Anionic and Cationic Bi- and Tri-nuclear *tert*-Butylimido Complexes of Manganese-(V) and -(VI)†

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Dimeric anionic complexes have been obtained by reduction of $MnCl(NBu^t)_3$ or $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **1** with lithium powder in 1,2-dimethoxyethane (dme) to give $[Li(dme)]_2[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]$ **2**, or with sodium amalgam in tetrahydrofuran (thf) to give $[Na(thf)][\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]$ **3** which have oxidation states V,V and V,VI respectively. Interaction of **1** with iodine gave a mixed-valence (VI,V,VI) compound, $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2\}_2Mn]I_3$ **4**. Interaction of **3** with $HgCl_2$ gave $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2\}_2Mn]_2[Hg_2Cl_6]\cdot 2CHCl_3$ **5a** and $[(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2Mn(NHBu^t)(NBu^t)]_2[Hg_3Cl_8]$ **5b**. Oxidation of **1** by silver trifluoromethanesulfonate resulted in an unisolable cation in CH_2Cl_2, presumably $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]^+$, the EPR spectrum of which suggests that the single electron is located on one N atom of the terminal imide groups. The interaction of this cation with thf resulted in abstraction of H to give the manganese(VI) amido species $[(Bu^tN)(Bu^tNH)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]^+$ which is also formed on protonation of **1** with stoichiometric amounts of CF_3SO_3H. The amido cation has been isolated with the anions $CF_3SO_3^-$ **6** and $[B(C_6F_5)_4]^-$ **7**, but use of $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ produces, after crystallisation from toluene, the salts of the amido cation **8** and of an oxo species $[Mn_3(\mu\text{-}O)(\mu\text{-}NBu^t)_3(NBu^t)_4]^+$ **9**. Interaction of $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]^+$ *in situ* with dry O_2 gave a mixture **10** of $[\{(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2\}_2Mn]^+$ and $[\{(Bu^tN)_2Mn(\mu\text{-}O)(\mu\text{-}NBu^t)\}_2Mn]^+$ which cocrystallise and cannot be separated. Thermal decomposition of the alkoxide $Mn(NBu^t)_3[OCH(CF_3)_2]$ gave the manganese(V) dimer $[Mn(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2$. The structures of compounds **3**, **4**, **5a**, **5b**, **7**, **9** and the mixture **10** have been confirmed by single-crystal X-ray studies. In all cases the Mn atoms have distorted-tetrahedral geometry. The Mn–N bonds to terminal imide ligands lie in the range 1.554–1.674 Å, whilst bridging distances vary considerably from 1.724 to 1.872 Å, reflecting differences for Mn atoms which are co-ordinated only by bridging imides and those which are also bonded to terminal ligands. The Mn–O bonds in the oxo-bridged species are slightly longer than the analogous Mn–N (bridging) distances, indicating less multiple bonding. The structure of the $[Hg_3Cl_8]^{2-}$ ion in **5b** shows it to conform quite closely to the 'composite' species $[(Cl_2Hg)(Cl_2HgCl_2)(HgCl_2)]^{2-}$

The synthesis of the first non-oxo manganese-(VII) and -(VI) compounds, $MnCl(NBu^t)_3$ and $[Li(dme)]_2[Mn(NBu^t)_4]$ (dme = 1,2-dimethoxyethane), as well as a number of derivatives obtained by substitution of Cl in the former have been described.[1] A second paper[2] described the dimer, $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$, a nitrido anion, $[MnN(NBu^t)_3]^{2-}$, and various dimeric alkyl compounds made by interaction of $MnCl(NBu^t)_3$ with LiMe, dialkylzincs and Al_2Me_6. An unusual Schiff-base complex, $Mn[NBu^t{=}C(H)C_6H_3(Me)NH]_2$, of Mn^{II} was also obtained on interaction of $MnCl(NBu^t)_3$ with $LiNHC_6H_3Me_2$-2,6.

We have now prepared various anionic and cationic species; the principal reactions are shown in Scheme 1. Analytical and physical data for new compounds are given in Table 1.

Results and Discussion

Anionic Species.—The reduction of $[Mn^{VI}(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **1**,[2] in 1,2-dimethoxyethane by stoichiometric amounts of lithium powder yields a very air-sensitive green dimanganese(V) dianion isolated as the salt $[Li(dme)]_2[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]$ **2**. Although X-ray-quality crystals could not be obtained, the formulation is confirmed by analysis and by the quantitative oxidation by dry oxygen of **2** to give **1** (which is unaffected by oxygen[2]). Reduction of **1** in tetrahydrofuran (thf) by Li also gives green solutions. In both cases the ^1H and ^7Li NMR spectra are broad, probably due to the paramagnetism of the anion.

The reduction of compound **1** in thf by sodium amalgam led to the orange-brown, air-sensitive, mixed-valence manganese(V,VI) dimer $[Na(thf)][\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}_2]$ **3** which can also be obtained directly from $MnCl(NBu^t)_3$ in thf using 2 equivalents of sodium; this provides the most convenient synthesis for **3**. This mixed-valence compound is paramagnetic and gives the complicated EPR spectrum shown in Fig. 1. The exposure of solutions of **3** to oxygen, as in the case of **2**, quantitatively regenerates the dimer **1**. Cyclic voltammetry of **1** in CH_2Cl_2 gave only irreversible reduction waves.

The structure of compound **3** as determined by X-ray crystallography is shown in Fig. 2; selected bond lengths and angles are given in Table 2. Several features of the anion structure are worthy of comment. First the central Mn_2N_2 ring is almost square, with all angles close to 90°, and with only small differences in the bridging Mn–N bond lengths. These data may be taken to indicate equivalence of the Mn atoms, with an 'average' manganese oxidation state of 5.5. On the other hand

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† Non-oxo Chemistry of Manganese in High Oxidation States. Part 3.[2]

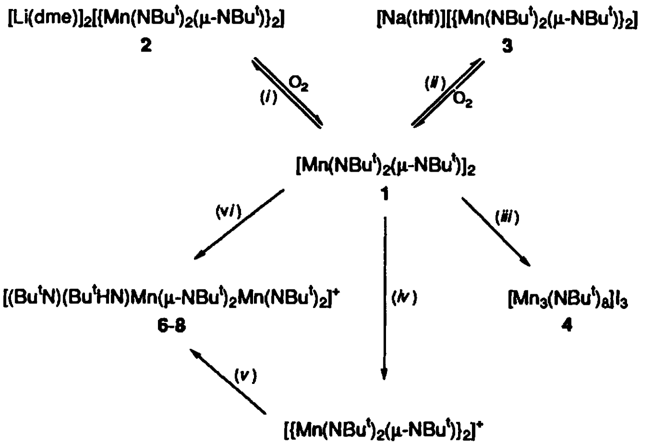
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: G = 10^{-4} T.

Table 1 Analytical and physical data for new compounds

	Compound	Colour	M.p./°C	Analysis (%)[a] C	H	N
2	$[\mathrm{Li(dme)}]_2[\{\mathrm{Mn(NBu^t)_2(\mu\text{-}NBu^t)}\}_2]$	Green	> 240	48.1 (48.3)	8.9 (9.3)	10.1 (10.5)
3	$[\mathrm{Na(thf)}][\{\mathrm{Mn(NBu^t)_2(\mu\text{-}NBu^t)}\}_2]$	Orange-brown	171–173 (decomp.)	52.8 (53.2)	9.5 (9.8)	12.8 (13.3)
4	$[\mathrm{Mn_3(NBu^t)_4(\mu\text{-}NBu^t)_4}]\mathrm{I_3}$	Red	195–197	32.8 (34.5)	6.2 (6.4)	9.8 (10.0)
6	$[\mathrm{Mn_2(NBu^t)_3(\mu\text{-}NBu^t)_2(NHBu^t)}][\mathrm{CF_3SO_3}]$	Red-brown	183–184	46.8 (47.3)	7.6 (8.0)	12.4 (12.4)
7	$[\mathrm{Mn_2(NBu^t)_3(\mu\text{-}NBu^t)_2(NHBu^t)}][\mathrm{B(C_6F_5)_4}]$	Red	172–173	43.7 (43.8)	9.2 (9.2)	13.2 (13.2)
8[b]	$[\mathrm{Mn_2(NBu^t)_3(\mu\text{-}NBu^t)_2(NHBu^t)}]\text{-}[\mathrm{B\{C_6H_3(CF_3)_2\text{-}3,5\}_4}]$	Red				
9[b]	$[\mathrm{Mn_3(\mu\text{-}O)(NBu^t)_4(\mu\text{-}NBu^t)_3}]\text{-}[\mathrm{B\{C_6H_3(CF_3)_2\text{-}3,5\}_4}]$	Red				
11[c]	$[\mathrm{Mn(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)}]_2$	Red-brown	Oil			

[a] For mass spectra see Experimental section. [b] Mixture, see text. [c] Mass spectrum only.



Scheme 1 Principal reactions giving anionic and cationic species. (*i*) Li, dme; (*ii*) Na, thf; (*iii*) $\mathrm{I_2}$, $\mathrm{CH_2Cl_2}$; (*iv*) $\mathrm{AgO_3SCF_3}$, $\mathrm{CH_2Cl_2}$; (*v*) abstraction of H from thf, *etc.*; $\mathrm{CF_3SO_3}^-$ for **6**, $[\mathrm{B(C_6F_5)_4}]^-$ for **7**, $[\mathrm{B\{C_6H_3(CF_3)_2\text{-}3,5\}\}_4}]$ for **8**; (*vi*) $\mathrm{CF_3SO_3H}$, light petroleum

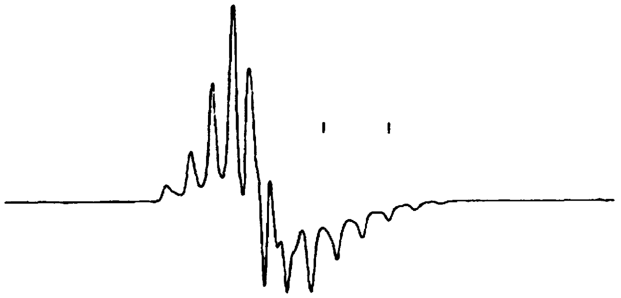


Fig. 1 X-Band EPR spectrum of the manganese(v,vi) dimer $[\mathrm{Na(thf)}][\{\mathrm{Mn(NBu^t)_2(\mu\text{-}NBu^t)}\}_2]$ **3** in toluene at 77 K; scale = 200 G

there are differences in the geometries of the terminal imido bonding. Those at Mn(1) give very similar Mn–N bond lengths, but different Mn–N–C angles, whilst those at Mn(2) give different angles *and* bond lengths. The smaller angles of *ca.* 133° at N(2) and N(6) are clearly linked to the involvement of those atoms in co-ordination to the sodium ion, whilst those at N(3) (160°) and N(5) (148°) are typical of terminal imides. The differences in bond lengths might be correlated with small differences in multiple-bond character ($\mathrm{M{=}N^{\diagup R}}$ *vs.* $\mathrm{Mn{\equiv}N{-}R}$). Such variations have been found in other structures studied.[1,2] It is difficult, however, to decide whether this is an indication of a difference in the oxidation state of the two metal atoms, especially since other features as mentioned above are to the contrary.

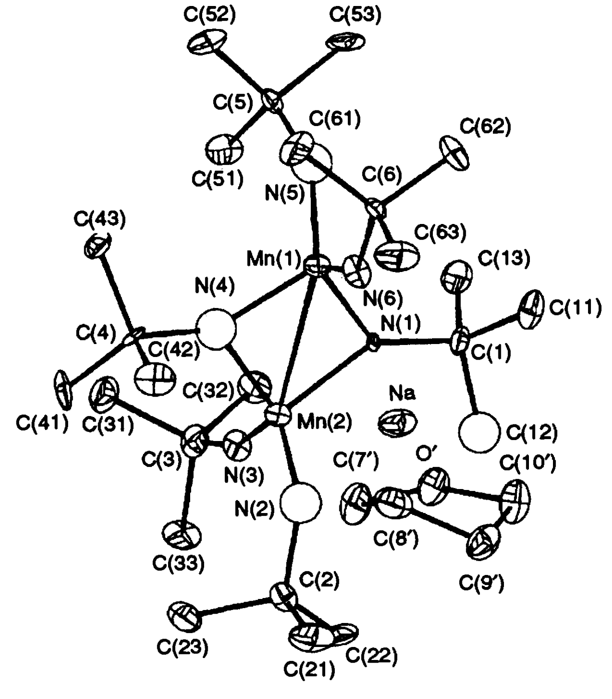


Fig. 2 Structure of the compound $[\mathrm{Na(thf)}][\{\mathrm{Mn(NBu^t)_2(\mu\text{-}NBu^t)}\}_2]$ **3**

The environment around the sodium ion is rather unusual. Short contacts to the thf oxygen (O) and two terminal imido nitrogens [N(2) and N(6)] form a pyramid to one side of the ion. The other side is blocked by a segment of the anion, typified by longer contacts to N(1), Mn(1) and Mn(2). This environment is depicted in Fig. 3, and relevant contact lengths and angles are included in Table 2.

Cationic Species.—On addition of an excess of iodine to compound **1** in $\mathrm{CH_2Cl_2}$, followed by work-up, a trinuclear ion can be isolated as its triiodide, $[\{\mathrm{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2}\}_2\mathrm{Mn}]\mathrm{I_3}$ **4**. Formally, **4** can be considered as having two manganese(VI) centres and one $\mathrm{Mn^V}$; an alternative formulation, $\mathrm{Mn^{VII}}$–$\mathrm{Mn^{IV}}$–$\mathrm{Mn^{VI}}$, seems unlikely as the outer Mn atoms are identical crystallographically.

The molecular structure of compound **4** is shown in Fig. 4; selected bond lengths and angles are given in Table 3. The cation is essentially a linear trimer comprising three edge-shared tetrahedra; the central manganese atom lies on a two-fold axis of symmetry. The imido bridges are strongly unsymmetrical, with Mn–N distances to the outer manganese averaging 1.87 and to the inner 1.77 Å. Similar asymmetry was noted in the $\mathrm{Mn_2N_2}$ ring in the structure of $\mathrm{(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2Mn\text{-}}$

Table 2 Selected bond lengths (Å) and angles (°) for $[\text{Na(thf)}][\{\text{Mn(NBu}^t)_2(\mu\text{-NBu}^t)\}_2]$ **3** with estimated standard deviations (e.s.d.s) in parentheses

Mn(1)–Mn(2)	2.587(2)	N(3)–C(3)	1.454(9)
Mn(1)–N(1)	1.828(6)	N(4)–C(4)	1.485(8)
Mn(1)–N(4)	1.809(5)	N(5)–C(5)	1.418(8)
Mn(1)–N(5)	1.707(6)	N(6)–C(6)	1.457(8)
Mn(1)–N(6)	1.702(6)	Na ··· N(1)	2.826(8)
Mn(2)–N(1)	1.824(5)	Na ··· N(2)	2.355(7)
Mn(2)–N(2)	1.735(5)	Na ··· N(6)	2.410(7)
Mn(2)–N(3)	1.648(6)	Na ··· O′	2.299(6)
Mn(2)–N(4)	1.859(6)	Na ··· Mn(1)	3.044(5)
N(1)–C(1)	1.486(8)	Na ··· Mn(2)	3.053(5)
N(2)–C(2)	1.480(8)		
N(1)–Mn(1)–N(4)	90.1(2)	C(6)–N(6)–Mn(1)	134.4(5)
N(1)–Mn(1)–N(5)	114.6(3)	C(2)–N(2)–Mn(2)	132.6(5)
N(1)–Mn(1)–N(6)	111.6(3)	C(3)–N(3)–Mn(2)	160.0(6)
N(4)–Mn(1)–N(5)	115.2(3)	N(1) ··· Na ··· N(2)	67.3
N(4)–Mn(1)–N(6)	110.5(3)	N(1) ··· Na ··· N(6)	67.2
N(5)–Mn(1)–N(6)	112.8(3)	N(1) ··· Na ··· O′	173.0
N(1)–Mn(2)–N(2)	108.9(3)	N(2) ··· Na ··· N(6)	112.7
N(1)–Mn(2)–N(3)	116.9(3)	N(2) ··· Na ··· O′	117.3
N(1)–Mn(2)–N(4)	88.7(2)	N(6) ··· Na ··· O′	113.7
N(2)–Mn(2)–N(3)	112.5(3)	Mn(1) ··· Na ··· Mn(2)	50.2
N(2)–Mn(2)–N(4)	111.0(3)	Mn(1) ··· Na ··· N(1)	36.0
N(3)–Mn(2)–N(4)	116.5(3)	Mn(1) ··· Na ··· N(2)	83.4
Mn(1)–N(1)–Mn(2)	90.2(2)	Mn(1) ··· Na ··· N(6)	33.9
Mn(1)–N(4)–Mn(2)	89.7(2)	Mn(1) ··· Na ··· O	146.6
C(1)–N(1)–Mn(1)	134.7(5)	Mn(2) ··· Na ··· N(1)	35.9
C(1)–N(1)–Mn(2)	135.0(5)	Mn(2) ··· Na ··· N(2)	34.5
C(4)–N(4)–Mn(1)	133.7(5)	Mn(2) ··· Na ··· N(6)	82.7
C(4)–N(4)–Mn(2)	129.0(5)	Mn(2) ··· Na ··· O	150.0
C(5)–N(5)–Mn(1)	148.1(5)		

Primed atoms are related by the symmetry transformation $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

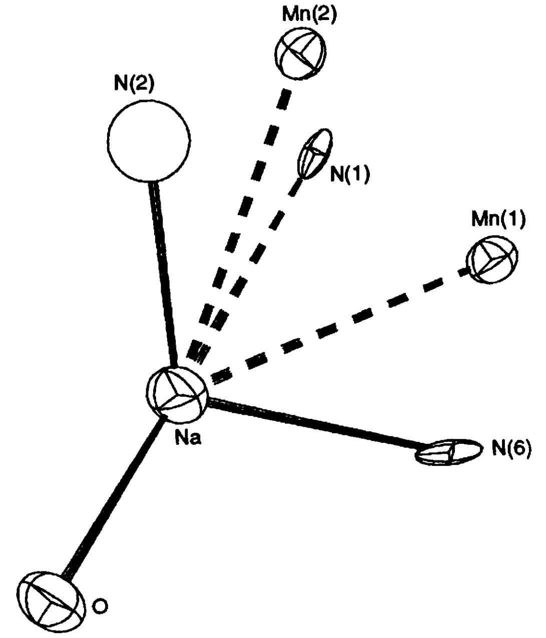


Fig. 3 Diagram of the sodium ion co-ordination of compound **3**

$(\mu\text{-NBu}^t)_2\text{ZnMe}$[2] and we are of the view that the smaller values may be typical for a manganese atom bonded only to bridging imido functions; for the outer manganese atoms N→Mn π bonding will come predominantly from the 6e terminal ligands. In this case the Mn–N distances are not therefore reliable indicators of oxidation states, and discussion of this must rely on spectroscopic data.

Although the VI,V,VI oxidation-state formulation would imply two unpaired electrons, these may be extensively delocalised or coupled, since the ^{1}H NMR spectra are sharp. In thf at room temperature or at 77 K no EPR signal is observed. Analytical samples show a somewhat low carbon content despite the use of a combustion catalyst (WO_3), but the purity of compound **4** can be established by ^{1}H NMR spectroscopy. The *tert*-butylimido resonances at δ 1.26 (terminal) and 1.60 (bridging) are in the usual regions and with a correct ratio. From the $^{13}\text{C-}\{^1\text{H}\}$ NMR spectrum the value $\Delta_{C_\alpha-C_\beta}$[3] is *ca.* 44, only slightly larger than the Δ value[2] for compound **1** possibly due to the positive charge on the cation.

Table 3 Selected bond lengths (Å) and angles (°) for $[\text{Mn}_3(\text{NBu}^t)_4(\mu\text{-NBu}^t)_4]\text{I}_3$ **4** with e.s.d.s in parentheses

Mn(1)–Mn(2)	2.492(1)	Mn(2)–N(4)	1.882(6)
Mn(1)–N(1)	1.756(6)	N(1)–C(1)	1.525(9)
Mn(1)–N(4)	1.780(7)	N(2)–C(2)	1.453(10)
Mn(2)–N(1)	1.861(6)	N(3)–C(3)	1.465(10)
Mn(2)–N(2)	1.641(6)	N(4)–C(4)	1.456(9)
Mn(2)–N(3)	1.621(7)		
Mn(2′)–Mn(1)–Mn(2)	178.2(1)	N(2)–Mn(2)–N(4)	112.3(3)
I(2″)–I(1)–I(2)	178.6(1)	N(3)–Mn(2)–N(4)	113.0(3)
N(1′)–Mn(1)–N(1)	116.0(4)	Mn(1)–N(1)–Mn(2)	87.0(3)
N(1′)–Mn(1)–N(4′)	97.1(3)	Mn(1)–N(4)–Mn(2)	85.7(3)
N(1)–Mn(1)–N(4′)	117.3(3)	C(1)–N(1)–Mn(1)	139.7(6)
N(4′)–Mn(1)–N(4)	113.4(4)	C(1)–N(1)–Mn(2)	133.3(5)
N(1)–Mn(2)–N(2)	110.8(3)	C(4)–N(4)–Mn(1)	138.9(6)
N(1)–Mn(2)–N(3)	114.3(3)	C(4)–N(4)–Mn(2)	135.3(6)
N(1)–Mn(2)–N(4)	90.2(3)	C(2)–N(2)–Mn(2)	159.3(7)
N(2)–Mn(2)–N(3)	114.1(3)	C(3)–N(3)–Mn(2)	172.3(6)

Primed and doubly primed atoms are related by the symmetry transformations $-x + \frac{3}{2}, y, -z + \frac{1}{2}$ and $-x + \frac{1}{2}, y, -z + \frac{1}{2}$.

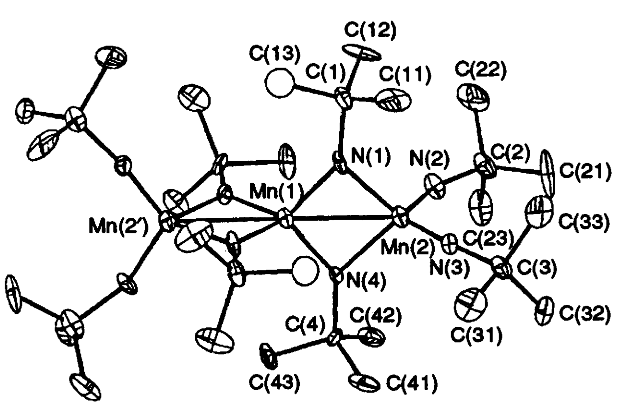


Fig. 4 Structure of the trinuclear cation $[\{\text{Mn(NBu}^t)_2(\mu\text{-NBu}^t)_2\}_2\text{Mn}]^+$ in the triiodide **4**

The mechanism of formation of compound **4** from the dimer is not clear; other products are formed in the reaction but **4** is the only one we have been able to isolate. The formal reduction of one Mn^{VII} to Mn^{V} is accompanied by a change in the NBu^t to Mn ratio, *ca.* 2.6:1 in compound **4** to 3.0:1 in **1**. Reductive de-imidation was found to occur in the reaction of Cl_2 with $\text{CrCl}_2(\text{NBu}^t)_2$ to give $\text{CrCl}_3(\text{NBu}^t)$[4] and similar peculiarities occurred in the reaction of iodine and $\text{Os(NBu}^t)_4$,[5] where Os^{VIII} was converted into two osmium(VI)dinuclear complexes, $(\text{Bu}^t\text{N})_2\text{Os}(\mu\text{-NBu}^t)_2\text{Os(NBu}^t)\text{I}_2$ and $[\{\text{Os(NBu}^t)_2(\mu\text{-NBu}^t)\}_2]^+\text{I}_3^-$.

The interaction of compound **3** with HgCl_2 gives, on work-up, low yields of the manganese compound $[\{\text{Mn(NBu}^t)_2(\mu\text{-NBu}^t)_2\}_2\text{Mn}]_2{}^+[\text{Hg}_2\text{Cl}_6]^{2-}\cdot 2\text{CHCl}_3$ **5a**. The structure (Fig. 5) contains two independent trinuclear cations, which are in fact analogous to that found in compound **4**. Selected bond lengths and angles are given in Table 4. In spite of the difficulties in refining some of those structures, the details of the geometry for the cations in **4** and this compound are reassuringly consistent.

Table 4 Selected bond lengths (Å) and angles (°) for $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2\}_2Mn]_2[Hg_2Cl_6]\cdot 2CHCl_3$, with e.s.d.s in parentheses

$[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2\}_2Mn]^+$ cations

	n = 1	*n* = 2		*n* = 1	*n* = 2
Mn(*n*1)–Mn(*n*2)	2.485(1)	2.488(1)	Mn(*n*3)–N(*n*6)	1.628(5)	1.626(5)
Mn(*n*2)–Mn(*n*3)	2.487(1)	2.481(1)	Mn(*n*3)–N(*n*7)	1.637(5)	1.633(5)
Mn(*n*1)–N(*n*1)	1.864(5)	1.866(5)	Mn(*n*3)–N(*n*8)	1.864(5)	1.858(5)
Mn(*n*1)–N(*n*2)	1.625(6)	1.626(5)	N(*n*1)–C(*n*1)	1.481(7)	1.474(7)
Mn(*n*1)–N(*n*3)	1.633(5)	1.621(5)	N(*n*2)–C(*n*2)	1.443(9)	1.474(8)
Mn(*n*1)–N(*n*4)	1.869(5)	1.860(5)	N(*n*3)–C(*n*3)	1.437(8)	1.453(8)
Mn(*n*2)–N(*n*1)	1.751(5)	1.758(5)	N(*n*4)–C(*n*4)	1.483(7)	1.474(7)
Mn(*n*2)–N(*n*4)	1.751(5)	1.759(5)	N(*n*5)–C(*n*5)	1.472(7)	1.475(7)
Mn(*n*2)–N(*n*5)	1.762(5)	1.758(5)	N(*n*6)–C(*n*6)	1.454(8)	1.451(8)
Mn(*n*2)–N(*n*8)	1.753(5)	1.760(5)	N(*n*7)–C(*n*7)	1.433(8)	1.436(8)
Mn(*n*3)–N(*n*5)	1.871(5)	1.870(5)	N(*n*8)–C(*n*8)	1.486(7)	1.471(7)

$[Hg_2Cl_6]^{2-}$ anion

Hg(1)···Hg(2)	3.75(1)	Hg(1)–Cl(3)	2.591(2)	Hg(2)–Cl(3)	2.611(2)	Hg(2)–Cl(5)	2.426(2)
Hg(1)–Cl(1)	2.396(2)	Hg(1)Cl(6)	2.615(2)	Hg(2)–Cl(4)	2.394(2)	Hg(2)–Cl(6)	2.607(2)
Hg(1)–Cl(2)	2.430(2)						

	n = 1	*n* = 2		*n* = 1	*n* = 2
Mn(*n*1)–Mn(*n*2)–Mn(*n*3)	179.2(1)	177.8(1)	N(*n*7)–Mn(*n*3)–N(*n*8)	113.7(2)	112.9(2)
N(*n*1)–Mn(*n*1)–N(*n*2)	112.9(3)	111.7(2)	Mn(*n*1)–N(*n*1)–Mn(*n*2)	86.8(2)	86.7(2)
N(*n*1)–Mn(*n*1)–N(*n*3)	113.9(2)	114.6(2)	Mn(*n*1)–N(*n*4)–Mn(*n*2)	86.7(2)	86.8(2)
N(*n*1)–Mn(*n*1)–N(*n*4)	89.4(2)	89.7(2)	Mn(*n*2)–N(*n*5)–Mn(*n*3)	86.4(2)	86.2(2)
N(*n*2)–Mn(*n*1)–N(*n*3)	112.9(3)	114.2(3)	Mn(*n*2)–N(*n*8)–Mn(*n*3)	86.8(2)	86.6(2)
N(*n*2)–Mn(*n*1)–N(*n*4)	112.7(2)	112.0(2)	C(*n*1)–N(*n*1)–Mn(*n*1)	134.7(4)	133.5(4)
N(*n*3)–Mn(*n*1)–N(*n*4)	112.9(2)	112.2(2)	C(*n*1)–N(*n*1)–Mn(*n*2)	138.5(4)	139.8(4)
N(*n*1)–Mn(*n*2)–N(*n*4)	97.2(2)	96.8(2)	C(*n*2)–N(*n*2)–Mn(*n*1)	165.0(5)	163.2(5)
N(*n*1)–Mn(*n*2)–N(*n*5)	115.3(2)	115.9(2)	C(*n*3)–N(*n*3)–Mn(*n*1)	163.4(5)	169.0(5)
N(*n*1)–Mn(*n*2)–N(*n*8)	116.3(2)	116.2(2)	C(*n*4)–N(*n*4)–Mn(*n*1)	133.3(4)	133.7(4)
N(*n*4)–Mn(*n*2)–N(*n*5)	116.6(2)	117.6(2)	C(*n*4)–N(*n*4)–Mn(*n*2)	140.0(4)	139.4(4)
N(*n*4)–Mn(*n*2)–N(*n*8)	115.7(2)	114.5(2)	C(*n*5)–N(*n*5)–Mn(*n*2)	140.1(4)	140.7(4)
N(*n*5)–Mn(*n*2)–N(*n*8)	97.1(2)	97.1(2)	C(*n*5)–N(*n*5)–Mn(*n*3)	133.5(4)	133.0(4)
N(*n*5)–Mn(*n*3)–N(*n*6)	112.6(2)	113.6(2)	C(*n*6)–N(*n*6)–Mn(*n*3)	163.7(5)	160.5(5)
N(*n*5)–Mn(*n*3)–N(*n*7)	112.8(2)	113.1(2)	C(*n*7)–N(*n*7)–Mn(*n*3)	163.9(5)	165.0(5)
N(*n*5)–Mn(*n*3)–N(*n*8)	89.7(2)	90.1(2)	C(*n*8)–N(*n*8)–Mn(*n*2)	139.0(4)	138.1(4)
N(*n*6)–Mn(*n*3)–N(*n*7)	113.3(3)	112.6(3)	C(*n*8)–N(*n*8)–Mn(*n*3)	134.2(4)	135.4(4)
N(*n*6)–Mn(*n*3)–N(*n*8)	112.6(2)	112.8(2)			

Cl(1)–Hg(1)–Cl(2)	118.97(7)	Cl(2)–Hg(1)–Cl(6)	114.99(6)	Cl(3)–Hg(2)–Cl(6)	87.78(5)	Cl(5)–Hg(2)–Cl(6)	104.27(6)
Cl(1)–Hg(1)–Cl(3)	119.59(6)	Cl(3)–Hg(1)–Cl(6)	88.02(5)	Cl(4)–Hg(2)–Cl(5)	118.92(7)	Hg(1)–Cl(3)–Hg(2)	92.32(5)
Cl(1)–Hg(1)–Cl(6)	107.04(6)	Cl(3)–Hg(2)–Cl(4)	107.02(6)	Cl(4)–Hg(2)–Cl(6)	120.20(6)	Hg(1)–Cl(6)–Hg(2)	91.88(5)
Cl(2)–Hg(1)–Cl(3)	104.45(6)	Cl(3)–Hg(2)–Cl(5)	114.81(6)				

The terminal imido functions give Mn–N distances in the range 1.621–1.637 Å, inner bridging Mn–N distances of 1.751–1.762 Å, outer bridging distances of 1.858–1.871 Å and Mn–Mn distances of 2.481–2.488 Å.

The geometry of the $[Hg_2Cl_6]^{2-}$ ion [Fig. 7(*a*) and Table 4] is based on a classical bitetrahedron, as found in a number of other structures.*[6] The terminal and bridging Hg–Cl bond lengths are 2.394(2)–2.430(2) and 2.591(2)–2.615(2) Å respectively.

A second species $[\{(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2Mn(NHBu^t)(NBu^t)\}]_2{}^+[Hg_3Cl_8]^{2-}$ **5b** has a cation possessing a Mn(NHBu^t) group. The structure contains two independent dinuclear cations with quite similar geometries. A diagram of one of them is given in Fig. 6; selected bond lengths and angles in Table 5. This structure determination has provided the first full characterisation of the $[Hg_3Cl_8]^{2-}$ ion, Fig. 7(*b*) and Table 5 (the only other recorded structure was incommensurate[7]). The central Hg atom has a distorted, but recognisable tetrahedral $HgCl_4$ geometry, with Hg–Cl distances in the range 2.471(4)–2.497(4) Å and Cl–Hg–Cl angles of 95.2(2)–121.5(2)°. The outer Hg atoms are weakly bonded to the bridging chlorines from the centre [Hg···Cl 2.746(5)–2.859(5) Å], whilst the terminal chlorines are strongly bound [Hg–Cl 2.301(5)–2.339(5) Å] and show an open arrangement [Cl–Hg–Cl 146.2(2), 149.4(2)°], suggestive of a representation $[(Cl_2Hg)(Cl_2HgCl_2)(HgCl_2)]^{2-}$. Interestingly, there are no other contacts to the outer Hg atoms less than 3.85 Å. Details of the cation structure are discussed below, along with those of the analogous species found in compound **7** where the anion is $[B(C_6F_5)_4]^-$.

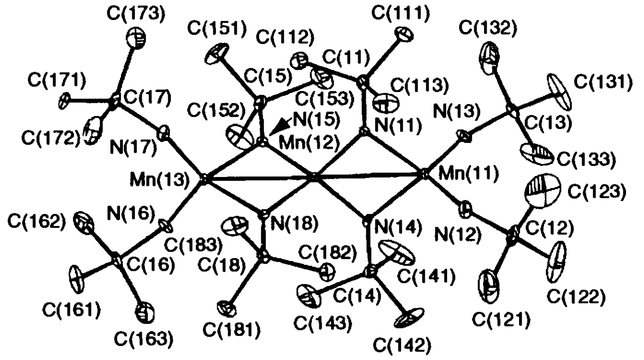


Fig. 5 Structure of one of the trinuclear cations $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)_2\}_2Mn]^+$ in the $[Hg_2Cl_6]^{2-}$ salt **5a**

The oxidation of compound **1** with AgO_3SCF_3 in CH_2Cl_2

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* Cambridge Structural Database System, compound reference codes: BETPAR, BOCDIG, BOCDIG10, COCBUR, DEYMUP, DUCVAY, DUCVAY10, FOCLEO, FTFHGC, FTFHGC10, KASTED, MESFLV, MESFLV01, MESFLV10, NBUPHG, PEYKIP, PIDCIO, SERGOL, VAYHOS, VUWVAK, VUWVEO and YAWNOZ.

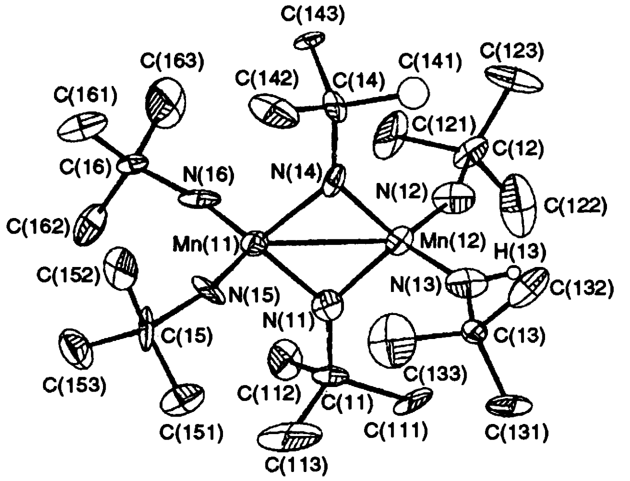


Fig. 6 Structure of one of the dinuclear cations $[(Bu^tN)(Bu^tHN)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]^+$ in the $[Hg_3Cl_8]^{2-}$ salt **5b**, analogous to **7**

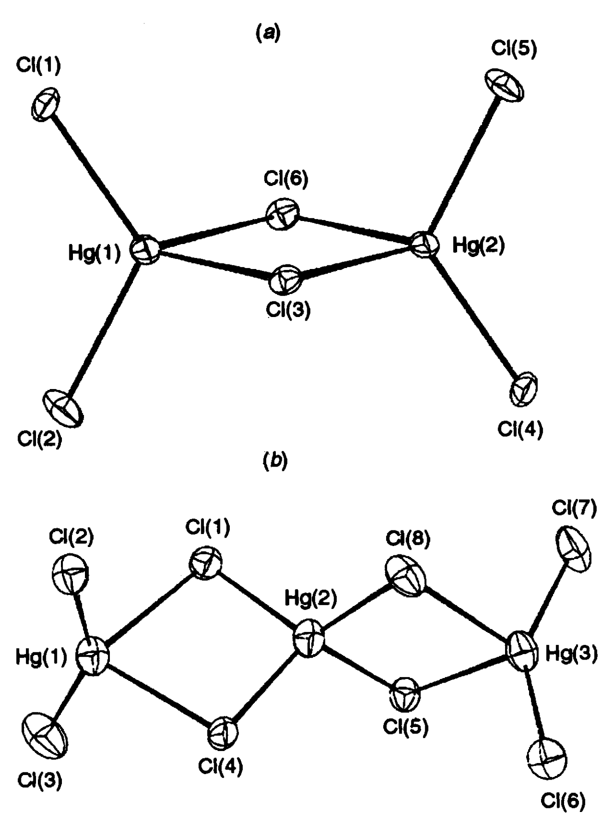


Fig. 7 Structures of (*a*) the $[Hg_2Cl_6]^{2-}$ anion of compound **5a** and (*b*) the $[Hg_3Cl_8]^{2-}$ anion of compound **5b**

Table 5 Selected bond lengths (Å) and angles (°) for the analogous cations of compounds $[(Bu^tN)(Bu^tNH)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]_2[Hg_3Cl_8]$ **5b** and $[(Bu^tN)(Bu^tNH)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]_2[B(C_6F_5)_4]_2$ **7**. The parameters are included for the $[Hg_3Cl_8]^{2-}$ counter anion of compound **5b**, with e.s.d.s in parentheses

	5b		**7**	
	n = 1	*n* = 2	*n* = 1	*n* = 2
Mn(*n*1)–Mn(*n*2)	2.473(4)	2.463(4)	2.490(8)	2.490(8)
Mn(*n*1)–N(*n*1)	1.843(12)	1.809(14)	1.872(7)	1.849(7)
Mn(*n*1)–N(*n*4)	1.799(13)	1.869(14)	1.850(9)	1.857(7)
Mn(*n*1)–N(*n*5)	1.615(14)	1.58(2)	1.621(7)	1.608(8)
Mn(*n*1)–N(*n*6)	1.597(12)	1.63(2)	1.620(7)	1.624(6)
Mn(*n*2)–N(*n*1)	1.724(13)	1.77(2)	1.750(8)	1.758(7)
Mn(*n*2)–N(*n*2)	1.554(13)	1.66(2)	1.674(7)	1.668(7)
Mn(*n*2)–N(*n*3)	1.779(12)	1.724(13)	1.720(7)	1.712(8)
Mn(*n*2)–N(*n*4)	1.739(12)	1.722(12)	1.759(6)	1.755(6)
N(*n*1)–C(*n*1)	1.52(2)	1.50(2)	1.466(8)	1.477(8)
N(*n*2)–C(*n*2)	1.48(2)	1.45(2)	1.442(9)	1.451(9)
N(*n*3)–C(*n*3)	1.50(2)	1.50(2)	1.463(9)	1.451(9)
N(*n*4)–C(*n*4)	1.54(2)	1.48(2)	1.461(8)	1.467(9)
N(*n*5)–C(*n*5)	1.41(2)	1.54(2)	1.459(8)	1.473(9)
N(*n*6)–C(*n*6)	1.47(2)	1.47(2)	1.449(8)	1.441(8)

Hg(1) ··· Hg(2)	3.78(1)	Hg(2)–Cl(4)	2.496(5)
Hg(2) ··· Hg(3)	3.72(1)	Hg(2)–Cl(5)	2.497(4)
Hg(1)–Cl(1)	2.859(5)	Hg(2)–Cl(8)	2.476(5)
Hg(1)–Cl(2)	2.311(5)	Hg(3)–Cl(5)	2.780(4)
Hg(1)–Cl(3)	2.301(5)	Hg(3)–Cl(6)	2.339(5)
Hg(1)–Cl(4)	2.808(4)	Hg(3)–Cl(7)	2.305(5)
Hg(2)–Cl(1)	2.471(4)	Hg(3)–Cl(8)	2.746(5)

	5b		**7**	
	n = 1	*n* = 2	*n* = 1	*n* = 2
N(*n*1)–Mn(*n*1)–N(*n*4)	88.7(6)	90.1(6)	89.4(3)	89.6(3)
N(*n*1)–Mn(*n*1)–N(*n*5)	112.9(5)	109.7(6)	113.6(3)	114.4(3)
N(*n*1)–Mn(*n*1)–N(*n*6)	112.5(6)	112.4(6)	113.6(3)	111.9(3)
N(*n*4)–Mn(*n*1)–N(*n*5)	114.1(6)	114.2(6)	111.9(3)	112.8(3)
N(*n*4)–Mn(*n*1)–N(*n*6)	112.7(6)	112.7(6)	113.1(3)	113.6(3)
N(*n*5)–Mn(*n*1)–N(*n*6)	113.6(8)	115.1(8)	113.1(3)	112.7(3)
N(*n*1)–Mn(*n*2)–N(*n*2)	115.1(6)	113.6(7)	114.1(3)	114.8(3)
N(*n*1)–Mn(*n*2)–N(*n*3)	115.7(5)	114.9(6)	114.2(3)	113.9(4)
N(*n*1)–Mn(*n*2)–N(*n*4)	94.6(6)	96.4(7)	96.5(3)	96.0(3)
N(*n*2)–Mn(*n*2)–N(*n*3)	103.2(7)	104.0(8)	104.3(4)	103.4(4)
N(*n*2)–Mn(*n*2)–N(*n*4)	113.7(5)	114.5(6)	114.1(3)	114.2(3)
N(*n*3)–Mn(*n*2)–N(*n*4)	115.2(5)	113.9(6)	114.1(3)	115.1(3)
Mn(*n*2)–N(*n*1)–Mn(*n*1)	87.7(5)	86.9(6)	86.8(3)	87.3(3)
Mn(*n*2)–N(*n*4)–Mn(*n*1)	88.7(5)	86.5(6)	87.2(3)	87.1(3)
C(*n*1)–N(*n*1)–Mn(*n*1)	132.0(11)	138.8(13)	133.5(4)	134.9(4)
C(*n*1)–N(*n*1)–Mn(*n*2)	139.8(11)	134.2(13)	139.6(4)	137.7(4)
C(*n*2)–N(*n*2)–Mn(*n*2)	160.3(12)	157(2)	157.1(5)	158.2(5)
C(*n*3)–N(*n*3)–Mn(*n*2)	132.3(12)	142.3(14)	146.5(5)	146.9(6)
C(*n*4)–N(*n*4)–Mn(*n*2)	133.1(11)	138.7(12)	139.1(4)	137.0(4)
C(*n*4)–N(*n*4)–Mn(*n*1)	135.9(11)	134.3(11)	133.0(4)	134.6(4)
C(*n*5)–N(*n*5)–Mn(*n*1)	169.1(13)	166.1(14)	165.5(5)	164.8(4)
C(*n*6)–N(*n*6)–Mn(*n*1)	160.4(13)	162.7(13)	165.3(4)	166.0(4)

Cl(1)–Hg(1)–Cl(2)	96.6(2)	Cl(5)–Hg(2)–Cl(8)	95.2(2)
Cl(1)–Hg(1)–Cl(3)	105.7(2)	Cl(5)–Hg(3)–Cl(6)	105.1(2)
Cl(1)–Hg(1)–Cl(4)	81.95(13)	Cl(5)–Hg(3)–Cl(7)	100.74(14)
Cl(2)–Hg(1)–Cl(3)	149.4(2)	Cl(5)–Hg(3)–Cl(8)	83.27(13)
Cl(2)–Hg(1)–Cl(4)	100.9(2)	Cl(6)–Hg(3)–Cl(7)	146.2(2)
Cl(3)–Hg(1)–Cl(4)	102.6(2)	Cl(6)–Hg(3)–Cl(8)	105.7(2)
Cl(1)–Hg(2)–Cl(4)	96.85(14)	Cl(7)–Hg(3)–Cl(8)	98.7(2)
Cl(1)–Hg(2)–Cl(5)	114.83(13)	Hg(1)–Cl(1)–Hg(2)	90.12(14)
Cl(1)–Hg(2)–Cl(8)	121.5(2)	Hg(1)–Cl(4)–Hg(2)	90.78(14)
Cl(4)–Hg(2)–Cl(5)	114.0(2)	Hg(2)–Cl(5)–Hg(3)	89.55(12)
Cl(4)–Hg(2)–Cl(8)	115.9(2)	Hg(2)–Cl(8)–Hg(3)	90.8(2)

gives a precipitate of silver and the solution contains a paramagnetic species the X-band EPR spectrum of which at 293 K is a triplet with $g = 2.00$, $\alpha_N = 15$ G. This species, which thus evidently has the unpaired electron located on one N atom, is quite long lived (hours) in CH_2Cl_2. It cannot be detected in non-chlorinated solvents and is very reactive toward solvents from which hydrogen can be abstracted. A study of the interaction of **1** with an excess of AgO_3SCF_3 in CH_2Cl_2 was possible by ^1H NMR spectroscopy only in the initial stages when bulk paramagnetism had not developed. Signals assigned to the terminal *tert*-butylimido groups of **1** showed broadening that could be due to interaction of the electrophilic Ag^+ ion with lone pairs localised on the terminal N atoms or in Mn≡N bonds. The μ-NBu^t peaks in the ^1H NMR spectrum are unaffected at this stage but after 6–8 h the solution paramagnetism wipes out all the signals. It is interesting that the interaction of the rhenium analogue of **1**, *i.e.* $Re_2(NBu^t)_6$,[8] with AgO_3SCF_3 under the same conditions gives a silver-containing species, $[AgRe_2(NBu^t)_2(\mu\text{-}NBu^t)_4]^+$, characterised by X-ray diffraction,[9] which can be described as having $AgRe_2$ triangular moieties with two NBu^t groups bridging Re atoms and one

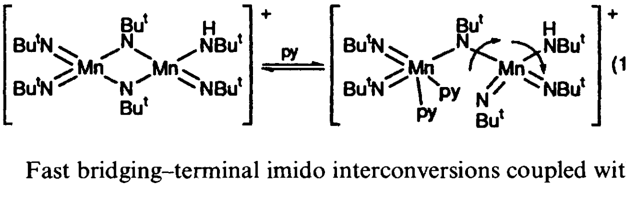
NBu^t group bridging each Ag–Re and with each Re retaining one terminal NBu^t group. In the case of Mn the NAg$^+$ species are clearly unstable undergoing electron transfer to form the radical cation.

The addition to the triflate solution in CH_2Cl_2 of $Li[B(C_6F_5)_4]$, which is reported[10] to contain 'active hydrogen' (we have confirmed that the IR spectrum of the solid shows typical OH stretching bands), allowed the isolation of red crystals of compound **7**. The IR and ^1H NMR spectra clearly indicated the presence of the amido, Bu^{t}NH, group,[11] 3340 cm^{-1} and δ *ca.* 9.6, the position of the latter varying slightly depending on the anion. Of equal significance was the ^1H NMR spectrum in the NBu^t region where five discrete lines in a ratio 2 : 1 : 1 : 1 : 1 were observed. One of these bands in the upfield region could be attributed to NHBu^t, while the band of relative intensity 2 at δ 1.75 can be assigned to bridging μ-NBu^t groups. The lowering of the molecular symmetry from a $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ dimer to $[(Bu^tN)(Bu^tHN)Mn(\mu\text{-}NBu^t)_2Mn(NBu^t)_2]^+$ should give rise to a five-line pattern as observed. This asymmetry was confirmed by the X-ray data for the $[B(C_6F_5)_4]^-$ salt and by consideration of the Mn–N bond lengths.

The hydride transfer to the N atom of the radical cation in the CH_2Cl_2 solution to give the amido species required that protonation of compound **1** should give the same cation. Careful reaction of **1** with CF_3SO_3H in stoichiometric amounts in light petroleum gave the triflate salt of the cation, with identical IR and NMR spectra to those of the other salts. It may be noted too that the triflate salt **6** can also be obtained directly by interaction of **1** and AgO_3SCF_3 in thf from which H is abstracted.

Bond lengths and angles for the structure of compound **7** are given in Table 5. As mentioned above, the structure of the cation, of which there are two in the asymmetric unit, is analogous to that found in compound **5b**. Again, the geometry parameters show good consistency over the four species. The two manganese atoms are clearly different and the positions of the amide ligand is well defined at N(13) and N(23) in both compounds **5b** and **7**. The terminal imide ligands give Mn–N distances in the range 1.554(13)–1.674(7) Å. The imido bridges are unsymmetrical, with the distances to the manganese atoms carrying the amides [Mn(12), Mn(22)] in both **5b** and **7** shorter [1.724(13)–1.77(2) Å] than those to the manganese atoms bonded to two terminal imides [1.799(14)–1.872(7) Å]. The Mn–Mn distances lie in the range 2.463(8)–2.490(8) Å.

A variable-temperature NMR study of the triflate **6** in chlorinated solvents between −20 and −30 °C shows broadening of the band at δ 0.85 assigned to the NHBu^t group. The rest of the spectrum does not change from +60 ($CDCl_3$) to −90 °C (CD_2Cl_2). The broadening is probably due to slowing of the rotation of the amide group about the Mn–N axis.[12] The spectrum of **6** in $[^2H_5]$pyridine at room temperature (*ca.* 22 °C) shows broadened peaks at δ 1.20 and 1.11 superimposed on a broad peak centred at δ 0.90 and a sharp one at δ 1.75. The latter peak is unchanged within the range +50 to −40 °C. The band at δ 0.90 separates initially into a broad peak at δ 0.85 at *ca.* 0 °C which in turn splits into two bands at *ca.* 20 °C. Meanwhile the peaks at δ 1.20 and 1.11 collapse to a broad peak at *ca.* −20 °C. The amido peak sharpens above +40 °C. Although the dynamic changes in pyridine solutions of the cation are not fully understood, a plausible picture involves rotation around the Mn–N(H)Bu^t bond similar to that observed in chlorinated solvents, in addition to a bridge-breaking formation process as shown in equation (1).



(1)

Fast bridging–terminal imido interconversions coupled with dissociation–association of pyridine (py) and rotation around the Mn–N bonds could explain the broadness of bridging and terminal imide groups associated with the manganese atom having the NHBu^t groups. Similar behaviour is observed in chlorinated solvents after addition of 2,2′-bipyridine. No products could be isolated from the solutions, however. When the reaction of compound **1** and AgO_3SCF_3 is carried out in $MeNO_2$ only intractable products are formed. However, in MeCN as solvent the only product that could be isolated, although in low yield, is the triflate salt[1] of $[Mn(NBu^t)_3(NH_2Bu^t)]^+$. In this case an intermediate similar to the one proposed for pyridine, followed by abstraction of H from MeCN *via* a radical or polar mechanism, could lead to the observed product.

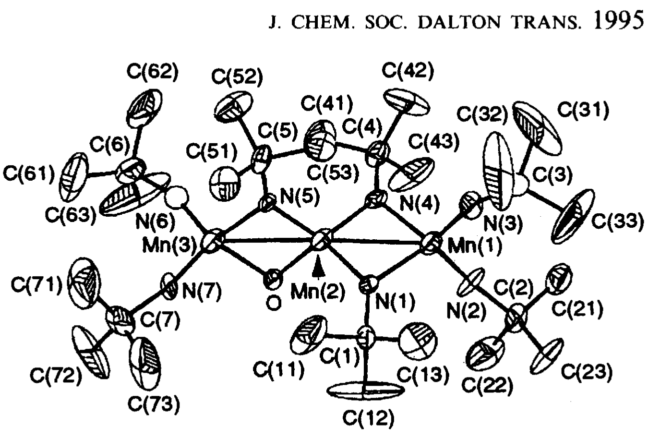
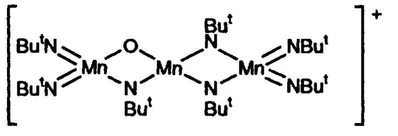


Fig. 8 Structure of the trinuclear cation $[Mn_3(\mu\text{-}O)(\mu\text{-}NBu^t)_3(NBu^t)_4]^+$ of compound **9** in the $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ salt



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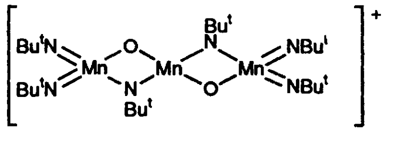

II

The interaction of compound **1** and AgO_3SCF_3 in CH_2Cl_2 with addition of $Na[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$[13] and work-up gave a mixture of the $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ salt **8** of the amido cation discussed above and the salt **9** of a new cation the structure of which was determined by X-ray crystallography and found to be a trinuclear compound similar to **4** but with a single oxo-bridge as in diagram **I**.

It is not clear where the oxygen came from since direct interaction of O_2 with the solution from the interaction of compound **1** with AgO_3SCF_3 in CH_2Cl_2 gives a different product (see below). Although **8** and **9** cannot be separated by fractional crystallisation from, *e.g.* Et_2O or toluene, due to similar solubility properties, an assignment of the mixture is possible since **8** gives five peaks in the ^1H NMR spectrum with a 2 : 1 : 1 : 1 : 1 ratio at the same chemical shift as the peaks of **6** or **7**. The remaining peaks can be assigned to **9**. The crystal structure of **9** was determined on a hand-picked crystal, Fig. 8; bond lengths and angles are given in Table 6. The presence of the one oxo bridge has very little effect on the geometry parameters, which are very similar to those in the trinuclear compounds **4** and **5a**, except that the Mn–O distances are slightly larger than the analogous Mn–N distances, suggesting less O→Mn π bonding here.

The interaction of the radical cation $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2^+$ made *in situ* in CH_2Cl_2 from compound **1** and AgO_3SCF_3 with

Table 6 Selected bond lengths (Å) and angles (°) for $[\mathrm{Mn_3(\mu\text{-}O)(NBu^t)_4(\mu\text{-}NBu^t)_3}][\mathrm{B\{C_6H_3(CF_3)_2\text{-}3,5\}_4}]\cdot\mathrm{C_6H_5Me}$ **9**, with e.s.d.s in parentheses

Mn(1)–Mn(2)	2.485(3)	Mn(3)–N(5)	1.836(9)
Mn(2)–Mn(3)	2.458(3)	Mn(3)–N(6)	1.621(11)
Mn(1)–N(1)	1.866(7)	Mn(3)–N(7)	1.661(8)
Mn(1)–N(2)	1.571(10)	N(1)–C(1)	1.489(12)
Mn(1)–N(3)	1.679(10)	N(2)–C(2)	1.474(14)
Mn(1)–N(4)	1.865(9)	N(3)–C(3)	1.360(14)
Mn(2)–O	1.777(7)	N(4)–C(4)	1.424(12)
Mn(2)–N(1)	1.732(9)	N(5)–C(5)	1.522(14)
Mn(2)–N(4)	1.761(8)	N(6)–C(6)	1.43(2)
Mn(2)–N(5)	1.728(9)	N(7)–C(7)	1.409(13)
Mn(3)–O	1.848(7)		
Mn(1)–Mn(2)–Mn(3)	176.8(1)	N(6)–Mn(3)–O	111.7(4)
N(1)–Mn(1)–N(2)	113.9(5)	N(7)–Mn(3)–O	112.9(4)
N(1)–Mn(1)–N(3)	113.2(4)	Mn(1)–N(1)–Mn(2)	87.3(4)
N(1)–Mn(1)–N(4)	89.2(4)	Mn(1)–N(4)–Mn(2)	86.4(4)
N(2)–Mn(1)–N(3)	111.3(5)	Mn(2)–O–Mn(3)	85.4(3)
N(2)–Mn(1)–N(4)	113.5(4)	Mn(2)–N(5)–Mn(3)	87.2(4)
N(3)–Mn(1)–N(4)	114.1(5)	C(1)–N(1)–Mn(1)	133.4(7)
N(1)–Mn(2)–N(4)	97.1(4)	C(1)–N(1)–Mn(2)	139.0(7)
N(1)–Mn(2)–N(5)	117.9(4)	C(2)–N(2)–Mn(1)	169.8(9)
N(4)–Mn(2)–N(5)	118.6(4)	C(3)–N(3)–Mn(1)	162.4(10)
N(1)–Mn(2)–O	113.1(4)	C(4)–N(4)–Mn(1)	136.8(7)
N(4)–Mn(2)–O	114.6(4)	C(4)–N(4)–Mn(2)	136.8(8)
N(5)–Mn(2)–O	96.8(4)	C(5)–N(5)–Mn(2)	140.1(7)
N(5)–Mn(3)–N(6)	112.3(5)	C(5)–N(5)–Mn(3)	132.8(7)
N(5)–Mn(3)–N(7)	113.5(4)	C(6)–N(6)–Mn(3)	163.2(8)
N(6)–Mn(3)–N(7)	113.6(4)	C(7)–N(7)–Mn(3)	162.9(9)
N(5)–Mn(3)–O	90.7(4)		

Table 7 Selected bond lengths (Å) and angles (°) for $[\{[\mathrm{(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2}]_2\mathrm{Mn}\}_{0.5}\{[\mathrm{(Bu^tN)_2Mn(\mu\text{-}O)(\mu\text{-}NBu^t)}]_2\mathrm{Mn}\}_{0.5}][\mathrm{CF_3SO_3}]$ **10**, with e.s.d.s in parentheses

Mn(1)–Mn(2)	2.460(1)	Mn(3)–O(2)	1.849(4)
Mn(2)–Mn(3)	2.457(1)	Mn(3)–N(4)	1.870(4)
Mn(1)–O(1)	1.848(4)	Mn(3)–N(5)	1.621(4)
Mn(1)–N(1)	1.631(4)	Mn(3)–N(6)	1.634(4)
Mn(1)–N(2)	1.621(4)	N(1)–C(1)	1.437(7)
Mn(1)–N(3)	1.858(4)	N(2)–C(2)	1.417(6)
Mn(2)–O(1)	1.747(4)	N(3)–C(3)	1.479(6)
Mn(2)–O(2)	1.748(4)	N(4)–C(4)	1.480(6)
Mn(2)–N(3)	1.737(4)	N(5)–C(5)	1.436(7)
Mn(2)–N(4)	1.734(4)	N(6)–C(6)	1.444(6)
Mn(1)–Mn(2)–Mn(3)	177.4(1)	N(5)–Mn(3)–O(2)	115.1(2)
N(1)–Mn(1)–O(1)	112.8(2)	N(5)–Mn(3)–N(6)	114.0(2)
N(1)–Mn(1)–N(2)	113.9(2)	N(6)–Mn(3)–O(2)	110.8(2)
N(1)–Mn(1)–N(3)	112.3(2)	Mn(1)–O(1)–Mn(2)	86.3(2)
N(2)–Mn(1)–O(1)	114.0(2)	Mn(1)–N(3)–Mn(2)	86.3(2)
N(2)–Mn(1)–N(3)	111.7(2)	Mn(2)–O(2)–Mn(3)	86.1(2)
N(3)–Mn(1)–O(1)	89.9(2)	Mn(2)–N(4)–Mn(3)	85.9(2)
N(3)–Mn(2)–O(1)	97.4(2)	C(1)–N(1)–Mn(1)	159.0(4)
N(3)–Mn(2)–O(2)	116.4(2)	C(2)–N(2)–Mn(1)	173.6(4)
N(3)–Mn(2)–N(4)	115.4(2)	C(3)–N(3)–Mn(1)	135.0(3)
N(4)–Mn(2)–O(1)	116.4(2)	C(3)–N(3)–Mn(2)	138.7(4)
N(4)–Mn(2)–O(2)	97.9(2)	C(4)–N(4)–Mn(2)	140.5(3)
O(1)–Mn(2)–O(2)	114.5(2)	C(4)–N(4)–Mn(3)	133.5(3)
N(4)–Mn(3)–O(2)	89.8(2)	C(5)–N(5)–Mn(3)	177.1(4)
N(4)–Mn(3)–N(5)	111.8(2)	C(6)–N(6)–Mn(3)	154.1(4)
N(4)–Mn(3)–N(6)	113.0(2)		

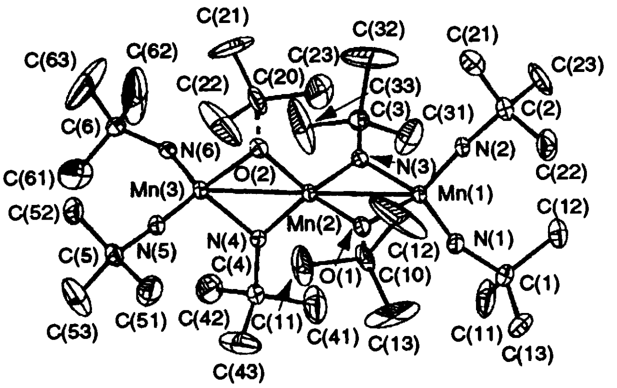

Fig. 9 Structure of the disordered trinuclear cation of the mixed compound **10** $[\{[\mathrm{(Bu^tN)_2Mn(\mu\text{-}NBu^t)_2}]_2\mathrm{Mn}\}_{0.5}\{[\mathrm{(Bu^tN)_2Mn(\mu\text{-}O)(\mu\text{-}NBu^t)}]_2\mathrm{Mn}\}_{0.5}]^+$ as the $\mathrm{CF_3SO_3}^-$ salt

an excess of dry oxygen for 24 h leads, on work-up, to crystals from toluene that consist of a trinuclear compound similar to **4** according to ^{1}H NMR spectra together with another compound as shown in diagram **II**. Repeated attempts at crystallisation from the same solvent under carefully controlled conditions did not alter the molar ratios (*ca.* 1 : 1) of the two components. The difference from the mixture of **8** and **9** is that in this case the two trinuclear compounds cocrystallise giving rise to disorder whereas crystals of **8** and **9** can be physically separated.

The ^{1}H NMR spectrum has signals at the same chemical shift as those of compound **4** (δ 1.27, 1.60, 1 : 1) and there are three additional peaks in 1 : 1 : 1 ratio at δ 1.63, 1.59 and 1.16 which can be assigned to the μ-oxo trimanganese cation in the mixture **10** shown in diagram **II**. The crystal structure of the mixed crystal is shown in Fig. 9; selected bond lengths and angles are in Table 7. Packing disorder occurs so that at each 'oxygen' site mixing of oxide and imide occurs. We interpret the disorder in terms of the occupancy of two sites related by a centre of inversion by an imide function on one molecule and an oxide function on the other and mixing of these. This disorder occurs at two centres of inversion in the unit cell, at 0,0,0 and 0.5,0,0. The other two bridging sites are occupied only by imide groups. Within the limits of experimental error, the geometry parameters are comparable with those in the other trinuclear compounds.

Finally, as noted previously,[1] the decomposition of $\mathrm{Mn(NBu^t)_3[OCH(CF_3)_2]}$ gives $\mathrm{(CF_3)_2CO}$ and the amido dimer $[\mathrm{Mn(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)}]_2$ **11**. Since the IR spectrum shows two NH stretches the compound is most likely a *cis* + *trans* mixture.

Experimental

Analyses were by the Imperial College Microanalytical Laboratory. The general techniques and starting materials were as previously described.[1,2] Infrared spectra were recorded in Nujol mulls and NMR spectra in $\mathrm{C_6D_6}$ referenced to $\mathrm{SiMe_4}$ on a JEOL-ES-270 spectrometer unless otherwise stated. Commercial chemicals were from Aldrich, Jannsen and Avocado Chemicals. The light petroleum used throughout had b.p. 40–60 °C. All solvents were purified by standard methods and degassed before use. All manipulations were carried out under purified Ar or N_2 using a Vacuum Atmospheres dry-box, or in vacuum.

Bis[(1,2-*dimethoxyethane*)*lithium*] *Bis*[(μ-tert-*butylimido*)*di*(tert-*butylimido*)*manganate*(V)] **2**.—To a suspension of lithium powder (0.08 g, 1.2 mmol) in dme (30 cm^3) was added at 0 °C a solution of compound **1** (0.3 g, 0.56 mmol) in dme (20 cm^3) and the mixture stirred at room temperature (12 h). During the first 0.5 h the colour changed from brown to bluish green then finally after *ca.* 1 h to green when the solvent was removed in vacuum. Extraction of the residue with light petroleum (2 × 20 cm^3), filtration and concentration to *ca.* 2 cm^3 with cooling (−20 °C) gave green-brown, extremely air-sensitive crystals. Yield: 0.16 g, *ca.* 40%. IR: 1195 cm^{-1} ($\mathrm{Mn{=}NBu^t}$). ^{1}H NMR: δ 3.2 and 2.9 (br, 8 H and 12 H, dme protons), 1.68 [s, br, 18 H, $\mu\text{-}\mathrm{NC(CH_3)_3}$] and 1.32 [s, br, 36 H, terminal $\mathrm{NC(CH_3)_3}$].

Table 8 Details of data collection and refinement for compounds **3**, **4**, **5a**, **5b**, **7**, **9** and **10**

	3	**4**	**5a**	**5b**	**7**	**9**	**10**
Formula	$C_{28}H_{62}Mn_2N_6NaO$	$C_{32}H_{72}I_3Mn_3N_8$	$C_{66}H_{146}Cl_{12}Hg_2Mn_6N_{16}$	$C_{48}H_{110}Cl_8Hg_3Mn_4N_{14}$	$C_{96}H_{110}B_2F_{40}Mn_4N_{12}$	$C_{67}H_{83}BF_{24}Mn_3N_7O$	$C_{29}H_{63}F_3Mn_3N_7O_4S$
M_r	631.71	557.25	2320.23	1960.61	2433.34	1634.03	827.74
T/K	120	120	120	150	140	200	150
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2/n$	$P2_1/a$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	10.825(2)	14.840(2)	19.559(5)	10.622(3)	11.29(4)	19.559(5)	11.073(4)
b/Å	11.808(2)	9.375(3)	18.276(1)	18.149(9)	22.27(5)	17.944(4)	13.298(7)
c/Å	27.32(2)	17.168(6)	27.688(6)	39.780(4)	23.02(9)	23.843(2)	15.862(2)
α/°	90	90	90	90	72.3(2)	90	109.54(1)
β/°	90	103.66(2)	96.915(6)	92.52(2)	82.6(2)	109.42(2)	99.79(3)
γ/°	90	90	90	90	79.9(2)	90	99.77(1)
U/Å^3	3492(3)	2321(1)	9825(3)	7661	5410	7892	2104
Z	4	2	4	4	2	4	2
D_c/g cm^{-3}	1.202	1.595	1.569	1.700	1.494	1.375	1.307
F(000)	1364	1108	4672	3832	2480	3352	872
μ(Mo-Kα)/mm^{-1}	0.764	2.828	4.200	6.942	0.575	0.550	0.949
Crystal size/mm	0.18 × 0.18 × 0.07	0.2 × 0.2 × 0.08	0.5 × 0.25 × 0.2	0.18 × 0.09 × 0.03	0.68 × 0.64 × 0.10	0.47 × 0.05 × 0.05	0.33 × 0.18 × 0.12
θ Range for data/°	1.88–25.12	2.17–24.94	1.85–25.08	1.90–25.11	1.84–24.97	1.81–25.13	1.92–25.25
hkl Ranges	−8 to 11, −13 to 12, −27 to 29	−15 to 16, −7 to 10, −20 to 19	−21 to 16, −20 to 20, −30 to 30	−11 to 7, −20 to 20, −27 to 46	−13 to 13, −24 to 12, −26 to 26	−17 to 23, −19 to 20, −27 to 28	−7 to 12, −15 to 15, −18 to 17
Reflections collected	14 127	8492	38 205	18 393	16 065	26 162	8225
Independent reflections	5267	3434	14 130	10 075	13 989	11 143	5762
R_{int}	0.1092	0.0856	0.0635	0.0893	0.0443	0.1257	0.0579
Data, restraints, parameters	5265, 0, 376	3431, 0, 225	14 130, 0, 965	10 073, 0, 712	13 986, 0, 1327	11 141, 45, 900	5760, 0, 480
Maximum, minimum absorption correction factors	1.182, 0.759	1.072, 0.691	1.421, 0.891	1.158, 0.850	1.123, 0.631	—	1.080, 0.909
Maximum peak and hole/e Å^{-3}	0.632, −0.658	0.627, −0.485	4.538, −0.905	1.070, −0.873	0.750, −0.391	0.418, −0.247	0.566, −0.327
Goodness of fit on F^2	0.644	0.516	0.954	0.612	0.578	0.592	0.882
$R1$	0.0473	0.0357	0.0474	0.0474	0.0571	0.0658	0.0473
wR^2 (all data)	0.1044	0.0718	0.1156	0.1059	0.2067	0.1403	0.1175

Goodness of fit = $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n = number of reflections and p = total number of parameters; $R1 = \Sigma|F_o - F_c|/\Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (gP)^2]$. Weighting parameters, g, were 0.0000 for compounds **3**, **4**, **5b** and **7** and 0.0612, 0.0206 and 0.0508 for **5a**, **9** and **10** respectively; $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 9 Fractional atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Mn(1)	7 825(1)	1 266(1)	1 381(1)
Mn(2)	7 711(1)	−861(1)	1 158(1)
O	2 096(5)	4 290(5)	1 950(2)
Na	8 241(3)	−349(3)	2 234(1)
N(1)	8 957(4)	151(5)	1 262(3)
N(2)	7 573(5)	−1 726(4)	1 669(2)
N(3)	7 754(6)	−1 586(5)	643(2)
N(4)	6 595(5)	333(5)	1 186(3)
N(5)	8 012(6)	2 458(5)	1 035(2)
N(6)	7 701(6)	1 549(5)	1 990(2)
C(1)	10 327(6)	108(7)	1 233(3)
C(2)	7 371(7)	−2 958(6)	1 727(3)
C(3)	7 735(8)	−1 832(7)	122(3)
C(4)	5 242(6)	304(7)	1 276(3)
C(5)	7 874(7)	2 997(6)	575(3)
C(6)	7 551(6)	2 579(6)	2 278(3)
C(7)	3 422(7)	4 173(9)	1 826(3)
C(8)	3 495(8)	4 506(7)	1 299(4)
C(9)	2 270(7)	4 065(7)	1 099(3)
C(10)	1 367(7)	4 331(9)	1 499(3)
C(11)	10 862(6)	776(8)	1 664(3)
C(12)	10 745(6)	−1 131(6)	1 230(3)
C(13)	10 769(6)	674(8)	753(3)
C(21)	7 179(8)	−3 178(6)	2 268(3)
C(22)	8 528(6)	−3 598(7)	1 540(3)
C(23)	6 197(6)	−3 379(6)	1 442(3)
C(31)	6 570(7)	−1 315(8)	−113(3)
C(32)	8 897(6)	−1 284(7)	−127(3)
C(33)	7 732(8)	−3 112(6)	65(8)
C(41)	4 627(6)	−605(7)	950(3)
C(42)	4 969(7)	64(7)	1 815(3)
C(43)	4 715(6)	1 464(6)	1 144(3)
C(51)	7 698(8)	2 108(6)	177(3)
C(52)	6 800(7)	3 818(7)	579(3)
C(53)	9 047(6)	3 719(7)	485(3)
C(61)	6 452(7)	3 304(7)	2 106(3)
C(62)	8 754(6)	3 280(7)	2 247(3)
C(63)	7 291(8)	2 257(6)	2 817(3)

(Tetrahydrofuran)sodium Bis[(μ-tert-*butylimido*)*di*(tert-*butylimido*)*manganate*(V, VI)] **3**.—To $MnCl(NBu^t)_3$ (0.61 g, 2 mmol) in thf (40 cm^3) was added at 0 °C sodium amalgam (4.2 mmol, 1.7 cm^3 of 0.42% w/w) and the mixture shaken vigorously (8 h). The solution was removed from the mercury *via* a cannula and evaporated in vacuum. Extraction of the green-brown residue with light petroleum (2 × 20 cm^3), filtration, concentration to *ca.* 3 cm^3, and cooling (−20 °C) gave orange-brown plates of X-ray quality. Evaporation of the petroleum extract left a microcrystalline material which can be used for other syntheses. Yield: 0.37 g, *ca.* 60%. Direct reduction of compound **1** in thf by stoichiometric amounts of sodium (as amalgam) gives **3** in comparable yields but this procedure requires an extra step. IR: 1200 ($MnNBu^t$), 966, 920 cm^{-1} (thf). For EPR spectrum see Fig. 1.

Tetra-(μ-tert-*butylimido*)*tetra*(tert-*butylimido*)*trimanganese Triiodide* **4**.—To a solution of compound **1** (0.2 g, 0.38 mmol) in dichloromethane (30 cm^3) was added iodine (0.4 g, 1.6 mmol, excess) and the mixture refluxed (5 h). Evaporation and washing the residue with light petroleum, then Et_2O followed by extraction with CH_2Cl_2 (20 cm^3), filtering of the solution and layering this with petroleum gave red-brown crystals. Yield: 0.12 g, 28%. X-Ray-quality crystals were obtained by two recrystallisations *via* layering tetrahydrofuran solutions with Et_2O. NMR($CDCl_3$): ^1H, δ 1.26 [s, 36 H, $(CH_3)_3CN$] and 1.60 [s, 36 H, μ-$(CH_3)_3CN$]; ^{13}C-{^1H}, δ 31.7 [$(CH_3)_3CN$)], 34.0 [μ-$(CH_3)_3CN$], 74.6 [$(CH_3)_3CN$] and 79.6 [μ-$(CH_3)_3CN$].

Table 10 Fractional atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
Mn(1)	7 500*	4 176(2)	2 500*
Mn(2)	9 038(1)	4 135(1)	2 152(1)
I(1)	2 500*	538(1)	2 500*
I(2)	2 880(1)	500(1)	907(1)
N(1)	7 946(4)	5 169(6)	1 808(3)
N(2)	9 223(5)	3 105(7)	1 433(4)
N(3)	9 926(5)	5 089(7)	2 586(3)
N(4)	8 510(5)	3 133(7)	2 884(3)
C(1)	7 646(7)	6 339(10)	1 184(5)
C(2)	9 709(7)	2 443(10)	885(5)
C(3)	10 801(6)	5 832(9)	2 921(4)
C(4)	8 836(6)	2 066(9)	3 503(5)
C(11)	8 381(7)	7 504(10)	1 323(5)
C(12)	7 539(7)	5 621(10)	371(4)
C(13)	6 714(7)	6 929(11)	1 279(5)
C(21)	10 635(7)	3 178(10)	983(5)
C(22)	9 117(7)	2 611(10)	39(4)
C(23)	9 832(6)	843(9)	1 116(5)
C(31)	10 691(7)	6 654(10)	3 674(5)
C(32)	11 585(6)	4 692(9)	3 144(4)
C(33)	10 997(7)	6 835(10)	2 282(5)
C(41)	9 571(7)	2 717(10)	4 176(4)
C(42)	9 244(6)	806(9)	3 131(4)
C(43)	8 010(6)	1 518(9)	3 832(5)

* Invariant parameter.

The salt of the cation with $[Hg_2Cl_6]^{2-}$ as anion, **5a**, was made as follows. To a solution of compound **3** (0.1 g, 0.16 mmol) in thf was added a solution of $HgCl_2$ in thf (0.11 g, 0.42 mmol, in 20 cm^3). The green-brown mixture became red-brown. After stirring for 8 h, evaporation in vacuum, washing of the residue with light petroleum and diethyl ether followed by extraction of the residue with $CHCl_3$ and by layering with Et_2O gave red crystals. The ^1H NMR spectrum was identical with that of the triiodide. Compound **5b** was obtained by concentration of ether washings to *ca.* 2 cm^3, addition of an equal volume of petroleum and cooling (−20 °C).

(tert-*Butylamido*)*bis*(μ-tert-*butylimido*)*tri*(tert-*butylimido*)-*dimanganese*(VI) *salts* **6**–**8**.—*Method* 1, *protonation of compound* **1**. To a solution of compound **1** in light petroleum (0.3 g, 0.56 mmol, in 50 cm^3) at −78 °C was added dropwise a solution of CF_3SO_3H in CH_2Cl_2 (1.4 cm^3 of 0.5 mol dm^{-3} solution, 0.7 mmol). After warming to room temperature the precipitated solid was collected and dissolved in thf (30 cm^3). Layering with petroleum gave red-brown crystals of **6**. Yield: 0.26 g, *ca.* 70%.

Method 2, *interaction of compound* **1** *with* AgO_3SCF_3. To a solution of compound **1** (0.3 g, 0.56 mmol) in CH_2Cl_2 (30 cm^3) was added AgO_3SCF_3 (0.15 g, 0.6 mmol) in CH_2Cl_2 (30 cm^3), followed by solid '$Li[B(C_6F_5)_4]$' (0.41 g, 0.6 mmol) when compound **7** was required. The brown mixture was stirred for 48 h during which time silver was precipitated. The red-brown solution was evaporated in vacuum and the residue washed with petroleum. Extraction with Et_2O (50 cm^3), filtration and layering with petroleum gave **7**. Extraction of the solid with thf (30 cm^3), filtration and addition of an equal volume of Et_2O followed by cooling (−22 °C, 24 h) also gave **7**. Yield in both cases *ca.* 75%.

Method 3. To the sodium salt **3** (0.2 g, 0.32 mmol) in thf (20 cm^3) was added a thf solution of $Li[B(C_6F_5)_4]$ (0.14 g, 0.35 mmol) that had been *made in air*. The mixture immediately changed from green-brown to red-brown. After stirring for 6 h the solution was evaporated and the product worked up as above. Yield: 0.18 g, *ca.* 45%. In some reactions a red, oily contaminant was formed but this can be removed by crystallisation from Et_2O–petroleum. NMR($CDCl_3$) for **7**: ^1H, δ 1.75 [s, 18 H, μ-$(CH_3)_3CN$]; 1.49, 1.43, 1.32 [s, 9 H each, terminal $(CH_3)_3CN$], 0.85 [s, 9 H, $(CH_3)_3CNH$]; and 10.2 (s, br, 1 H, Me_3CNH); ^{19}F, δ −163.7, −164.1 and −165.7 (m, C_6F_5).

Table 11 Fractional atomic coordinates (× 10^4) for compound **5a**

Atom	*x*	*y*	*z*
Hg(1)	−52(1)	9 583(1)	2 869(1)
Hg(2)	95(1)	7 866(1)	2 146(1)
Cl(1)	18(1)	9 596(1)	3 739(1)
Cl(2)	−190(1)	10 735(1)	2 430(1)
Cl(3)	−902(1)	8 699(1)	2 374(1)
Cl(4)	14(1)	7 843(1)	1 276(1)
Cl(5)	231(1)	6 721(1)	2 590(1)
Cl(6)	953(1)	8 756(1)	2 643(1)
Mn(11)	2 900(1)	9 624(1)	−842(1)
Mn(12)	2 527(1)	9 572(1)	−16(1)
Mn(13)	2 168(1)	9 510(1)	815(1)
N(11)	3 164(2)	9 090(3)	−276(2)
N(12)	2 568(3)	9 116(3)	−1 292(2)
N(13)	3 495(2)	10 178(3)	−992(2)
N(14)	2 233(2)	10 099(3)	−527(2)
N(15)	2 815(2)	10 054(3)	521(2)
N(16)	1 559(2)	10 017(3)	990(2)
N(17)	2 523(2)	8 962(3)	1 241(2)
N(18)	1 900(2)	9 042(3)	224(2)
C(11)	3 673(3)	8 504(4)	−139(2)
C(12)	2 387(3)	8 781(4)	−1 762(3)
C(13)	3 968(3)	10 565(4)	−1 258(2)
C(14)	1 708(3)	10 664(4)	−682(2)
C(15)	3 304(3)	10 636(3)	696(2)
C(16)	1 049(3)	10 337(4)	1 268(2)
C(17)	2 723(3)	8 604(4)	1 696(2)
C(18)	1 380(3)	7 473(3)	61(2)
C(111)	4 371(3)	8 750(4)	−285(3)
C(112)	3 717(3)	8 365(4)	406(3)
C(113)	3 441(3)	7 805(4)	−421(3)
C(121)	1 699(4)	8 425(6)	−1 761(3)
C(122)	2 256(5)	9 424(6)	−2 140(3)
C(123)	2 950(5)	8 323(7)	−1 872(4)
C(131)	4 275(4)	10 034(5)	−1 582(4)
C(132)	4 528(4)	10 894(5)	−893(3)
C(133)	3 589(4)	11 166(6)	−1 550(4)
C(141)	2 058(4)	11 358(4)	−785(4)
C(142)	1 265(4)	10 397(5)	−1 143(3)
C(143)	1 243(4)	10 762(4)	−287(3)
C(151)	3 719(4)	10 375(4)	1 170(3)
C(152)	2 906(3)	11 320(4)	777(3)
C(153)	2 784(3)	10 758(4)	314(3)
C(161)	654(4)	9 713(4)	1 479(3)
C(162)	1 416(3)	10 822(4)	1 667(3)
C(163)	566(3)	10 791(4)	911(3)
C(171)	2 619(3)	9 122(4)	2 112(2)
C(172)	2 259(4)	7 925(4)	1 727(3)
C(173)	3 487(3)	8 392(5)	1 726(3)
C(181)	684(3)	8 733(4)	183(3)
C(182)	1 371(3)	8 365(4)	−480(2)
C(183)	1 581(3)	7 773(4)	333(3)
Mn(21)	2 893(1)	1 991(1)	4 120(1)
Mn(22)	2 538(1)	2 028(1)	4 953(1)
Mn(23)	2 143(1)	2 039(1)	5 771(1)
N(21)	3 158(2)	1 498(3)	4 703(2)
N(22)	2 516(2)	1 446(3)	3 706(2)
N(23)	3 488(2)	2 501(3)	3 934(2)
N(24)	2 262(2)	2 532(3)	4 424(2)
N(25)	2 833(2)	2 520(3)	5 482(2)
N(26)	1 546(2)	2 581(3)	5 923(2)
N(27)	2 447(2)	1 497(3)	6 215(2)
N(28)	1 879(2)	1 542(3)	5 194(2)
C(21)	3 663(3)	916(3)	4 847(2)
C(22)	2 304(3)	1 068(4)	3 242(2)
C(23)	3 971(3)	2 904(4)	3 676(2)
C(24)	1 783(3)	3 132(3)	4 264(2)
C(25)	3 358(3)	3 066(3)	5 663(2)
C(26)	1 046(3)	2 910(3)	6 204(2)
C(27)	2 600(3)	1 133(4)	6 675(2)
C(28)	1 353(3)	992(3)	5 029(2)
C(211)	4 366(3)	1 142(4)	4 705(3)
C(212)	3 423(3)	207(4)	4 587(3)
C(213)	3 704(3)	809(4)	5 402(2)
C(221)	2 619(4)	296(4)	3 286(3)
C(222)	1 530(3)	1 010(5)	3 176(3)
C(223)	2 563(5)	1 502(5)	2 834(3)
C(231)	4 464(4)	2 362(5)	3 504(4)
C(232)	3 583(3)	3 300(4)	3 243(3)
C(233)	4 362(4)	3 441(5)	4 027(3)
C(241)	1 419(4)	2 945(4)	3 758(3)
C(242)	2 205(3)	3 831(4)	4 239(3)
C(243)	1 265(3)	3 230(4)	4 629(3)
C(251)	3 761(3)	2 783(4)	6 128(2)
C(252)	2 996(3)	3 775(4)	5 764(3)
C(253)	3 844(3)	3 185(4)	5 283(3)
C(261)	706(4)	2 294(4)	6 470(3)
C(262)	1 425(3)	3 455(4)	6 566(3)
C(263)	505(3)	3 300(4)	5 853(3)
C(271)	2 625(4)	1 698(4)	7 091(3)
C(272)	2 027(4)	564(4)	6 706(3)
C(273)	3 305(3)	766(4)	6 685(3)
C(281)	661(3)	1 259(4)	5 167(3)
C(282)	1 317(3)	898(4)	4 481(2)
C(283)	1 546(3)	268(4)	5 289(3)
C(1)	34(5)	4 955(6)	2 982(4)
C(1′)	−74(5)	4 735(7)	2 869(4)
Cl(7)	−774(1)	4 916(1)	2 608(1)
Cl(8)	−98(1)	4 832(1)	3 590(1)
Cl(9)	589(1)	4 299(1)	2 799(1)
C(2)	−63(5)	2 473(6)	1 949(4)
C(2′)	24(5)	2 934(6)	2 118(4)
Cl(10)	−665(1)	3 092(1)	2 125(1)
Cl(11)	144(1)	2 692(1)	1 371(1)
Cl(12)	709(1)	2 518(1)	2 376(1)

Compounds **8** *and* **9**.—To a solution of compound **1** (0.2 g, 0.37 mmol) and AgO_3SCF_3 (0.12 g, 0.5 mmol) in CH_2Cl_2 was added $Na[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ (0.44 g, 0.5 mmol) and the mixture stirred for 2 h at *ca.* 24 °C. After filtration the volatiles were removed under vacuum and the residue extracted with hot toluene. On slow cooling red crystals were formed in *ca.* 90% yield. The ^1H NMR spectrum showed that they were a mixture of the two salts **8** and **9**. Five peaks at δ 1.74, 1.48, 1.40, 1.30 and 0.84 in a 2:1:1:1:1 ratio can be assigned to the amido cation as in **6** and **7**. The remaining peaks at 1.62, 1.56, 1.31 and 1.10 in a 2:2:2:1 ratio could be assigned to the μ-oxo complex **9**.

Interaction of Compound **1** *with* AgO_3SCF_3 *and* O_2.—A solution of compound **1** (0.12 g, 0.5 mmol) in CH_2Cl_2 was stirred for 12 h. After filtration to remove the precipitate of Ag the solution was exposed to dry O_2 for *ca.* 24 h with stirring. After evaporation the residue was washed with petroleum and extracted with boiling toluene; slow cooling gave red-brown plates of **4** + **10**. For NMR see text.

Bis[(tert-*butylamido*)(μ-tert-*butylimido*)(tert-*butylimido*)-*manganese*(V)] **11**.— To $MnCl(NBu^t)_3$ (0.3 g, *ca.* 1 mmol) in benzene (30 cm^3) cooled to −78 °C was added a solution of $TlOCH(CF_3)_2$[1] (0.41 g, 1 mmol) in benzene–light petroleum (30 cm^3). The solution was allowed to warm to room temperature and stirred for 2 h. The white precipitate (TlCl) was removed and the green solution heated at 50–60 °C for 2 h or stirred at room temperature for 2 d, when the solutions became red-brown. Removal of volatiles in vacuum and extraction of the residue into petroleum followed by filtration and evaporation under vacuum left a red-brown oil. Yield: *ca.* 60%. Mass spectrum (electron impact, EI): *m*/*z* 538 (M^+) and 466 ($M^+ - NHBu^t$). IR: 3325, 3180 (N–H) and 1180 cm^{-1} ($Mn{=}NBu^t$).

Table 12 Fractional atomic coordinates (× 10^4) for compound **5b**

Atom	*x*	*y*	*z*
Hg(1)	4243(1)	859(1)	1453(1)
Hg(2)	4273(1)	2884(1)	1228(1)
Hg(3)	3737(1)	4881(1)	1065(1)
Mn(11)	452(2)	7561(1)	215(1)
Mn(12)	1675(2)	7653(1)	−299(1)
Mn(21)	−1062(2)	2196(2)	2874(1)
Mn(22)	93(2)	2170(1)	2350(1)
Cl(1)	5942(4)	1938(2)	1211(1)
Cl(2)	3622(4)	381(2)	933(1)
Cl(3)	4848(5)	671(3)	2009(1)
Cl(4)	2652(4)	2090(2)	1484(1)
Cl(5)	4850(4)	4002(2)	1567(1)
Cl(6)	1706(4)	5122(3)	1241(1)
Cl(7)	5497(4)	5355(3)	824(1)
Cl(8)	3564(4)	3575(3)	718(1)
N(11)	1959(10)	7191(7)	76(3)
N(12)	1465(10)	7152(7)	−613(3)
N(13)	2886(9)	8264(6)	−418(3)
N(14)	308(10)	8077(6)	−171(3)
N(15)	614(11)	8064(7)	549(4)
N(16)	−604(11)	6939(7)	239(4)
N(21)	435(12)	1817(7)	2759(4)
N(22)	4(13)	1524(8)	2053(4)
N(23)	1187(11)	2784(7)	2209(4)
N(24)	−1329(11)	2565(7)	2438(4)
N(25)	−838(12)	2807(8)	3151(3)
N(26)	−2077(12)	1557(7)	2965(4)
C(11)	2877(15)	6634(9)	233(5)
C(12)	1014(15)	6533(10)	−828(5)
C(13)	3533(13)	8900(8)	−240(5)
C(14)	−740(14)	8516(9)	−359(4)
C(15)	540(17)	8442(11)	858(5)
C(16)	−1622(14)	6492(9)	371(5)
C(21)	1488(16)	1364(9)	2915(5)
C(22)	−443(15)	855(11)	1885(6)
C(23)	1857(17)	3488(10)	2301(5)
C(24)	−2395(16)	2939(9)	2256(4)
C(25)	−855(19)	3295(11)	3468(5)
C(26)	−3092(15)	1148(9)	3122(5)
C(111)	3524(15)	6949(9)	551(5)
C(112)	2188(14)	5979(9)	321(5)
C(113)	3836(15)	6444(10)	−5(5)
C(121)	225(15)	6780(9)	−1125(4)
C(122)	2134(20)	6214(11)	−972(6)
C(123)	332(17)	5978(9)	−626(5)
C(131)	4 894(14)	8719(8)	−207(5)
C(132)	3370(14)	9558(8)	−469(5)
C(133)	3010(16)	9059(9)	103(5)
C(141)	−295(15)	8845(10)	−678(5)
C(142)	−1742(13)	8001(9)	−453(4)
C(143)	−1223(16)	9078(10)	−119(5)
C(151)	1562(18)	8934(12)	898(6)
C(152)	−711(22)	8864(13)	859(6)
C(153)	460(21)	7955(12)	1135(6)
C(161)	−2804(12)	6983(9)	391(5)
C(162)	−1208(15)	6202(9)	725(4)
C(163)	−1963(14)	5876(10)	118(4)
C(211)	2537(13)	1251(10)	2686(5)
C(212)	949(16)	709(9)	3043(5)
C(213)	1987(16)	1809(11)	3205(6)
C(221)	−1313(17)	480(11)	2130(5)
C(222)	728(20)	370(11)	1842(5)
C(223)	−1123(17)	1008(10)	1555(5)
C(231)	3201(14)	3339(9)	2353(5)
C(232)	1655(14)	3961(11)	2007(5)
C(233)	1294(20)	3774(11)	2615(6)
C(241)	−1961(14)	3212(11)	1945(5)
C(242)	−2888(17)	3532(11)	2482(5)
C(243)	−3468(12)	2381(9)	2196(4)
C(251)	396(15)	3692(9)	3496(5)
C(252)	−1954(16)	3829(11)	3413(5)
C(253)	−1076(17)	2768(11)	3767(5)
C(261)	−4064(15)	1616(9)	3211(5)
C(262)	−2525(15)	750(10)	3422(5)
C(263)	−3625(18)	584(11)	2854(5)

Table 13 Fractional atomic coordinates (× 10^4) for compound 7

Atom	*x*	*y*	*z*
Mn(11)	14 205(1)	6 615(1)	−4 118(1)
Mn(12)	13 276(1)	5 814(1)	−3 253(1)
Mn(21)	4 176(1)	1 045(1)	1 453(1)
Mn(22)	5 179(1)	1 868(1)	648(1)
N(11)	13 119(4)	6 044(2)	−4 040(2)
N(12)	13 829(5)	5 045(3)	−2 965(2)
N(13)	11 948(4)	5 917(3)	−2 813(2)
N(14)	14 281(4)	6 344(2)	−3 278(2)
N(15)	15 492(4)	6 440(2)	−4 475(2)
N(16)	13 626(4)	7 355(2)	−4 371(2)
N(21)	3 843(4)	1 918(2)	1 127(2)
N(22)	6 230(5)	2 263(3)	744(3)
N(23)	4 972(6)	2 174(3)	−116(2)
N(24)	5 538(4)	1 036(2)	907(2)
N(25)	4 497(4)	815(2)	2 155(2)
N(26)	3 141(4)	683(2)	1 334(2)
C(11)	12 463(5)	5 898(3)	−4 478(2)
C(12)	14 675(5)	4 468(3)	−2 904(3)
C(13)	10 917(5)	6 366(3)	−2 677(2)
C(14)	15 028(5)	6 475(3)	−2 870(2)
C(15)	16 611(5)	6 455(3)	−4 872(2)
C(16)	13 387(5)	8 025(3)	−4 702(3)
C(21)	2 895(5)	2 421(3)	1 254(3)
C(22)	7 045(5)	2 463(3)	1064(2)
C(23)	4 354(6)	2 156(3)	−623(2)
C(24)	6 572(6)	556(3)	837(3)
C(25)	4 539(5)	498(3)	2 816(2)
C(26)	2 238(6)	282(3)	1 386(3)
C(111)	13 330(7)	5 784(4)	−5 000(3)
C(112)	11 505(7)	6 477(3)	−4 722(3)
C(113)	11 818(6)	5 329(3)	−4 152(3)
C(41)	10 235(3)	3 971(2)	−1 012(1)
C(42)	9 902(3)	3 887(2)	−393(1)
C(43)	10 534(3)	4 126(2)	−54(1)
C(44)	11 499(3)	4 449(2)	−334(2)
C(45)	11 831(3)	4 534(2)	−953(2)
C(46)	11 199(3)	4 295(2)	−1 292(1)
F(42)	9 000(3)	3 589(2)	−101(1)
F(43)	10 208(3)	4 051(2)	539(1)
F(44)	12 110(3)	4 692(2)	−9(2)
F(45)	12 751(3)	4 855(2)	−1 230(2)
F(46)	11 548(3)	4 425(2)	−1 881(1)
C(51)	9 728(3)	3 895(2)	−2 170(1)
C(52)	9 065(3)	4 312(2)	−2 636(1)
C(53)	9 432(3)	4 338(2)	−3 242(1)
C(54)	10 462(3)	2 948(2)	−3 382(1)
C(55)	11 125(3)	3 531(2)	−2 916(2)
C(56)	10 759(3)	3 505(2)	−2 309(1)
F(52)	8 058(3)	4 677(2)	−2 546(1)
F(53)	8 810(3)	4 726(2)	−3 694(1)
F(54)	10 808(3)	3 963(2)	−3 973(1)
F(55)	12 089(3)	3 140(2)	−3 052(1)
F(56)	11 444(3)	3 131(2)	−1 891(1)
C(61)	7 911(2)	4 175(2)	−1 240(2)
C(62)	7 879(3)	4 831(2)	−1 384(2)
C(63)	6 859(3)	5 205(1)	−1 209(2)
C(64)	5 871(3)	4 923(2)	−890(2)
C(65)	5 902(3)	4 268(2)	−746(2)
C(66)	6 923(3)	3 894(1)	−921(2)
F(62)	8 787(3)	5 121(2)	−1 681(1)
F(63)	6 844(3)	5 835(2)	−1 346(2)
F(64)	4 882(3)	5 292(2)	−710(2)

Table 13 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(121)	15 678(7)	4 573(4)	−3 425(3)	F(65)	4 949(3)	4 001(2)	−436(2)
C(122)	15 185(6)	4 291(3)	−2 273(3)	F(66)	6 864(3)	3 278(2)	−748(1)
C(123)	13 981(6)	3 951(3)	−2 931(3)	C(71)	9 489(3)	−389(1)	3 607(2)
C(131)	10 746(5)	6 250(3)	−1 986(3)	C(72)	8 954(3)	141(2)	3 177(2)
C(132)	9 808(5)	6 238(3)	−2 913(3)	C(73)	9 178(3)	746(1)	3 142(2)
C(133)	11 208(7)	7 033(4)	−2 999(3)	C(74)	9 937(3)	820(1)	3 537(2)
C(141)	15 093(7)	7 175(3)	−3 057(3)	C(75)	10 472(3)	290(2)	3 967(2)
C(142)	16 299(5)	6 106(4)	−2 928(3)	C(76)	10 248(3)	−315(1)	4 002(1)
C(143)	14 459(5)	6 235(3)	−2 206(2)	F(72)	8 201(3)	113(2)	2 803(1)
C(151)	16 277(6)	6 672(4)	−5 539(3)	F(73)	8 677(3)	1 256(2)	2 734(2)
C(152)	17 310(6)	6 934(4)	−4 771(3)	F(74)	10 187(3)	1 406(2)	3 496(2)
C(153)	17 322(8)	5 797(4)	−4 706(3)	F(75)	11 192(3)	365(2)	4 352(2)
C(161)	14 468(6)	8 350(3)	−4 693(3)	F(76)	10 780(3)	−791(2)	4 404(1)
C(162)	13 216(6)	8 081(3)	−5 372(2)	C(81)	10 533(2)	−1 643(2)	3 594(2)
C(163)	12 272(6)	8 320(3)	−4 396(3)	C(82)	10 461(3)	−2 288(2)	3 725(2)
C(211)	3 080(11)	2 486(5)	1 860(3)	C(83)	11 442(3)	−2 698(1)	3 568(2)
C(212)	3 045(8)	3 058(3)	794(4)	C(84)	12 495(3)	−2 462(2)	3 281(2)
C(213)	1 701(6)	2 242(4)	1 215(6)	C(85)	12 567(2)	−1 817(2)	3 149(2)
C(221)	6 800(8)	2 157(4)	1 746(3)	C(86)	11 586(3)	−1 408(1)	3 306(2)
C(222)	8 336(5)	2 239(4)	838(3)	F(82)	9 464(3)	−2 536(2)	3 967(1)
C(223)	6 775(6)	3 182(3)	898(3)	F(83)	11 388(3)	−3 322(2)	3 697(2)
C(231)	5 297(7)	2 026(5)	−1 111(3)	F(84)	13 454(3)	−2 866(2)	3 133(2)
C(232)	3 619(7)	2 823(4)	−883(3)	F(85)	13 574(3)	−1 592(2)	2 865(2)
C(233)	3 503(8)	1 692(4)	−405(4)	F(86)	11 754(3)	−811(2)	3 166(1)
C(241)	6 162(7)	−46(4)	896(4)	C(91)	8 616(3)	−1 333(2)	4 466(1)
C(242)	7 375(7)	457(4)	1 397(3)	C(92)	7 566(3)	−941(2)	4 580(1)
C(243)	7 363(6)	792(4)	265(3)	C(93)	7 031(3)	−1 031(2)	5 173(2)
C(251)	3 246(5)	505(3)	3 108(3)	C(94)	7 545(3)	−1 514(2)	5 652(1)
C(252)	5 146(6)	−197(3)	2 902(3)	C(95)	8 595(3)	−1 906(2)	5 538(1)
C(253)	5 254(5)	864(3)	3 069(3)	C(96)	9 130(3)	−1 815(2)	4 945(1)
C(261)	2 750(7)	−401(3)	1 683(3)	F(92)	7 036(3)	−497(2)	4 147(1)
C(262)	1 150(6)	485(4)	1 805(4)	F(93)	6 052(3)	−638(2)	5 296(2)
C(263)	1 847(11)	396(5)	764(4)	F(94)	7 003(3)	−1 618(2)	6 229(1)
B(1)	9 269(5)	3 745(3)	−1 401(3)	F(95)	9 059(3)	−2 373(2)	5 999(1)
B(2)	9 235(5)	−1 147(3)	3 715(3)	F(96)	10 148(3)	−2 181(2)	4 885(1)
C(31)	9 200(3)	2 952(1)	−1 205(2)	C(101)	8 326(3)	−1 267(2)	3 242(1)
C(32)	8 505(3)	2 767(2)	−1 559(1)	C(102)	7 328(3)	−1 584(2)	3 447(1)
C(33)	8 486(3)	2 124(2)	−1 478(2)	C(103)	6 741(3)	−1 751(2)	3 036(2)
C(34)	9 163(4)	1 666(1)	−1 042(2)	C(104)	7 151(3)	−1 600(2)	2 421(1)
C(35)	9 858(3)	1 851(2)	−688(2)	C(105)	8 149(3)	−1 283(2)	2 215(1)
C(36)	9 876(3)	2 493(2)	−769(2)	C(106)	8 736(3)	−1 116(2)	2 626(1)
F(32)	7 815(3)	3 166(2)	−1 954(1)	F(102)	6 877(3)	−1 752(2)	4 015(1)
F(33)	7 854(3)	1 938(2)	−1 828(2)	F(103)	5 812(3)	−2 077(2)	3 232(2)
F(34)	9 147(4)	1 035(2)	−959(2)	F(104)	6 597(4)	−1 769(2)	2 020(2)
F(35)	10 496(3)	1 408(2)	−278(2)	F(105)	8 546(3)	−1 142(2)	1 621(1)
F(36)	10 599(3)	2 632(2)	−440(2)	F(106)	9 698(3)	−830(2)	2 400(1)

Table 14 Fractional atomic coordinates (× 10^4) for compound **9**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	2490(1)	3531(1)	2622(1)	F(13)	1445(6)	4485(5)	5620(3)
Mn(2)	2783(1)	2951(1)	1783(1)	F(14)	792(4)	4254(4)	4841(4)
Mn(3)	3037(1)	2315(1)	960(1)	F(15)	1787(5)	4451(5)	4924(5)
O	2756(3)	1993(3)	1587(2)	F(16)	258(5)	1615(4)	4351(4)
N(1)	1972(4)	3272(4)	1837(3)	F(17)	1034(5)	895(6)	4628(5)
N(2)	2252(4)	3093(4)	3097(3)	F(18)	448(6)	1094(7)	5114(3)
N(3)	2512(5)	4453(5)	2744(3)	F(19)	3388(4)	898(6)	4250(3)
N(4)	3329(4)	3152(4)	2518(3)	F(20)	4285(7)	385(6)	4506(3)
N(5)	3047(4)	3286(4)	1206(3)	F(21)	4278(6)	1490(6)	4581(3)
N(6)	3839(4)	2016(4)	1016(3)	F(22)	4452(9)	−477(5)	7045(4)
N(7)	2418(4)	2150(4)	301(3)	F(23)	4847(8)	−853(8)	6440(7)
C(1)	1188(5)	3281(6)	1477(4)	F(24)	3899(7)	−1080(7)	6410(6)
C(2)	1967(5)	2808(6)	3555(4)	C(101)	3789(3)	2839(3)	6419(4)
C(3)	2444(7)	5133(6)	2972(4)	C(102)	3931(4)	3132(4)	5929(3)
C(4)	4072(5)	3070(6)	2871(4)	C(103)	4364(4)	3762(5)	5993(3)
C(5)	3226(5)	4019(6)	966(3)	C(104)	4656(3)	4098(3)	6547(4)
C(6)	4431(6)	1637(7)	910(4)	C(105)	4514(4)	3805(4)	7036(3)
C(7)	2047(6)	1851(7)	−266(5)	C(106)	4081(4)	3176(4)	6972(3)
C(11)	1146(5)	3289(8)	852(4)	C(107)	4516(6)	4056(6)	5505(5)
C(12)	866(7)	2576(8)	1577(7)	C(108)	4818(6)	4132(6)	7612(5)
C(13)	803(6)	3892(7)	1651(5)	C(201)	3108(6)	1851(6)	6927(5)
C(21)	2477(5)	2985(5)	4153(3)	C(202)	3645(6)	1653(5)	7439(5)
C(22)	1939(6)	1988(6)	3494(4)	C(203)	3561(6)	1398(6)	7943(5)
C(23)	1241(5)	3125(6)	3469(4)	C(204)	2844(7)	1352(7)	7990(4)
C(31)	3137(7)	5409(9)	3375(9)	C(205)	2271(6)	1531(6)	7485(5)
C(32)	2257(12)	5695(7)	2503(6)	C(206)	2434(7)	1788(6)	6979(4)
C(33)	2039(11)	5120(9)	3390(9)	C(207)	4179(6)	1195(5)	8473(4)

Table 14 (*continued*)

Atom	*x*	*y*	*z*
C(41)	4496(5)	2635(8)	2583(4)
C(42)	4415(6)	3793(6)	3075(5)
C(43)	4091(5)	2622(7)	3390(4)
C(51)	2741(5)	4118(6)	347(3)
C(52)	3993(5)	3997(6)	998(4)
C(53)	3107(5)	4620(5)	1348(4)
C(61)	4289(7)	1599(10)	262(4)
C(62)	5078(6)	2106(7)	1164(5)
C(63)	4543(7)	929(7)	1240(7)
C(71)	2272(8)	2277(9)	−701(5)
C(72)	2075(9)	1036(7)	−290(6)
C(73)	1294(6)	2093(12)	−404(6)
B	3226(6)	2100(7)	6323(4)
F(1)	5043(7)	4495(9)	5568(4)
F(2)	4597(8)	3608(6)	5119(5)
F(3)	4028(6)	4438(8)	5131(5)
F(4)	5433(6)	4449(7)	7737(4)
F(5)	4977(6)	3722(5)	8073(3)
F(6)	4457(6)	4664(8)	7724(5)
F(7)	4684(5)	852(5)	8348(3)
F(8)	4544(4)	1741(4)	8761(3)
F(9)	4046(4)	824(5)	8882(3)
F(10)	1471(4)	1061(5)	7929(3)
F(11)	1312(4)	2141(6)	7652(3)
F(12)	1034(4)	1311(5)	7016(3)
C(208)	1500(7)	1498(6)	7513(3)
C(301)	2428(3)	2347(5)	5821(2)
C(302)	2234(4)	3092(4)	5716(3)
C(303)	1565(5)	3283(3)	5308(3)
C(304)	1090(3)	2728(6)	5004(2)
C(305)	1284(4)	1983(5)	5108(3)
C(306)	1953(5)	1792(3)	5516(3)
C(307)	1426(5)	4076(6)	5183(4)
C(308)	776(5)	1450(5)	4819(4)
C(401)	3547(3)	1362(4)	6053(4)
C(402)	3593(3)	1412(4)	5485(3)
C(403)	3879(4)	822(5)	5255(2)
C(404)	4118(3)	184(4)	5594(4)
C(405)	4072(4)	135(4)	6162(4)
C(406)	3787(4)	724(5)	6392(2)
C(407)	3973(5)	908(6)	4691(4)
C(408)	4302(7)	−509(6)	6485(5)
C(500)	−3012(7)	1016(8)	2212(4)
C(501)	−2418(5)	962(10)	2852(3)
C(502)	−2369(6)	255(7)	3102(7)
C(503)	−1908(8)	132(5)	3679(7)
C(504)	−1496(5)	714(10)	4007(3)
C(505)	−1545(6)	1420(7)	3756(6)
C(506)	−2006(7)	1544(5)	3179(7)

Table 15 Fractional atomic coordinates (× 10^4) for compound **10**

Atom	*x*	*y*	*z*
Mn(1)	4700(1)	731(1)	2609(1)
Mn(2)	3480(1)	1853(1)	2034(1)
Mn(3)	2255(1)	3015(1)	1531(1)
S	1645(1)	2917(1)	−3418(1)
O(1)	4445(3)	1031(3)	1544(3)
O(2)	1953(3)	1536(3)	1343(3)
O(3)	1665(3)	3724(3)	−2556(3)
O(4)	2759(3)	2517(3)	−3445(3)
O(5)	1137(5)	3146(4)	−4201(3)
F(1)	−626(3)	1984(3)	−3430(3)
F(2)	824(4)	1398(3)	−2815(3)
F(3)	286(3)	907(3)	−4276(3)
N(1)	6147(4)	1255(4)	3238(3)
N(2)	4157(4)	−549(3)	2444(3)
N(3)	3607(4)	1586(3)	3041(3)
N(4)	3909(4)	3230(3)	2189(3)
N(5)	2224(4)	3287(3)	612(3)
N(6)	1384(4)	3618(3)	2176(3)
C	480(6)	1745(5)	−3496(5)
C(1)	7353(5)	1313(5)	3784(4)
C(2)	3811(5)	−1658(4)	2366(4)
C(3)	3123(5)	1887(5)	3882(4)
C(4)	5025(5)	4179(4)	2580(4)
C(5)	2137(5)	3545(5)	−203(4)
C(6)	538(5)	4326(4)	2411(4)
C(11)	7830(7)	2454(5)	4516(5)
C(12)	7206(6)	478(5)	4234(4)
C(13)	8229(6)	1075(7)	3146(6)
C(21)	2477(6)	−2169(5)	1765(5)
C(22)	4744(6)	−2265(5)	1912(5)
C(23)	3888(7)	−1673(5)	3339(4)
C(31)	4144(7)	2009(8)	4685(5)
C(32)	2021(8)	930(8)	3711(6)
C(33)	2764(12)	2946(8)	4061(6)
C(41)	5975(7)	3977(6)	3252(6)
C(42)	4630(6)	5192(4)	3032(5)
C(43)	5548(7)	4260(7)	1784(5)
C(51)	2942(6)	2924(6)	−781(5)
C(52)	774(6)	3220(6)	−735(4)
C(53)	2657(8)	4796(5)	98(5)
C(61)	1036(8)	5372(6)	2336(9)
C(62)	437(12)	4519(11)	3358(8)
C(63)	−704(8)	3791(8)	1794(9)
C(10)	4789(12)	573(9)	657(7)
C(11)	4143(16)	1005(13)	−22(9)
C(12)	4211(26)	−707(13)	222(15)
C(13)	6 127(15)	889(23)	791(13)
C(20)	870(12)	576(8)	781(9)
C(21)	−238(13)	683(14)	1113(16)
C(22)	654(19)	500(15)	−266(12)
C(23)	1292(14)	−423(9)	792(13)

^1H (C_6D_6) NMR: δ 1.75 (s, br, 18 H, μ-NC*Me*$_3$), 1.30 (s, br, 18 H, NC*Me*$_3$), 0.85 (s, br, 18 H, NHC*Me*$_3$) and 2.4 (s, N*H*CMe$_3$).

X-Ray Crystallography.—The X-ray measurements were made on crystals handled under nitrogen with standard Schlenk procedures, and mounted on glass fibres using a variety of coating and adhesive media (depending on the solubility properties of the crystal being measured). The unit-cell and intensity data for all compounds were collected using a Delft-Instruments FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) following previously described procedures.[5] The data collection and refinement details are given in Table 8. Structures **3** and **5a** were solved by direct methods whilst those for **4**, **5b**, **7**, **9** and **10** were solved using the Patterson instruction of SHELXS 86.[14] All refinements were by full-matrix least squares on F^2 (SHELXL 93).[15] The data for compounds **3**, **4**, **5a**, **5b**, **7** and **10** were corrected for absorption using the program DIFABS[16] adapted for FAST geometry.[17] The maximum and minimum absorption correction factors are given in Table 8. The data for compound **9** were not corrected for absorption due to the large proportion of unobserved reflections in the data set. The non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms in each compound were placed in calculated positions (C–H 0.96 Å, C–C–H and H–C–H 109.5°). As a result of the generally poor crystal quality, coupled with disorder/high thermal motion of the Bu^t groups, four atoms in compound **3**, two in **4**, one in **5b** and two in **9** showed non-positive definite thermal parameters. These atoms were refined isotropically. The asymmetric unit of compound **5a** includes two trinuclear entities, $[Hg_2Cl_6]^{2-}$ and two disordered molecules of $CHCl_3$. The carbon atoms of the solvent molecules were assigned a fixed occupancy of 0.5 in two sites, and all of the C–Cl bond lengths were refined using a free-variable value of 1.718 Å.

The pentafluorophenyl rings of the two counter ions $[B(C_6F_5)_4]^-$ in compound **7** were refined as rigid bodies with C–C 1.39 Å and C–C–C 120°. Both the substituted phenyl rings of the counterion $[B(C_8H_3F_6)_4]^-$ and lattice toluene molecule of compound **9** were refined as rigid bodies (C–C 1.39 Å and C–C–C 120°). Some disorder is evident in the CF_3 groups. This was successfully modelled by fixing the C–F and C–C bond lengths using free-variable values for all of the groups present in the molecule. One *tert*-butyl group was assigned fractional occupancy due to evident disorder, and hydrogen atoms were not included for this group or for the toluene molecule. For compound **10** the cocrystallised mixture of oxo- and imido-bridged species, two of the bridging sites are shared between oxide and imide. The carbon atoms were initially refined with a fixed thermal parameter of 0.05 Å^2, and the occupancy for each group was allowed to refine with a free variable. For both groups the occupancy refined to approximately 0.5, therefore in the final refinement the carbon occupancies were fixed at 0.5 and the thermal parameters were allowed freely to refine. The bridging atoms were assigned as oxygen with fixed occupancies of 0.9375, to represent $\frac{1}{2}(O + N)$. Fractional atomic coordinates are given in Tables 9–15.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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