Synthesis and Reactivity towards Dioxygen of Some Manganese(II) Complexes of Tertiary Amines. Crystal Structures of $[\{MnI_2(NEt_3)\}_2]$, $[\{MnI_2(NPr^n_3)\}_2]$ and $[NHMe_3][MnI_3(NMe_3)]$ †

Helen P. Lane, Stephen M. Godfrey,* Robin G. Pritchard and Charles A. McAuliffe*
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

Some manganese(II)–tertiary amine complexes of stoichiometry $MnX_2(NR_3)$ have been prepared for the first time. Magnetic susceptibility and X-ray crystallographic studies on $[MnI_2(NR_3)]$ (R = Et or Pr^n) indicate that the complexes have a dimeric structure, in contrast to the analogous tertiary phosphine complexes which are polymeric. The crystal structure of $[NHMe_3][MnI_3(NMe_3)]$ which contains a mononuclear manganese site has also been determined. This complex is postulated to arise from reaction of a solution of $[MnI_2(NMe_3)]$ with trace quantities of moisture. The reaction of the complexes with dioxygen has also been examined: $[MnBr_2(NMe_3)]$ shows no interaction, $[MnI_2(NEt_3)]$ absorbs 2 mol of dioxygen per mol of complex, whereas $[MnI_2(NPr^n_3)]$ absorbs only 1. In contrast to the analogous tertiary phosphine complexes, the $[MnI_2(NR_3)]$ complexes do not exhibit reversible binding of dioxygen.

Fifteen years ago almost no manganese(II)–tertiary phosphine co-ordination chemistry was known. Since then simple complexes have been prepared and crystallographically characterised by Wilkinson[1,2] and Kohler[3] and their co-workers. However, most of the published work has derived from our investigations of complexes of stoichiometry $MnX_2(PR_3)$ and $MnX_2(PR_3)_2$, the former being polymers which can exist in isomeric forms depending on the method of synthesis[4,5] and the latter tetrahedral and monomeric;[6] complexes of intermediate stoichiometry are also known, for example $MnI_2(PPhMe_2)_{1.33}$.[6] Our chief interest has been in the interaction of these complexes with molecular oxygen and other small molecules such as carbon monoxide,[7] nitric oxide,[8] sulfur dioxide[9] and carbon disulfide.[10] At low temperatures the $Mn–O_2$ interaction has been shown to be reversible, but, generally, at room temperature it is not and, for example, species such as $[Mn_4I_6O(PPr^n_3)_4]$ [11] and $[MnI_3(PMe_3)_2]$ [12] are generated.

We have now turned our attention to tertiary amine complexes of manganese(II). Surprisingly, little work has been published on tertiary amine complexes of *any* metal ion, other than with trimethylamine. For platinum(II) and palladium(II), complexes with trimethylamine, $[MCl_2(NMe_3)_2]$, are known,[13] as are $[ZrCl_4(NMe_3)_2]$ and $[TiCl_4(NMe_3)_2]$,[14] and the trivalent metal species $[MnCl_3(NMe_3)]$ and $[MnCl_3(NMe_3)_2]$,[15] though few of these have been crystallographically characterised.

Within this background manganese(II) complexes have received even less attention. The interaction of the relatively 'soft' nitrogen (*i.e.* tertiary amine) donor ligands with the hard manganese(II) cation is expected to be weak. In addition, complexes of manganese(II) with tertiary amines are extremely air and moisture sensitive and great care is required in maintaining strictly anaerobic and anhydrous conditions throughout their preparation. Consequently there are only four reported examples of manganese(II) halide complexes of tertiary amines, and of these only two have been thoroughly characterised. Prasad and Kacker[16] reported the preparation of a series of complexes of stoichiometry $MnCl_2L$ (L = NMe_2Ph, NEt_2Ph, $NMe_2(C_6H_4Me)$ or NEt_3) in ethanolic solutions. No evidence was given to suggest that anaerobic conditions were employed. Moreover, no spectroscopic data were provided and it seems unlikely that these were true manganese(II) complexes. In an infrared study of a series of transition-metal complexes of trimethylamine, Guilbault and Billedeaux[17] reported the formation of stable complexes of $MnCl_2$ and $MnBr_2$, prepared by the reaction of the gaseous amine with a thin layer of the metal salt in a purpose-built infrared cell. These complexes were also not fully characterised. More recently the manganese chloride complex $[MnCl_2(NMe_3)]$ was reported by Willey and co-workers.[18] This was prepared by the direct reaction of the amine with manganese(II) chloride in the absence of any solvent. Attempts to crystallise it from acetonitrile, however, resulted in the formation of the ionic complexes $[NHMe_3][MnCl_3]$ and $[NHMe_3]_2[MnCl_4]$. No other manganese(II) complex containing monodentate tertiary amines is known. However, the tetradentate compound tris(2-dimethylaminoethyl)amine has been shown to form five-co-ordinate ionic complexes of stoichiometry $[Mn\{N(CH_2CH_2NMe_2)_3\}X]X$ (X = Br or I) on reaction with the metal halide in hot butanol under anaerobic conditions.[19]

Results and Discussion

Preparation and Characterisation of Complexes of Stoichiometry MnI_2L (L = NEt_3, $NMeEt_2$ *or* NPr^n_3).—The complexes $[MnI_2(NR_3)]$ (R_3 = Et_3, Et_2Me or Pr^n_3) were prepared by reaction of the tertiary amine with anhydrous manganese(II) iodide in dry diethyl ether; rigorously anaerobic and anhydrous conditions were employed throughout. Elemental analyses are given in Table 1.

By comparison with the manganese(II) phosphine complexes of this stoichiometry[4,5] it was expected that the tertiary amine complexes would be at least oligomeric, if not polymeric. The room-temperature magnetic moments of these complexes, Table 1, support this, values of 4.8–5.1 μ_B being recorded. These values are low compared to the spin-only value for

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

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Analytical data for complexes of stoichiometry $[MnX_2(NR_3)]$

		Analysis (%) *					Infrared
Complex	Colour	C	H	N	X	μ_{eff}/μ_B	$\tilde{\nu}$(Mn–N)/cm^{-1}
$[MnI_2(NMeEt_2)]$	Pink-orange	15.5 (15.2)	3.6 (3.3)	3.4 (3.5)	64.5 (64.1)	5.1	329
$[MnI_2(NEt_3)]$	Peach	17.5 (17.6)	3.8 (3.7)	3.3 (3.4)	61.7 (61.9)	4.8	321
$[MnI_2(NPr^n_3)]$	Orange	23.8 (23.9)	4.9 (4.6)	3.0 (3.1)	56.4 (56.2)	4.8	322
$[MnBr_2(NMe_3)]$	Off-white	13.4 (13.1)	3.0 (3.3)	4.8 (5.1)	58.4 (58.4)		

* Calculated values in parentheses.

manganese(II), 5.9 μ_B, thus implying that antiferromagnetic interactions occur between adjacent paramagnetic centres. It is unlikely, in view of the chemistry of manganese(II), that metal–metal bonding occurs, and the interaction is proposed to take place *via* superexchange through bridging iodine atoms.

The nature of these complexes has rendered further characterisation difficult. Strong fluorescence bands are seen in their low-frequency Raman spectra; thus, ν(Mn–I) frequencies cannot be recorded. The low-frequency infrared spectra were recorded down to 200 cm^{-1}. Unfortunately, the ν(Mn–I) frequency would be expected to occur below this; however, a broad band at *ca.* 320 cm^{-1} was seen for each complex, assignable to ν(Mn–N), Table 1. Attempts to record the EPR spectra in the solid state at both room temperature and at 77 K revealed no fine structure, only broad unresolved bands being displayed. The low solubility of the $[MnI_2(NR_3)]$ compounds in most organic solvents, and their extreme sensitivity to minute amounts of moisture or dioxygen, particularly in solution, has precluded any EPR studies being made in solution.

Recrystallisation of $[MnI_2(NEt_3)]$ and $[MnI_2(NPr^n_3)]$ in diethyl ether under dry argon produced orange-pink crystals of both complexes suitable for X-ray diffraction studies. The crystal structures were determined and are shown in Figs. 1 and 2. Both complexes are dinuclear with pseudo-tetrahedral manganese centres bridged by two iodine atoms; the two structures are very similar. The bridged Mn_2I_2 moiety is planar in each case; however, a slight lengthening of the bridge Mn–I bonds is seen for the tri-*n*-propylamine complex compared to the triethylamine analogue. This is probably due to the more sterically demanding *n*-propyl groups. Selected bond distances and angles for both complexes are given in Table 2. These are the first two crystallographically characterised examples of manganese(II) halide complexes containing tertiary amine bonds.

The formation of a dinuclear complex rather than the expected polymeric structure may be explained by steric considerations. Recent studies extending the cone-angle concept to nitrogen-donor ligands show a greater steric requirement for tertiary amines than for their phosphorus analogues.[20] The Tolman cone angle, θ, for PEt_3 is 132°, whereas those of NEt_3 and NPr^n_3 are 150 and 160°, respectively. The manganese(II) complexes $[MnBr_2(PEt_3)]$ and $[MnI_2(PMeEt_2)]$[21] have been shown by X-ray diffraction to be polymeric with five-co-ordinate trigonal-bipyramidal geometry at each manganese centre. In the present study, the greater steric requirements of the tertiary amines may be too large to allow for five-co-ordination at the manganese, thus leading to the observed four-co-ordinate dinuclear structures. It is also interesting that the only dimeric manganese(II) phosphine complex of stoichiometry $[MnI_2(PR_3)]_2$ contains the ligand $P(NMe_2)_3$,[22] which has an unusually large cone angle of 157°, *i.e.* very similar to that of NPr^n_3, again supporting the assertion that it is the steric requirements of the ligands which is crucial in determining the structure of the resultant manganese complex.

Table 2 Selected bond lengths (Å) and angles (°) for $[\{MnI_2(NEt_3)\}_2]$ and $[\{MnI_2(NPr_3)\}_2]$ *

	$[\{MnI_2(NEt_3)\}_2]$	$[\{MnI_2(NPr^n_3)\}_2]$
I(1)–Mn(1)	2.634(6)	2.632(6)
I(2)–Mn(1)	2.765(5)	2.782(8)
I(2)–Mn(1)	2.764(5)	2.804(8)
Mn(1)–N(1)	2.18(3)	2.17(4)
Mn(1)–I(2)–Mn(1)	80.6(1)	83.1(3)
I(1)–Mn(1)–I(2)	109.8(2)	112.5(3)
I(1)–Mn(1)–I(2)	109.2(2)	112.5(3)
I(1)–Mn(1)–N(1)	114.9(6)	110.7(9)
I(2)–Mn(1)–I(2)	99.4(1)	96.9(3)
I(2)–Mn(1)–N(1)	111.6(8)	113(1)
I(2)–Mn(1)–N(1)	110.9(6)	111(1)

* Estimated standard deviations in the least significant figure are given in parentheses.

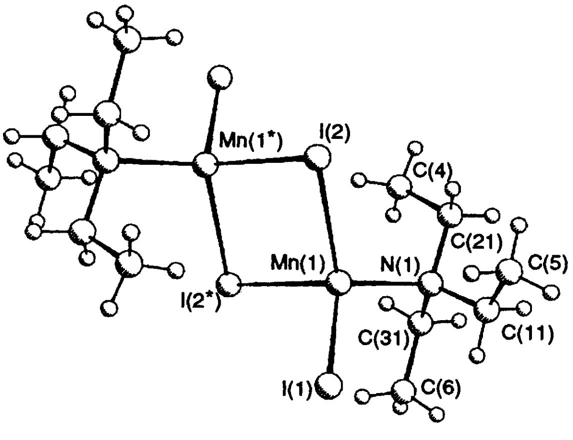

Fig. 1 Crystal structure of $[\{MnI_2(NEt_3)\}_2]$

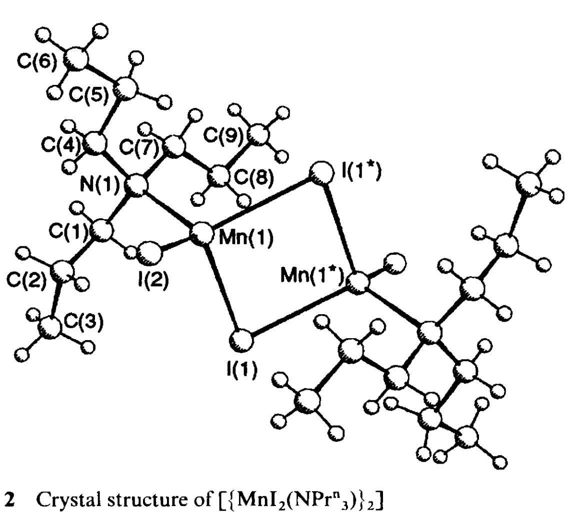

Fig. 2 Crystal structure of $[\{MnI_2(NPr^n_3)\}_2]$

Reaction of Trimethylamine with Manganese(II) *Halides*.—The complex $[MnBr_2(NMe_3)]$ was prepared by the reaction of freshly distilled trimethylamine with manganese(II) bromide in a toluene slurry under strictly anhydrous and anaerobic conditions. The off-white solid product could not be obtained from diethyl ether, 1,2-dichloroethane or tetrahydrofuran, there being no reaction in these solvents. Elemental analyses for the complex are given in Table 1. The infrared spectrum was recorded but was rather poorly resolved and unambiguous identification of ν(Mn–N) was not possible. Attempts to record the magnetic moment were also unsuccessful since decomposition of the sample occurred, thus rendering the results somewhat ambiguous. Attempts to prepare the diiodo- and dichloro-analogues in toluene were less successful. No complex of manganese(II) chloride with trimethylamine could be prepared, which may be due to the low solubility of the manganese(II) salt in most organic solvents.

Reaction of trimethylamine with manganese(II) iodide in diethyl ether yielded a series of beige products with varied stoichiometry. In each case the molar ratio of manganese : amine was in excess of 1. It is possible that a mixture of the bis and mono adducts, $[MnI_2(NMe_3)_2]$ and $[MnI_2(NMe_3)]$ was obtained in varying proportions. In an attempt to recrystallise the adducts from diethyl ether light orange crystals were formed. Single-crystal X-ray analysis showed that these were the ionic complex $[NHMe_3][MnI_3(NMe_3)]$. The structure (Fig. 3, Table 3) consists of a tetrahedral anion with a trimethylammonium counter ion. The presence of a proton in the ammonium ion could not be confirmed by X-ray diffraction alone. However, the infrared spectrum of the complex shows a broad band at 2739 cm^{-1}, indicative of ν(N–H) in an ammonium ion.

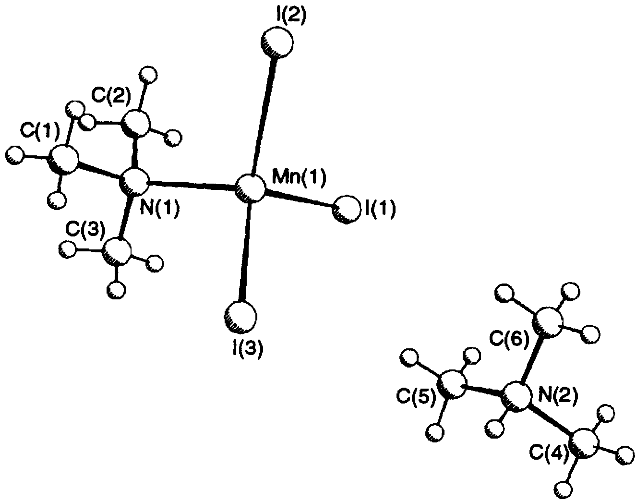

Fig. 3 Crystal structure of $[NHMe_3][MnI_3(NMe_3)]$

Table 3 Selected bond lengths (Å) and angles (°) for $[NHMe_3][MnI_3(NMe_3)]$

I(1)–Mn(1)	2.784(8)	I(3)–Mn(1)	2.680(7)
I(2)–Mn(1)	2.680(7)	Mn(1)–N(1)	2.20(2)
I(1)–Mn(1)–I(2)	111.9(2)	I(2)–Mn(1)–I(3)	113.4(3)
I(1)–Mn(1)–I(3)	114.7(2)	I(2)–Mn(1)–N(1)	107.0(6)
I(1)–Mn(1)–N(1)	103.3(6)	I(3)–Mn(1)–N(1)	105.6(5)

It seems unlikely that the proton in the ammonium ion is derived from the solvent, diethyl ether. We therefore believe that the formation of this ionic complex is due to the presence of a trace quantity of moisture. The reaction of transition-metal complexes of trimethylamine with moisture to yield the trimethylammonium cation is not unknown. Willey and co-workers[18] observed the formation of the polymeric complexes $[NHMe_3][MnCl_3]$ and $[NHMe_3][CdCl_3]$ from the reaction of $[MCl_2(NMe_3)]$ with trace quantities of water. Without any knowledge of the parent molecule in this case, however, it is not possible to speculate upon how the ionic complex was formed.

Reaction of Complexes $[MnX_2(NR_3)]$ (X = I *or* Br; R = *alkyl*) *with Dioxygen.*—The three complexes $[MnI_2(NR_3)]$ (R = Me, Et or Pr^n) react rapidly with dioxygen in the solid state at room temperature. Quantitative measurements were made of the amount of dioxygen absorbed by these under anhydrous conditions over a period of up to 25 d, Table 4.

The O_2 : Mn ratio for the dioxygen uptake measurements of the trimethylamine complex $[MnBr_2(NMe_3)]$ is only 7.4×10^{-4} : 1, essentially indicating that this complex does not react with dioxygen at ambient temperatures. For the other complexes, $[MnI_2(NEt_3)]$ and $[MnI_2(NPr^n_3)]$, initial reaction of the solid with dioxygen occurs within 1–2 min of exposure to the gas. This can be observed by the intense darkening of the solid samples from pale orange/peach to dark brown. Initial uptake of dioxygen is small, however, and it is thought that the intense colouration is due to dioxygen absorption on the surface of the sample. Further reaction of the complex with dioxygen is then diffusion controlled. The complexes were measured to take up between 1.64 and 1.98 mol of dioxygen per mol of manganese by weight increase. Elemental analysis of the dioxygen adducts revealed that whilst the NEt_3 complex takes up 2 mol of dioxygen in the solid state its tri-*n*-propylamine analogue takes up only 1 mol, Table 5. The larger uptake of dioxygen, Table 5, recorded for the quantitative measurements of $[MnI_2(NPr^n_3)]$ may be explained by the presence of some labile dioxygen which is rapidly removed on reduction of the partial pressure of dioxygen above the sample, but attempts to remove all the dioxygen from the complexes by heat or vacuum were unsuccessful. The adducts remained the same at temperatures from 20 to 80 °C. Thus, in contrast to the reaction of their phosphine analogues, the manganese(II) amine complexes do not bind dioxygen reversibly.

The reaction of these complexes with dioxygen was also studied at lower temperatures. It was the same although somewhat slower at temperatures from 0 to −20 °C. Below this temperature no reaction occurred. The reaction with dioxygen must therefore be thermodynamically controlled. After exposure of the amine complexes to dioxygen an intractable brown tar resulted which was insoluble in common organic solvents and exhibited no bands in the infrared spectrum which could result from dioxygen binding. Clearly the complexes had decomposed.

Conclusion

Four complexes of manganese(II) halides with tertiary amines have been prepared; $[MnX_2(NR_3)]$ (X = I, R_3 = $MeEt_2$, Et_3 or Pr^n_3; X = Br, R_3 = Me_3). The two iodo-complexes,

Table 4 Solid-state dioxygen uptake measurements for $[MnX_2(NR_3)]$ complexes at room temperature

	Initial mass			Mass of O_2		
Complex	g	10^4 mol	Final mass/g	g	10^4 mol	Total uptake O_2 : Mn
$[MnBr_2(NMe_3)]$	0.4634	16.9	0.4653	4.0×10^{-4}	0.125	7.40×10^{-4}
$[MnI_2(NEt_3)]$	0.3558	8.678	0.4108	0.055	17.19	1.98
$[MnI_2(NPr^n_3)]$	0.2257	4.99	0.2518	0.0261	8.16	1.64

$[MnI_2(NEt_3)]$ and $[MnI_2(NPr^n{}_3)]$, have been characterised by X-ray crystallography, and shown to consist of a dimeric iodide-bridged structure with tetrahedral manganese centres. These are the first structurally characterised examples of molecular manganese(II) tertiary amine complexes.

An attempt was made to grow crystals of the diiodo-complex $[MnI_2(NMe_3)]$, from diethyl ether. Trace moisture contamination of the complex resulted in the formation of the ammonium salt, $[NHMe_3][MnI_3(NMe_3)]$, which was crystallographically characterised. In contrast to its chloride complex $[NHMe_3][MnCl_3]$, which adopts a polymeric structure,[18] the structure of this complex consists of a discrete tetrahedral, monomeric anion with a trimethylammonium counter ion. The presence of the anion as a monomer rather than a polymer must be due to the greater steric bulk of the iodide ligands, compared with that of the chloride anions.

A comparison has been made of the dioxygen activity of some of these complexes with that of the phosphorus analogues, $[MnI_2(PR_3)]$. The phosphine complexes have previously been shown to bind dioxygen reversibly in the solid state, the dioxygen being removed at room temperature or above. The amine analogues, however, react irreversibly with dioxygen. Intractable black tars are formed which have not been characterised. The reaction with dioxygen is thought to lead to a breakdown of the tertiary amine complexes, resulting ultimately in the formation of manganese(IV) oxide. This could not be verified with absolute certainty, however, since analytical data on a series of samples exhibited some inconsistency in the manganese content. However, the infrared spectra recorded for the brown tars which resulted from exposure of the $[MnI_2(NEt_3)]$ and $[MnI_2(Pr^n{}_3)]$ complexes to dioxygen showed single broad bands at 544 and 592 cm^{-1}, respectively. These values are not inconsistent with other recorded[23] values for ν(Mn–O) and therefore support our assertion that the brown tars are essentially crude samples of MnO_2.

Table 5 Microanalyses of complexes $[MnX_2(NR_3)]$ and their products upon dioxygen uptake in the solid state

Product	Analysis (%)[a]			
	C	H	N	X
$[MnBr_2(NMe_3)]$[b]	12.8 (13.1)	3.2 (3.3)	4.7 (5.1)	58.6 (58.4)
$[MnI_2(NEt_3)]\cdot 2O_2$[b,c]	15.3 (15.2)	3.1 (3.2)	3.0 (3.2)	55.3 (53.6)
$[MnI_2(NEt_3)]$[d]	17.3 (17.6)	3.9 (3.7)	3.3 (3.4)	
$[MnI_2(NPr^n{}_3)]\cdot O_2$[b]	22.7 (22.3)	4.4 (4.3)	2.7 (2.9)	52.9 (52.5)
$[MnI_2(NPr^n{}_3)]$[d]	23.3 (23.9)	4.7 (4.6)	2.8 (3.1)	56.3 (56.2)

[a] Calculated values in parentheses. [b] Solid state, room temperature. [c] Mn 11.9 (11.6)%. [d] Solid state, −20 °C.

Experimental

The manganese complexes reported are extremely sensitive to air and moisture. All manipulations were therefore made under strictly anhydrous and anaerobic conditions employing a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried over sodium wire for 24 h and then distilled over CaH_2 under nitrogen prior to use. Analytical grade toluene (Vickers) was distilled over sodium–benzophenone prior to use. Both solvents were distilled into pre-dried reaction vessels and degassed thoroughly prior to use. Extreme care must be taken in the drying of the manganese salts MnI_2 and $MnBr_2$ as trace moisture contamination precludes any reaction with the tertiary amines. Finely ground $[MnX_2(H_2O)_4]$ (X = I or Br) (BDH) was heated *in vacuo* at 150 (X = Br) or 80 °C (I) for 7 h. The powder was reground and heated for 2 h at 150 (X = Br) or 100 °C (I), *in vacuo*. The temperature was then slowly increased to 180 (X = Br) or 120 °C (I) for 5–6 h. The dry salts were stored in air-tight jars in an argon-filled dry-box. Reagent-grade tertiary amines, NEt_3, $NPr^n{}_3$ and $NMeEt_2$ (Aldrich), were dried over sodium hydroxide pellets, and freshly distilled under argon prior to use. Trimethylamine (BDH) was stored in a gas-tight vessel and distilled directly into the reaction vessel.

Preparation of Manganese(II) *Amine Complexes*, $[MnX_2(NR_3)]$.—The diiodo-complexes, $[MnI_2(NR_3)]$ (R_3 = $MeEt_2$,

Table 6 X-Ray data and refinement details for manganese complexes *

	$[\{MnI_2(NEt_3)\}_2]$	$[\{MnI_2(NPr^n{}_3)\}_2]$	$[NHMe_3][MnI_3(NMe_3)]$
M	819.88	452.02	554.88
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Crystal dimensions/mm	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.3
a/Å	7.541(1)	13.526(6)	13.163(4)
b/Å	11.305(2)	7.950(4)	10.805(2)
c/Å	14.557(2)	15.725(5)	11.872(4)
β/°	104.66(2)	111.84(3)	95.76(3)
θ range for cell determination/°	7.9–14.0	7.6–8.6	15.2–17.8
$U/Å^3$	1200.6(6)	1569(2)	1680(1)
Z	2	2	4
$D_c/g\ cm^{-3}$	2.268	1.913	2.194
F(000)	756	852	1012
$\mu(Mo\text{-}K\alpha)/cm^{-1}$	60.99	46.75	61.87
No. of measured reflections	3916	3136	3289
No. of reflections with $I \geqslant 3\sigma(I)$	1487	717	1154
θ Range/°	2–24	2–24	2–25
% Decomposition corrected for	10	16	7
Minimum/maximum transmission	0.83, 1.08	0.89, 1.05	0.70, 1.16
Diffractometer	CAD-4	Rigaku AFC6S	Rigaku AFC6S
k in weighting scheme	0.0001	0.01	0.01
No. of refined parameters	89	73	104
Maximum shift/e.s.d.	0.06	0.10	0.04
Maximum and minimum residual electron density/e $Å^{-3}$	1.48, −1.64	0.88, −0.83	0.76, −0.81
R	0.074	0.079	0.058
R'	0.064	0.062	0.059

* Details in common: monoclinic; λ(Mo-Kα) 0.710 69 Å; H atoms in calculated positions; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o) + kF_o^2]$.

Table 7 Fractional atomic coordinates for the non-hydrogen atoms of $[\{MnI_2(NEt_3)\}_2]$

Atom	*x*	*y*	*z*
I(1)	1.0434(3)	0.7932(1)	−0.1299(1)
I(2)	1.2766(2)	0.5127(1)	0.0765(1)
Mn(1)	0.9787(5)	0.6573(3)	0.0046(3)
N(1)	0.896(2)	0.754(1)	0.116(1)
C(4)	0.868(4)	0.572(2)	0.208(2)
C(5)	1.190(4)	0.867(2)	0.157(2)
C(6)	0.605(3)	0.834(2)	0.004(2)
C(11)	0.975(5)	0.866(3)	0.130(3)
C(12)	1.06(1)	0.821(7)	0.172(6)
C(21)	0.969(4)	0.691(3)	0.209(2)
C(22)	0.70(1)	0.71(1)	0.127(8)
C(31)	0.699(5)	0.771(4)	0.091(3)
C(32)	0.81(1)	0.870(5)	0.075(6)

Table 8 Fractional atomic coordinates for the non-hydrogen atoms of $[\{MnI_2(NPr^n{}_3)\}_2]$

Atom	*x*	*y*	*z*
I(1)	0.4201(3)	−0.2299(4)	0.4688(2)
I(2)	0.4805(3)	−0.0104(5)	0.7471(2)
Mn(1)	0.4236(5)	0.0561(8)	0.5714(3)
N(1)	0.271(3)	0.183(5)	0.519(2)
C(1)	0.183(3)	0.062(6)	0.477(2)
C(2)	0.171(3)	−0.061(6)	0.538(2)
C(3)	0.111(4)	−0.22(1)	0.485(3)
C(3B)	0.08(1)	−0.12(2)	0.496(7)
C(4)	0.254(3)	0.286(5)	0.586(2)
C(5)	0.332(3)	0.428(5)	0.626(2)
C(6)	0.330(3)	0.484(5)	0.722(2)
C(7)	0.266(2)	0.304(5)	0.437(2)
C(8)	0.283(2)	0.235(5)	0.356(2)
C(9)	0.300(3)	0.366(5)	0.293(2)

Table 9 Fractional atomic coordinates for the non-hydrogen atoms in $[NHMe_3][MnI_3(NMe_3)]$

Atom	*x*	*y*	*z*
I(1)	0.6881(2)	0.5734(1)	0.8548(2)
I(2)	0.8445(2)	0.5989(2)	0.5391(2)
I(3)	0.6360(2)	0.2788(2)	0.5834(2)
Mn(1)	0.7637(4)	0.4474(3)	0.6852(4)
N(1)	0.891(2)	0.342(2)	0.774(2)
C(1)	0.952(3)	0.273(3)	0.685(3)
C(2)	0.965(3)	0.423(3)	0.844(3)
C(3)	0.853(3)	0.253(3)	0.840(4)
N(2)	0.360(2)	0.382(2)	0.756(2)
C(4)	0.259(3)	0.414(2)	0.799(3)
C(5)	0.435(3)	0.339(2)	0.851(3)
C(6)	0.396(3)	0.484(3)	0.689(3)

Et_3 or $Pr^n{}_3$), were all prepared by a similar method. A pre-dried argon-filled reaction vessel was charged with manganese(II) iodide (2 g, 6.5 mmol). It was then degassed and filled with argon. Diethyl ether (50 cm^3) was distilled into the vessel and degassed thoroughly. The tertiary amine (6.5 mmol) was added to the mixture against a stream of argon and the vessel again degassed. The reaction mixture was stirred for *ca.* 7 d. The resultant peach-coloured solid was isolated using standard Schlenk techniques and dried *in vacuo*. The trimethylamine complexes were prepared in a similar manner with an excess of amine being used. The complex $[MnBr_2(NMe_3)]$ was prepared in toluene.

Reaction of $[MnI_2(NR_3)]$ *Complexes with Dioxygen in the Solid State*.—The manganese(II) amine complex was placed in a small pre-weighed, argon-filled Rotaflo tube against a flow of argon. The tube was evacuated, filled with argon and weighed, to determine the mass of sample used. It was again evacuated and the vacuum released with 1 atm (*ca.* 10^5 Pa) anhydrous dioxygen. The tube was reweighed and dioxygen added to the tube daily until the mass of the tube remained constant for 3 d.

Crystal Structure Determinations and Refinements.—Crystal data, details of X-ray measurements and computational methods for $[\{MnI_2(NEt_3)\}_2]$, $[\{MnI_2(NPr^n{}_3)\}_2]$ and $[NHMe_3][MnI_3(NMe_3)]$ are presented in Table 6. All samples were handled under dry argon and sealed in Lindeman tubes for X-ray investigation. Unit-cell parameters were derived from the setting angles of 25 accurately centred reflections and data collection was performed using ω–2θ scans. Lorentz, polarisation, decomposition and absorption (azimuthal scan technique) corrections were applied. The structures were solved using the SHELXS 86[24] program and refined by full-matrix least squares based on *F* using the TEXSAN suite of programs.[25]

Disorder of the three methylene carbons C(11), C(21), C(31) in $[\{MnI_2(NEt_3)\}_2]$ was represented by a set of three partially occupied (31%) carbon sites C(12), C(22), C(32) staggered relative to the major conformer. A terminal methyl group in $[\{MnI_2(NPr^n{}_3)\}_2]$ was also disordered over two sites (77:23). Final atomic coordinates for non-hydrogen atoms are presented in Tables 7–9.

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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