvent effects may be larger for the $(NH)_x$-containing complexes than for the complexes containing only tertiary amines. Replacing methyl by ethyl groups did not yield an appreciable change of the electrochemical properties, in agreement with expectations.

The four $[Mn^{IV}_2(\mu\text{-}O)_3L_2]^{2+}$ complexes exhibit reduction waves at around −0.5 V *vs.* SCE in acetonitrile. The complexes containing L^4–L^6 show irreversible reduction waves at scan rates of 100 and 200 mV s^{-1}. The complex with L^4 has been studied by Wieghardt *et al.*[4] who also observed irreversible redox chemistry. Apparently, the mixed-valence $Mn^{III}Mn^{IV}$ species formed upon reduction of the $Mn^{IV}Mn^{IV}$ complex is not stable under these conditions on voltammetry time-scales. The electrochemical experiments on compound **10** will be discussed in more detail in another paper.[19]

The compound containing L^7 shows quasi-reversible behaviour (Fig. 4). It has been studied using cyclic voltammetry with scan rates between 25 and 1000 mV s^{-1}. The wave never becomes completely reversible, as $i_{pc}/i_{pa} \approx 1.2$ for 1000 mV s^{-1} to > 10 for 25 mV s^{-1}. As shown in Table 6, the differential pulse polarograms of **10–13** exhibit very similar values. This is consistent with the electronic spectra of these complexes (see below) and the electrochemical properties of the dinuclear manganese(III) complexes (see above).

Electronic spectra

The absorption spectral data of the $[Mn_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]^{2+}$ complexes **1–7** with L = L^1–L^7 are presented in Table 7. Fig. 5 shows the spectra for the dinuclear complexes **1–4**. The absorption spectra for these μ-oxo-bis-μ-carboxylato dinuclear manganese(III) complexes are very similar to related complexes.[1,4,20–22]

The strong band in the region around 300 nm shows a clear shift to lower energy upon going from L^1 to L^4. The weak band around 660–720 nm also exhibits a shift to lower energy upon introducing more methyl groups. The typical 'twin peaks' around 500 nm are not influenced to a great extent upon introducing more methyl groups on the tacn ligand. These findings are not in disagreement with the suggestions made by Lippard and co-workers[20] concerning the assignments of the absorption bands for such compounds. The absorptions around 500 nm have been assigned to d–d transitions, as mononuclear manganese(III) complexes exhibit bands in this region as well. Resonance-Raman spectroscopy has revealed that some charge-transfer (c.t.) character is also present, thus explaining the higher intensity of these absorption bands on increasing methyl substitution.

As shown in Fig. 6, the oxidation potentials of the $Mn^{III}Mn^{III} \longrightarrow Mn^{III}Mn^{IV}$ redox couple (see below) and absorption bands around 230–244, 270–310 and 660–720 nm are clearly correlated. A similar relationship has been observed for the $Mn^{III}Mn^{IV} \longrightarrow Mn^{IV}Mn^{IV}$ redox couple and the same absorption bands as well. A number of papers have already dealt with the relationship between c.t. bands and electrochemical properties.[23–25] Especially ruthenium(II) complexes with various nitrogen donors have been investigated in detail and a good correlation found between the electrochemical potentials (oxidation or reduction or oxidation-reduction

Table 6 Electrochemical data for the complexes, as determined from differential pulse measurements in MeCN solution containing 0.1 mol dm^{-3} NBu_4ClO_4. All values in V *vs.* SCE. Cyclic voltammograms were run in order to judge the reversibility of the redox processes. rev. = reversible, irr. = irreversible and qr. = quasi-reversible

Complex	$E_{red}(Mn^{III}Mn^{III}–Mn^{III}Mn^{II})$	$E_{ox}(Mn^{III}Mn^{III}–Mn^{III}Mn^{IV})$	$E_{ox}(Mn^{III}Mn^{IV}–Mn^{IV}Mn^{IV})$	$E_{red}(Mn^{IV}Mn^{IV}–Mn^{IV}Mn^{III})$
$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$				
1	−0.25 (irr.)	0.60 (rev.)	1.20 (rev.)	—
2	−0.35 (irr.)	0.69 (rev.)	1.24 (rev.)	—
3	−0.26 (irr.)	0.80 (rev.)	1.38 (rev.)	—
4	−0.15 (irr.)	0.92 (rev.)	1.55 (rev.)	—
5	−0.14 (irr.)	0.96 (rev.)	1.55 (rev.)	—
6	−0.13 (irr.)	0.95 (rev.)	1.54 (rev.)	—
7	−0.12 (irr.)	0.94 (rev.)	1.53 (rev.)	—
$[Mn_2(\mu\text{-}O)_3L_2]$				
10	—	—	—	−0.58 (irr.)
11	—	—	—	−0.54 (irr.)
12	—	—	—	−0.53 (irr.)
13	—	—	—	−0.54 (qr.)

Table 7 Absorption spectroscopic data for the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]$ complexes in acetonitrile

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})				
1	230 (9 000)	274 (10 300)	484 (380)	518 (290)	660 (120)
2	235 (9 800)	280 (12 100)	484 (420)	516 (340)	666 (115)
3	241 (9 700)	296 (12 700)	484 (450)	517 (380)	686 (100)
4	244 (8 300)	310 (14 000)	484 (680)	520 (640)	720 (90)
5		311 (14 200)	485 (740)	521 (720)	
6*	247 (sh)	313 (11 000)	486 (570)	520 (550)	720 (90)
7		318 (13 300)	485 (700)	522 (720)	729 (130)

* Not recrystallized.

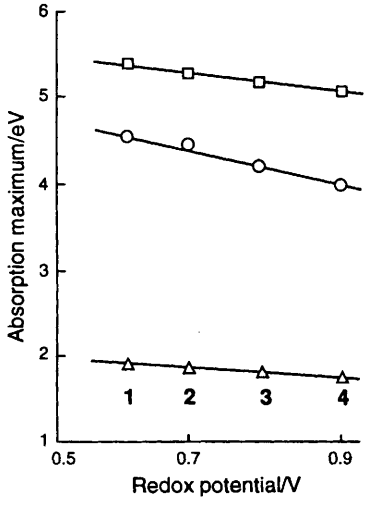


Fig. 6 Plot of absorption maxima to redox potentials of the $Mn^{III}Mn^{III} \longrightarrow Mn^{III}Mn^{IV}$ transition of the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]$ complexes **1**–**4** (□, 230–244; ○, 270–310; △, 660–720 nm absorption bands)

potential) and the absorption or emission metal-to-ligand charge-transfer (m.l.c.t.) bands. For the manganese(III) complexes **1**–**4** with the triazacyclononane ligands such a dicorrelation also is found, suggesting that a similar treatment can be given. When plotting the absorption energies in eV *vs.* the oxidation potentials (V), negative slopes of −0.5 to −1.7 eV per V have been found for the three absorption bands. The relationship observed in our case strongly suggests that these absorption bands are charge-transfer bands, in agreement with previous assignments.[20] No assignment has been made, however, for the low-energy band around 700 nm.[20] Our observations suggest that this band is a charge-transfer band as well. The differences in redox properties and absorption bands between compounds **1**–**4** can have electronic or steric effects. Intuitively, one would expect that methyl groups are better donating groups than hydrogen atoms, leading to *lower* oxidation potentials and *higher* energy absorption bands, *i.e.* positive slopes. Preliminary semiempirical Austin Model 1 (AM1) calculations on L^1 and L^4 have revealed that the electron density on the nitrogen atoms is lower for the methyl-substituted ligand, due to hyperconjugative interaction between the nitrogen atoms and the substituents of N for L^4.[26] Therefore, the methyl-substituted ligand donates less electron density than would be expected.

The five tris-μ-oxo dinuclear manganese(IV) complexes all exhibit very similar UV/VIS spectra (Table 8), which is consistent with the electrochemical data for these compounds (Table 6). The smaller molar absorption values found for **14** are probably due to impurities, as the small quantities did not allow recrystallization. The substituents on the nitrogen donor atoms are expected to exhibit similar donating abilities. It is interesting that the asymmetric complexes **11** and **12** also have similar absorption bands, suggesting that the asymmetry does not influence the electronic properties to a large extent. The metal-centred orbitals are not influenced by the relatively small variations on the nitrogen donors.

Conclusion

A new series of 1,4,7-triazacyclononanes has been prepared in which the three nitrogens were substituted one by one, first by methyl and subsequently by ethyl groups. Using an improved synthetic method the compounds obtained could be converted efficiently into their $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]^{2+}$ complexes. It was clearly shown that large nitrogen substituents inhibit the reaction as the 1,4,7-triethyl derivative gave low conversion and the 1,4,7-tripropyl gave very low conversion.

Replacement of hydrogens for methyl groups had the strongest effect on the properties of the complexes. When

Table 8 Absorption spectroscopic data for $[Mn_2(\mu\text{-}O)_3L_2]$ complexes in acetonitrile

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})				
10	236 (19 100)	270 (16 400)	314 (9 500)	396 (950)	491 (390)
11	238 (17 500)	273 (15 600)	315 (9 250)	394 (920)	495 (380)
12	240 (18 000)	274 (16 300)	315 (9 700)	395 (920)	494 (370)
13	244 (17 800)	278 (16 600)	317 (10 300)	395 (980)	497 (395)
14*	249 (12 000)	280 (11 600)	318 (7 000)	395 (690)	498 (310)

* Values based on impure product.

secondary amines are present oxidation yields no $Mn^{IV}_2(\mu\text{-}O)_3$ core. Their redox potentials gradually increased upon increasing substitution while their absorption maxima shifted to lower energy.

A new method was developed to prepare efficiently the oxidation products, *i.e.* the $[Mn^{IV}_2(\mu\text{-}O)_3L_2]^{2+}$ complexes, directly from macrocycle, manganese(II) chloride and alkaline hydrogen peroxide. Again macrocycles with large substituents (triethyl and tripropyl) gave low conversions. The gradual increase in substituent size (methyl ⟶ ethyl) gave only a small but significant shift in the absorption spectra.

The X-ray-resolved structure of complex **13** clearly shows that on replacing all the methyl by ethyl groups (**10** to **13**) the very short interatomic Mn···Mn distance does not change within experimental error (2.29 Å). The core determines the binding of the two halves of the molecule, while the extra steric requirements of the ethyl over the methyl groups do not seem to have significant influence. Although similar steric interactions are likely to apply for both the $[Mn^{III}_2(\mu\text{-}O)(O_2CMe)_2L_2]^{2+}$ and the $[Mn^{IV}_2(\mu\text{-}O)_3L_2]^{2+}$ complexes, as observed for their syntheses, their electronic properties (absorption spectroscopy, redox potentials) seem, however, to be only marginally affected on going from *N*-methyl to *N*-ethyl groups.

Experimental

Physical measurements

The NMR spectra were recorded on a JEOL 60 MHz and a Bruker 360 MHz spectrometer, absorption spectra on a Perkin-Elmer Lambda 3 spectrophotometer with a PC-data station using PECSS software for data processing, infrared spectra with a Philips PU9706 spectrophotometer and FAB-mass spectra on a VG7070 or Trio-2000 spectrometer. The positive-ion FAB mass spectra of the macrocycles were measured in glycerol. In general they show a $[M + H]$ ion. Those of the complexes do not show molecular ions in glycerol. After acidifying with acetic acid in most cases ions of composition $[L_2Mn_2(O_2CMe)_3]^+$ and $[LMn(O_2CMe)]^+$ can be seen. Using 3-nitrobenzyl alcohol as matrix the complexes sometimes show $[complex - X]^+$ and $[complex - 2X]^+$ (X is the counter ion). The negative-ion FAB mass spectra of the complexes were run in 3-nitrobenzyl alcohol as matrix. In general ions with the composition $[M]^-$, $[M - L + H]^-$ and $[M + X]^-$ are observed. Sometimes cluster ions of PF_6 and the matrix were present. The electrochemistry measurements were performed on an EG&G PAR C model 303 potentiostat with an EG&G polarographic analyser. A laboratory-made three-compartment cell was used with a glassy carbon electrode as working electrode, a SCE as reference and a platinum wire as auxiliary electrode. Solutions of the complexes were made in 0.1 mol dm^{-3} tetrabutylammonium perchlorate in acetonitrile and thoroughly purged with nitrogen. The scan rate for the differential pulse experiments was 10 mV s^{-1} and for the cyclic voltammograms 100 mV s^{-1} in a potential window of +2.0 to −2.0 V. Elemental analyses were carried out by Labor Pascher, Bonn, Germany.

Crystallography

Crystal data. $C_{24}H_{54}F_{15}K_{0.5}Mn_2N_6O_3P_{2.5}$, $M = 966.56$, tetragonal, space group $P4_2/n$, $a = b = 14.678(1)$, $c = 18.676(2)$ Å, $U = 4023.6(6)$ Å^3, $Z = 4$, $D_c = 1.595$ Mg m^{-3}, $F(000) = 1984$, μ(Mo-Kα) = 8.5cm^{-1}, λ(Mo-Kα) = 0.710 73Å. A red crystal of dimensions 0.25 × 0.50 × 0.50 mm was used.

Data collection and processing. Reflection data were measured with a TurboCAD-4 diffractometer on rotation anode (60 kV, 150 mA), ω–2θ scan width $\Delta\omega = 1.02 + 0.35 \tan\theta$, using graphite-monochromated Mo-Kα radiation at $T = 150$ K. A total of 5780 reflections were measured [$\theta < 27.5°$, $-h$, $-k$, $\pm l$], 4612 unique ($R_{av} = 0.06$), giving 2696 reflections with $I > 2.0\sigma(I)$. No decay was observed. Lorentz polarization correction, but not for absorption, was performed.

Structure solution and refinement. The structure was solved with DIRDIF 92[27] and refined by full-matrix least squares (SHELXL 93.[28]) Hydrogen atoms were taken into account at calculated positions. One of the PF_6 anions is disordered over a $\bar{4}$ site. A twinning model (on 100) was used to describe the disorder in the dinuclear manganese cation and '$[K(PF_6)_4]$' anionic unit. The corresponding twinning parameter refined to 50%. Convergence was reached at $R_1 = 0.087$, $wR_2 = 0.25$, with $w^{-1} = \sigma^2(F^2) + (0.1481P)^2$. Maximum residual density (1.03 e Å^{-3}) in the region of the disordered PF_6. Scattering factors were taken from ref. 29. The geometrical calculations, including the illustration, were done with PLATON 93[30] and PLUTON 93.[31]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Preparation of the macrocycles

The compounds L^1 (1,4,7-triazacyclononane),[32] L^3 (1,4-dimethyl-1,4,7-triazacyclononane)[33] (*via* 1-tosyl-1,4,7-triazacyclononane[10]) and L^4 (1,4,7-trimethyl-1,4,7-triazacyclononane)[34] were prepared by literature methods.

1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane II. Distilled L^1 (99.4 g) was warmed to 340 K (without solvent) and dimethylaminoformaldehyde dimethyl acetal (91.7 g) was added dropwise with vigorous stirring between 335 and 345 K. The mixture was refluxed for 16 h, cooled, low-boiling products evaporated and the residue distilled to give the methine-bridged triamine (99.9 g, 92%) as a slightly yellow oil, b.p. 350–351 K at 133 Pa. The NMR spectrum was in agreement with that in the literature.[12]

1-Methyl-4,7-diaza-1-azoniatricyclo[5.2.1.0^{4,10}]decane iodide IIIa. Methyl iodide (5.1 g) in tetrahydrofuran (thf, 30 cm^3) was added below 273 K to compound **II** (5.0 g) in thf (40 cm^3) and the mixture allowed to warm to room temperature. The precipitate obtained was filtered off, washed and dried to leave 9.85 g (97%) of the beige microcrystalline salt. NMR (D_2O): ^{1}H, δ 3.26 (3 H, s), 3.1–3.3 (4 H, m), 3.70 (8 H, m) and 5.58

(1 H, s); ^{13}C, δ 50.98, 54.39, 57.16, 63.95, and 122.01. Mass spectrum (FAB^+, glycerol): *m/z* 154 ($[M - I]^+$) and 435 ($[2M - I]^+$).

1-Methyl-1,4,7-triazacyclononane L². Although the synthesis has been reported before,[35] the following method was found to be more convenient. Compound **IIIa** (2.47 g) was dissolved in 4 mol dm^{-3} hydrochloric acid (21 cm^3) and left for 60 h at room temperature. After evaporation it was heated for 60 h at 80 °C with sodium hydroxide (4 g), water (4 cm^3) and ethanol (12 cm^3). The upper layer was separated and the lower aqueous phase extracted with dichloromethane. The combined organic layers were dried and evaporated to leave 1.05 g of oil which was distilled (bulb to bulb) to give L^2 (820 mg, 65%) as a colourless oil, b.p. up to 378 K at 65 Pa. NMR ($CDCl_3$): ^1H, δ 2.23 (3 H, s), 2.38 (4 H, m) and 2.75 (8 H, m); ^{13}C, δ 44.32, 46.34, 46.70 and 54.85. Mass spectrum (FAB^+, glycerol): *m/z* 144 ($[M + H]^+$).

1-Ethyl-4,7-diaza-1-azoniatricyclo[5.2.1.0^{4,10}]decane iodide IIIb. Compound **II** (8.0 g) was dissolved in thf (65 cm^3) and ethyl iodide (9.0 g) added. After standing for 2 d the precipitated microcrystalline solid was filtered off and washed with thf. After drying the iodide salt weighed 16.3 g (96%). NMR (CD_3OD): ^1H, δ 1.47 (3 H, t), 3.25 (4 H, m), 3.48 (4 H, m), 3.65 (2 H, q), 3.70 (4 H, m) and 5.58 (1 H, s); ^{13}C, δ 10.66, 53.00, 54.90, 56.58, 57.81 and 124.13. Mass spectrum (FAB^+, glycerol): *m/z* 168 ($[M - I]^+$) and 463 ($[2M - I]^+$).

1-Ethyl-4,7-dimethyl-1,4,7-triazacyclononane L⁵. Compound **IIIb** (7.0 g) was taken up in formic acid (21.0 g) and 37% aqueous formaldehyde (14.0 g) and heated at 373 K for 24 h. The mixture was evaporated, water added, re-evaporated, then 50% sodium hydroxide added to pH >12. Extraction with hexane, drying and evaporation gave an almost colourless oil which was distilled (bulb to bulb) to give the free amine (4.05 g, 92%) as a colourless oil, b.p. up to 383 K at 13 Pa. NMR ($CDCl_3$): ^1H, δ 1.00 (3 H, t), 2.35 (6 H, s) and 2.4–2.8 (14 H, m); ^{13}C, δ 12.87, 46.81, 52.59, 55.46, 57.20 and 57.83. Mass spectrum (FAB^+, glycerol): *m/z* 186 ($[M + H]^+$).

1,4-Diethyl-7-methyl-1,4,7-triazacyclononane L⁶. Compound L^2 (620 mg) was dissolved in acetic acid (25 cm^3) and at 323–328 K, pellets of $NaBH_4$, (1.58 g) were added in pieces over 1 h. The mixture was stirred at 328 K overnight, then some acetic acid was evaporated and $NaBH_4$ (0.58 g) added. The mixture was heated overnight at 328 K, then some water and concentrated HCl (10 cm^3) added (pH < 1). The mixture was evaporated to a tenth of its original volume, taken up in water and extracted with CH_2Cl_2. Sodium hydroxide was added to pH >12 and the mixture extracted with pentane. Evaporation of the pentane gave 530 mg of a yellow oil which was distilled (bulb to bulb) to yield L^6 (340 mg, 39%) as a colourless oil, b.p. 343–348 K at 13 Pa. NMR ($CDCl_3$): ^1H, δ 1.03 (6 H, t), 2.37 (3 H, s), 2.56 (4 H, q), 2.66 (4 H, s) and 2.74 (8 H, m); ^{13}C, δ 12.88, 46.64, 52.56, 55.28, 55.93 and 57.47. Mass spectrum (FAB^+, glycerol): *m/z* 200 ($[M + H]^+$).

1,4,7-Triethyl-1,4,7-triazacyclononane L⁷. The compound **I**·3HBr (5.58 g, 15 mmol) was suspended in acetic acid (154 cm^3, 2.7 mol) and $NaBH_4$ (10.26 g, 1 g pellets) added over 45 min, keeping the temperature at 328 K. The mixture was stirred at this temperature for 24 h and subsequently evaporated *in vacuo* using an oil pump. Water (25 cm^3) and CH_2Cl_2 (100 cm^3) were added to the residue giving a gelatinous mixture. While stirring and cooling (alcohol–CO_2) a solution of NaOH (65 g, 1.62 mol in 162 cm^3 water) was added, maintaining the temperature at 293 K. To the thick slurry water (25 cm^3) was added. The strongly alkaline mixture was filtered over Hyflo and the filter cake was washed with CH_2Cl_2. The organic layer was separated and the water layer extracted three times with CH_2Cl_2 (100 cm^3). The combined CH_2Cl_2 layers were evaporated, refiltered over Hyflo and completely evaporated giving 2.82 g of residue, which was distilled *in vacuo* at 353–358 K (24 Pa) to give 2.6 g (80% yield) of the product as a colourless oil of 98% purity (GC). NMR ($CDCl_3$): ^1H, δ 2.9 (12 H, s), 2.6 (6 H, q) and 1.1 (9 H, t). The compound could also be isolated as the HCl salt by dissolving the residue isolated from the dichloromethane extraction in a mixture of concentrated HCl (10 cm^3) and EtOH (10 cm^3). After addition of EtOH (150 cm^3) the turbid mixture was allowed to stand overnight at 278 K. It was then filtered, the filter cake discarded (62 mg, containing incompletely alkylated material), and the filtrate evaporated. Again concentrated HCl (5 cm^3) and methanol (MeOH, 15 cm^3) were added, and while cooling (CO_2–acetone) acetone (150 cm^3) was squirted into the mixture resulting in flocculation. The mixture was cooled in a refrigerator for 3 d and filtered. The solids were washed with acetone and hexane and dried *in vacuo* giving 3.9 g (80%) of a white hygroscopic powder. The material was stored over P_2O_5. NMR (D_2O + DCl): ^1H, δ 3.4 (12 H, s), 3.1 (6 H, m) and 1.2 (9 H, t). Mass spectrum (FAB^+, glycerol): *m/z* 214 ($[M + H]^+$). IR (KBr): ν 3410, 2980, 2530, 1400, 1025, 805 and 765 cm^{-1}.

1,4,7-Tripropyl-1,4,7-triazacyclononane L⁸. A procedure similar to that described for L^7 was followed. Propionic acid was used instead of acetic acid and the reaction was carried out on a 50 mmol scale under similar reaction conditions. Data for L^8·3HCl: ^1H NMR (D_2O + DCl) δ 3.4 (12 H, s), 3.1 (6 H, m), 1.7 (6 H, m) and 0.9 (9 H, t); mass spectrum (FAB^+, glycerol): *m/z* 256 ($[M + H]^+$); IR (KBr) ν 3440, 2980, 2530, 1450, 990 and 765 cm^{-1}.

Preparation of the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$ complexes.

Two methods were used, and optimized for L^4·3HCl (method A) and L^4 (method B) giving complex **4**.

In method A $Mn(O_2CMe)_3$·$2H_2O$ (536 mg, 2 mmol) was added to a stirred solution of L^4·3HCl (561 mg, 2 mmol), $NaHCO_3$ (420 mg, 5 mmol), NaO_2CMe (410 mg, 5 mmol) and KPF_6 (460 mg, 2.5 mmol) or $NaClO_4$ (306 mg, 2.5 mmol) in acetonitrile (30 cm^3, degassed) under argon. The temperature was raised gradually to 328 K (0.5 h) and stirring continued for 2.5 h at this temperature. Within a few minutes the brownish suspension turned brownish purple *via* dark greyish brown. After filtration the extent of conversion was 90% according to the absorption spectrum of the reaction mixture. Evaporation (303 K, vacuum) of the filtrate, stirring the residue with water, collection of the solidified products on a glass frit, washing with water and drying *in vacuo* yielded 659 mg (74%) of complex **4**. In the case of the perchlorate cation the filtrate was evaporated to half volume (the presence of potentially explosive perchlorate salts prohibits total evaporation), ethanol added and re-evaporated to half volume. On the third time this was repeated the complex precipitated and was filtered off, washed with ethanol and hexane, and dried (vacuum and argon) to give a dark purple solid. Purity similar to that reported[4] (ε 14 000 mol dm^{-3} cm^{-1}, at 310 nm).

In method B L^4 (5.15 mmol) was dissolved in acetonitrile (50 cm^3) in a Schlenk tube and toluene-*p*-sulfonic acid monohydrate (950 mg, 5 mmol) added. When the acid had dissolved a mixture of finely powdered $NaHCO_3$ (420 mg, 5 mmol), NaO_2CMe (1025 mg, 12.5 mmol), KPF_6 (1150 mg, 6.25 mmol) or $NaClO_4$ (765 mg, 6.25 mmol) and $Mn(O_2CMe)_3$·$2H_2O$ (1340 mg, 5 mmol) was added at room temperature with efficient stirring. The resulting thick brown suspension was heated in an oil-bath at 333 K. After 10 min the mixture was less viscous and had changed to brown-purple. The reaction was monitored by removing an aliquot and following the absorption coefficient by absorption spectroscopy. This reached a maximum after 40 min. The mixture was cooled, filtered into a graduated flask and

a more accurate determination of the conversion showed a yield of 95%. Work-up as described above gave a yield of 2060 mg (92%), purity 97% (UV/VIS [4]). For elemental analysis see Table 2, absorption data see Table 7.

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^1_2][ClO_4]_2$ 1. Method A was used: L^1·2.3HBr (630 mg, 2 mmol), $NaHCO_3$ (finely powdered, 386 mg, 4.6 mmol), NaO_2CMe (410 mg, 5 mmol), $NaClO_4$ (1224 mg, 10 mmol) and $Mn(O_2CMe)_3$·$2H_2O$ (536 mg, 2 mmol) in acetonitrile (30 cm^3). Yield: 512 mg (73%). IR (KBr): ν 3440, 3350, 3290, 1585, 1430, 1120, 850, 750 (sh), 740, 715, 668 and 631 cm^{-1}.

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^2_2][ClO_4]_2$ 2. Method B was used: L^2 (408 mg, 2.85 mmol). On addition of saturated $NaClO_4$–EtOH (3 cm^3) to the ethanolic solution obtained after reaction the complex crystallized. Yield: 712 mg (69%).

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^3_2][ClO_4]_2$ 3. Method A was used: L^3·3HBr (794 mg, 2 mmol) gave a yield of 288 mg (38%). Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 599 ($[M - L]^-$), 755 ($[M - H]^-$]) and 855 ($[M + ClO_4]^-$).

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^5_2][PF_6]_2$ 5. Method B was used: from L^5 (185 mg, 1 mmol). Trituration with water, filtering and washing with ethanol and diethyl ether gave an amorphous purple solid (220 mg, 48%).

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^6_2][PF_6]_2$ 6. Method B was used: from L^6 (107 mg, 0.53 mmol). After 4 h at 335–337 K and work-up a sticky product was obtained. Boiling in EtOH allowed the complex to be isolated as a purple powder, 127 mg (51%).

$[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L^7_2][PF_6]_2$ 7. Method A was used. A mixture of L^7·3HCl (3.3 g, 10 mmol), NaO_2CMe (2.5 g), KPF_6 (2.1 g) and $Mn^{III}(O_2CMe)_3$·$2H_2O$ (2.7 g) was stirred in MeCN (200 cm^3) at 328 K under argon. After 2 d of stirring the extent of conversion was about 10% as determined from the absorbance at 310 nm. Yield: 260 mg (5%) of a purple powder. Mass spectrum (FAB^+, glycerol + $MeCO_2H$): *m/z* 327 ($[L + Mn + O_2CMe]^+$) and 713 ($[2L + 2Mn + 3O_2CMe]^+$). IR (KBr): ν 3450, 1574, 841, 779, 732 and 661 cm^{-1}.

Preparation of the $[Mn^{IV}_2(\mu\text{-}O)_3L_2][PF_6]_2$ complexes

Two general methods were employed for the synthesis of the dinuclear $Mn_2(\mu\text{-}O)_3L_2$ complexes, the first (C) only for L^4, the second (D) for L^4–L^8.

$[Mn^{IV}_2(\mu\text{-}O)_3L^4_2][PF_6]_2$ 10. Method C, starting from the $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2L_2]X_2$ complexes, which is a modification of the synthesis reported by Wieghardt *et al.*[3e,4] Triethylamine (420 cm^3, 3.0 mol) was added to a solution of complex **4** (120 g, 0.134 mol) in ethanol–water (1:1, 2.4 dm^3). Oxygen was bubbled through the solution for 3.5 h at room temperature. After filtration the filtrate was concentrated to 0.3 dm^3 and the product left to crystallize. After standing overnight the product was filtered off and dried giving 86 g (85% yield) of red crystals. IR (KBr): ν 3540, 3400, 1465, 840, 798, 755 and 673 cm^{-1}. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 620 ($[M - L + H]^-$), 790 (M^-) and 935 ($[M + PF_6]^-$); (FAB^+, glycerol + $MeCO_2H$) 285 ($[L + Mn + O_2CMe]^+$) and 629 ($[2L + 2Mn + O_2CMe]^+$).

Method D; starting from $Mn^{II}Cl_2$·$4H_2O$ and L. Generally, compound L (1 mmol) was dissolved in EtOH–water (2:1, 6 cm^3) and $MnCl_2$ (1 mmol) and KPF_6 (1.5 mmol) were added simultaneously. Stirring for 20 min at 313–328 K gave a thinner cream suspension. The mixture was cooled (ice-bath) while stirring and after 10 min a freshly premixed solution containing hydrogen peroxide (H_2O_2, 1 cm^3, 1 mmol dm^{-3}) and NaOH (1 cm^3, 1.5 mmol dm^{-3}) was added dropwise during 3–5 min. After stirring for 11–15 min at ice-bath temperature, the mixture was neutralized to pH 8 with sulfuric acid (H_2SO_4, 2 mmol dm^{-3}), then Celite was added and the mixture filtered over a bed of Celite. The filter cake was washed with MeCN and the filtrate evaporated (vacuum, 313 K). To remove most salts, the product was dissolved in MeCN and again filtered into a graduated flask enabling measurement of the conversion by absorption spectroscopy. The filtrate was partially evaporated (vacuum, 313 K), EtOH added and again evaporated until the complex crystallized. The remainder (containing about 7 cm^3 EtOH per mmol complex) was stirred at 353 K for a while and left to crystallize at room temperature. Finally the complex was filtered off, washed with EtOH and hexane, and dried. Crystalline material was obtained after recrystallization(s) from EtOH–water mixtures.

This method, starting from L^4 (2 g, 11.4 mmol), gave 3.83 g (4.8 mmol, 84%) of complex **10**. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 620 ($[M - L + H]^-$), 790 (M^-) and 935 ($[M + PF_6]^-$).

$[Mn^{IV}_2(\mu\text{-}O)_3L^5_2][PF_6]_2$·$0.5KPF_6$·$0.5HPF_6$ 11. Prepared by method D: compound L^5 (3 g, 16.5 mmol) gave 6.64 g (6.7 mmol, 81%) complex. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 634 ($[M - L + H]^-$), 818 (M^-) and 963 ($[M + PF_6]^-$); (FAB^+, same matrix) 528 ($[M - 2PF_6]^+$) and 673 ($[M - PF_6]^+$); (FAB^+, glycerol + $MeCO_2H$) 299 ($[L + Mn + O_2CMe]^+$) and 657 ($[2L + 2Mn + 3O_2CMe]^+$).

$[Mn^{IV}_2(\mu\text{-}O)_3L^6_2][PF_6]_2$·$KPF_6$·$0.5H_2O$ 12. Prepared by method D: compound L^6 (2.3 g, 8.4 mmol) gave 2.75 g (2.7 mmol, 64%) complex. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 846 (M^-) and 991 ($[M + PF_6]^-$).

$[Mn^{IV}_2(\mu\text{-}O)_3L^7_2][PF_6]_2$·$0.5KPF_6$·$0.5H_2O$ 13. Prepared by method D: compound L^7 (4.1 g, 18.6 mmol) gave 651 mg (0.65 mmol, 7%) complex. Crystals suitable for X-ray analysis were obtained by recrystallization from ethanol–water (1:1). The 0.5 water molecule in the molecular formula was calculated from the oxygen analysis but was not observed in the crystal structure. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 662 ($[M - L + H]^-$), 874 (M^-) and 1019 ($[M + PF_6]^-$). IR (KBr): ν 3440, 1457, 842, 788, 738 and 665 cm^{-1}.

$[Mn^{IV}_2(\mu\text{-}O)_3L^8_2][PF_6]_2$ 14. Prepared by method D: compound L^8 (0.5 g, 2 mmol) gave a very low yield, 8 mg (0.01 mmol, 1%) of the complex. Mass spectrum (FAB^-, 3-nitrobenzyl alcohol): *m/z* 958 (M^-) and 1104 ($[M + PF_6]^-$); (FAB^+, same matrix) 668 ($[M - 2PF_6]^+$) and 813 ($[M - PF_6]^+$).

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