Syntheses of Nonacarbonylbis(μ_3-ethoxy)(μ_2-halogeno)trimanganese Complexes, the Crystal Structures of the Fluoride and Iodide, and the Crystal Structure of Octacarbonyl(dimethylphenylphosphine)bis(μ_3-ethoxy)(μ_2-ethoxy)trimanganese †

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Nonacarbonylbis(μ_3-ethoxy)(μ_2-ethoxy)trimanganese reacts with all four boron trihalides to give the corresponding halogeno-complexes [$Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}X)$] (X = F, Cl, Br, or I). The chloro- and bromo-complexes have also been made from the anhydrous hydrogen halides. *X*-Ray analyses of the fluoride and iodide have shown the structure to consist of three Mn(CO)$_3$ units in a scalene triangular cluster, with two face bridging ethoxy-groups and one edge-bridging halogeno-ligand. For comparison, we have also recorded the structure of [$Mn_3(CO)_8(PMe_2Ph)(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$].

PREVIOUSLY we have reported [1,2] the synthesis of the trimeric tricarbonylalkoxymanganese complexes. These have [1] a remarkable unsymmetrical trimanganese cluster structure.

We have already noted that it was possible to selectively replace edge-bridging alkoxy-groups by other alkoxy-groups as illustrated in equation (1). This

$$[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)] + ROH \longrightarrow [Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OR)] + EtOH \quad (1)$$

selective reaction was attributed to the edge-bridging alkoxy-group having nucleophilic character conferred by the remaining unco-ordinated lone pair of electrons. This prompted us to investigate further the nucleophilic character of the tricarbonylalkoxymanganese trimers.

RESULTS

Nonacarbonylbis(μ_3-ethoxy)(μ_2-ethoxy)trimanganese underwent immediate reaction with all four boron trihalides according to equation (2) (X = F, Cl, Br, or I).

$$[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)] + BX_3 \longrightarrow [Mn_3(CO)_9(OEt)_2X] + BX_2(OEt) \quad (2)$$

All of these ethoxyhalogenocarbonyls of manganese are formed as red crystals, which appeared indefinitely stable in air in solution and as solids. The rarity of metal carbonyl fluorides makes the isolation of the fluoride [$Mn_3(CO)_9(OEt)_2F$] *via* boron trifluoride especially interesting.

The chloride and bromide were also prepared by the action of the corresponding hydrogen halide upon the trimeric ethoxide according to equation (3) (X = Cl or Br).

$$[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)] + HX \longrightarrow [Mn_3(CO)_9(OEt)_2X] + EtOH \quad (3)$$

Hydrogen fluoride did not undergo this reaction, due presumably to the very strong H–F bond of the acid.

The i.r. spectra, in the metal carbonyl region, of the halides [$Mn_3(CO)_9(OEt)_2X$] (X = F, Cl, Br, or I) consisted of nine distinct bands, closely resembling [2] the corresponding spectra of the trimer [$Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$]. Whereas the ^1H and ^{13}C n.m.r. spectra of the trimer show distinctively the presence of the face- and edge-bridging ethoxy-groups, the n.m.r. spectra of the halides [$Mn_3(CO)_9(OEt)_2X$] (X = F, Cl, Br, or I) indicate the presence of only one type of ethoxy-group. The positions of the resonances suggest the retention of the μ_3-OEt groups, by analogy with the parent ethoxide. The ^{19}F n.m.r. spectrum of [$Mn_3(CO)_9(OEt)_2F$] showed one broad symmetrical resonance at 312.5 p.p.m. upfield of C_6F_6. This very high value is probably attributable to the shielding of the fluorine nucleus by the two manganese atoms with which it is associated. No proton–fluorine couplings were observed, and no temperature dependence of ^1H n.m.r. spectra of [$Mn_3(CO)_9(OEt)_2X$] (X = F, Cl, Br, or I) was observed between −80 and +90 °C.

The mass spectra of these halides did not show a molecular ion; in each case the highest observed *m/e* corresponded to $[M - 2CO]^+$. This was followed by consecutive loss of all carbon monoxide ligands to $[M - 9CO]^+$, which was the base peak in each case. The ion $[M - 9CO]^+$ then lost Mn–OEt in preference to Mn–X, since $[Mn_2(OEt)_2]^+$ was never observed. The ion $[Mn_2(OEt)X]^+$ then decomposed *via* two pathways to Mn^+.

We have determined the crystal structures of [$Mn_3(CO)_9(OEt)_2F$], [$Mn_3(CO)_9(OEt)_2I$], and [$Mn_3(CO)_8(PMe_2Ph)(OEt)_3$]. These are referred to as compounds (1), (2), and (3) respectively, in the ensuing discussion of structures.

DISCUSSION

The dimensions of the triangle of manganese atoms remain remarkably constant in the three compounds. The triangle has one long side with lengths in the range 3.15—3.22 Å, a side with the bridging X group having lengths in the range 2.83—2.87 Å, and a short side, showing the greatest variation in length, from 2.54 to 2.70 Å (Figure 1). The Mn–Mn bond is 2.92 Å in [$Mn_2(CO)_{10}$],[3] and the Mn ··· Mn separation is 3.743(8) Å in [$Mn_2(CO)_8Br_2$],[4] a structure where the non-bonded manganese atoms are separated by two bridging bromine atoms. The manganese atoms in all three compounds therefore have two strong metal bonds [Mn(1)–Mn(3) and Mn(2)–Mn(3)] and one weak bond [Mn(1)–Mn(2)]. The Mn(2)–X–Mn(3) angles are 93(1) (F), 60.9(2) (I), and 92.1(6)° (OEt). In each case this

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† Recommended names for complexes (1)—(3) whose structures were determined are: 1,1,1,2,2,2,3,3,3-nonacarbonyl-di-μ_3-ethoxo-1,2-μ-fluoro-trimanganese; 1,1,1,2,2,2,3,3,3-nonacarbonyl-di-μ_3-ethoxo-1,2-μ-iodo-trimanganese; and 1,1,2,2,2,3,3,3-octacarbonyl-dimethylphenylphosphine-1,2-μ-ethoxo-di-μ_3-ethoxo-trimanganese, respectively.

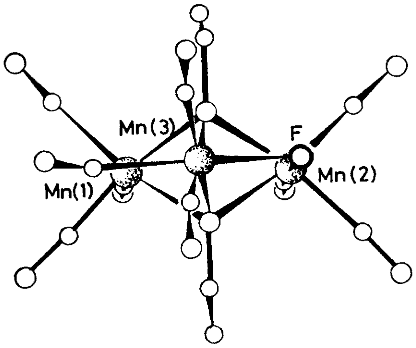
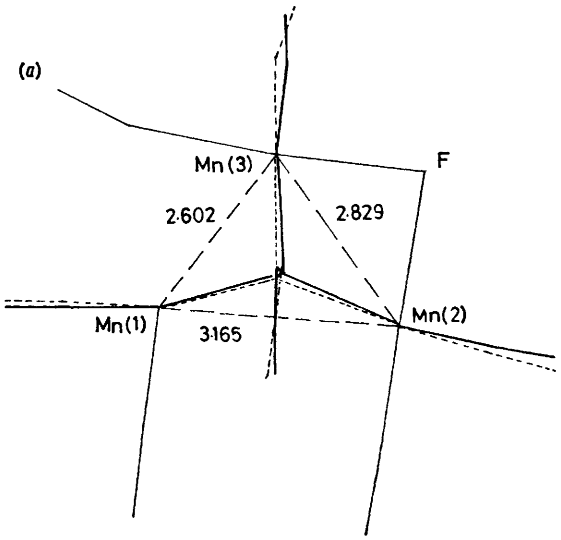


FIGURE 1 Compound (1) viewed at an angle of 5° to the Mn$_3$ plane

angle is more acute (very much more so for the iodine) than would be expected, and there must be some strain on the Mn(2)-Mn(3) bond which tends to lengthen it. The reduction in bond order in this Mn(2)-Mn(3) bond could well be compensated by an increase in the bond order of Mn(1)-Mn(2) which would otherwise have been effectively non-bonded. The two Mn-X bond lengths in the fluoride and ethoxide are practically equivalent (mean 1.95 for F, 1.99 Å for OEt), but those in the iodide are significantly different [I-Mn(2) 2.892(6), I-Mn(3) 2.689(6) Å]. The increase in Mn-X bond length from fluoride to iodide is responsible for the very acute Mn(2)-I-Mn(3) bond angle.

The two ethoxy-groups above and below the plane of the three metal atoms form equivalent bonds with each of the three manganese atoms. The mean O(1)-Mn and O(2)-Mn distances are 1.99 and 1.98 Å for compound (1), 2.04 and 2.08 Å for (2), and 2.05 and 2.05 Å for (3). The Mn-O-Mn angles reflect the differences in the three Mn-Mn distances; *e.g.* for compound (1) the angles about O(1) are Mn(1)-O(1)-Mn(2) 106°, Mn(1)-O(1)-Mn(3) 83°, and Mn(2)-O(1)-Mn(3) 90°. The mean values of these three angles and those about O(2) fall in the range 89—93° for the three compounds. The marked similarities in the bond lengths and angles suggest that these ethoxy-groups have the same function in all three compounds, although the bond lengths are slightly shorter and the mean angles slightly larger in the fluoride.



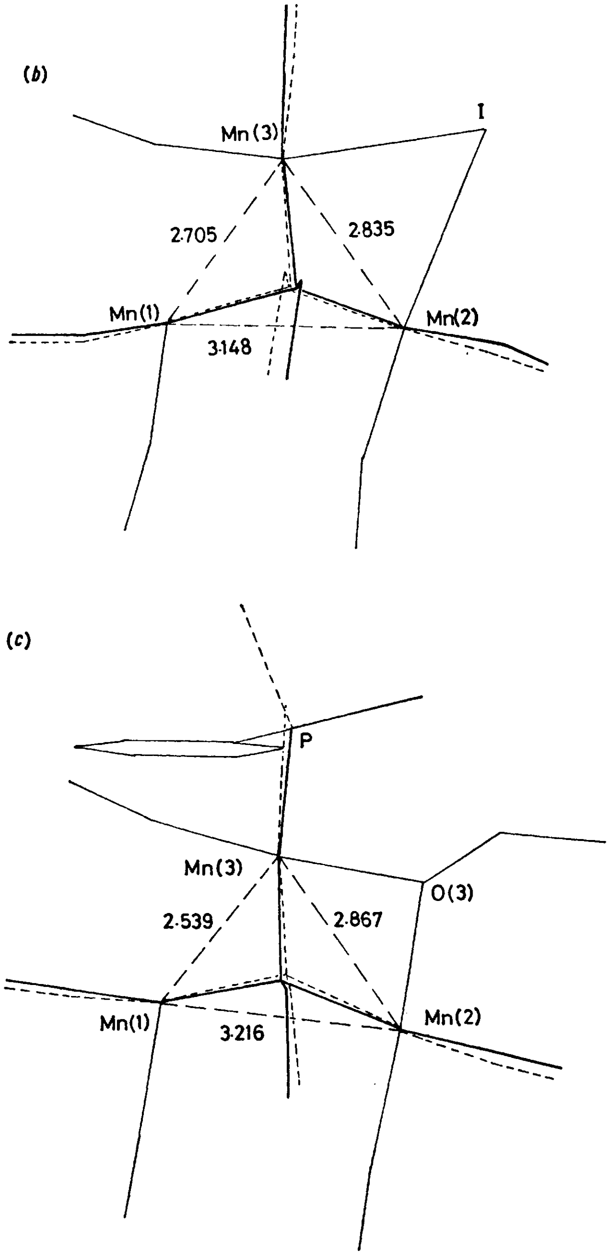


FIGURE 2 The molecules of the compounds (1)—(3) viewed perpendicular to the Mn$_3$ plane
(a) = F, (b) = I, (c) = OEt

The carbonyl groups on each manganese atom are arranged so that one is in the plane of the three manganese atoms, one is above it and the other below it (Figures 1 and 2). Many of these Mn-C-O groups show the not unusual deviation from linearity, the most acute angle being 159° [Mn(3)-C(31)-O(31) in the iodide]. The mean Mn-C-O angle of all groups in all three compounds is 173°. There is no distinguishable difference among the various Mn-C and C-O bond lengths, for

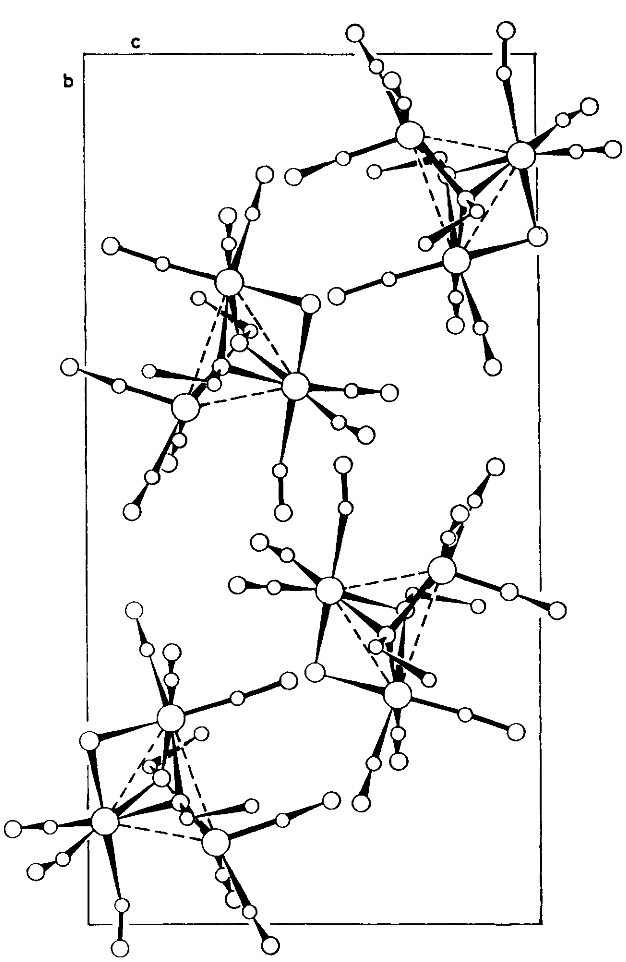


FIGURE 3 Unit cell of compound (1)

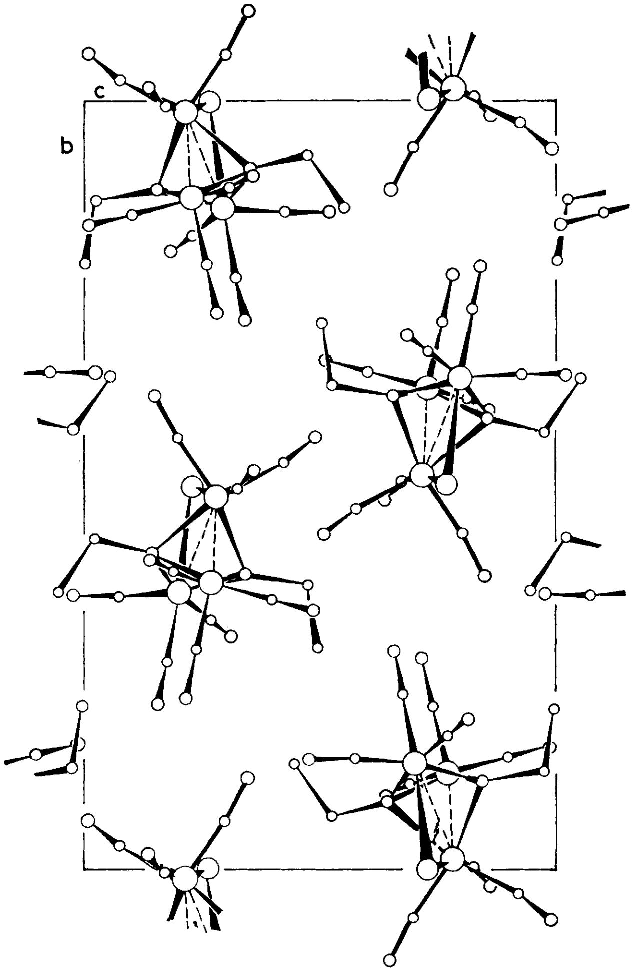


FIGURE 4 Unit cell of compound (2)

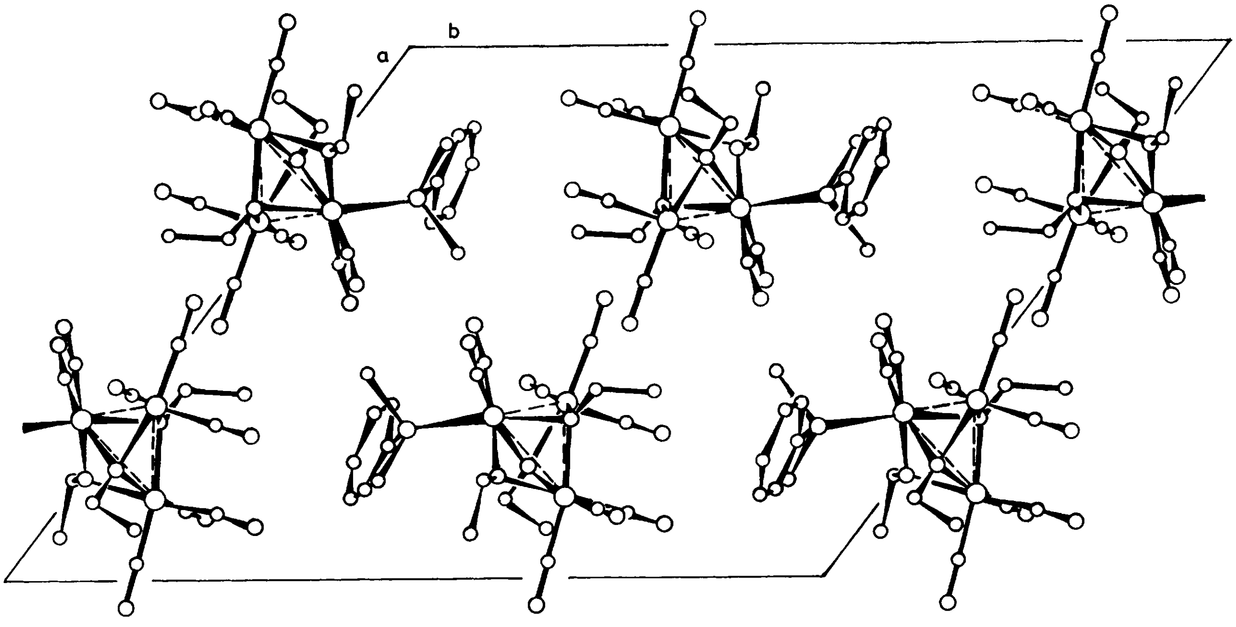


FIGURE 5 Unit cell of compound (3)

which the overall mean values are 1.76 and 1.15 Å respectively.

Bridging fluoride ions seem to be the least common amongst the halide ions. Nevertheless they are well established. Iridium fluoride, IrF_4, is constructed from octahedral IrF_6 units in which four vertices are common.[5] Similarly VOF_3 contains bent fluorine bridges [6] with a mean V–F bond length of 1.94 Å and a V–F–V angle of 106°, and bent fluorine bridges occur for most of the first transition metals, including manganese, in the system Ba_2MF_6, where M = Cr, Mn, Fe, Co, Ni, or Zn.[7] However, compound (1) is the first example of a bent fluorine bridge in a manganese carbonyl. A bent bridge has been observed in $[Re(CO)_5F]\cdot ReF_5$,[8] where the distance from fluorine to $Re(CO)_5$ is 2.17(4) Å and the Re–F–Re angle is 141(1)°. The average Mn–F distance is 1.95(2) Å. The difference between this and the Re–F distance may be attributed to the difference in the covalent radii of Mn and Re atoms.[9]

EXPERIMENTAL

All reactions were carried out routinely under an atmosphere of dry nitrogen, and all solvents were dried by distillation from potassium–benzophenone. Infrared spectra were recorded in hexane solution using calcium fluoride 0.1 mm cells on a Perkin-Elmer 257 spectrophotometer. Hydrogen-1 n.m.r. spectra were obtained on a JEOL MH100 spectrometer and ^{19}F spectra on a JEOL JNM-PS-100 spectrometer, all in deuteriochloroform solutions. Mass spectra were recorded on a Perkin-Elmer–Hitachi RMU-6 spectrometer.

Interactions of Nonacarbonylbis(μ_3-ethoxy)(μ_2-ethoxy)trimanganese.—With boron trifluoride. Through a stirred solution of the carbonyl (0.2 g) in hexane (20 cm^3) was bubbled boron trifluoride for 15 min. Solvent was then removed (20 °C, 10 mmHg *), and the remaining red solid further pumped (15 min at 20 °C, 0.01 mmHg) to remove last traces of boron trifluoride. The residue was dissolved in warm hexane (40 °C), the solution filtered, and the product crystallized at −20 °C as nonacarbonylbis(μ_3-ethoxy)(μ_2-fluoro)trimanganese (0.14 g, 75%), a red crystalline solid (Table 1).

With boron trichloride. To a stirred solution of the carbonyl (0.2 g) in hexane (20 cm^3) at 0 °C was added boron trichloride (1 g, an excess). After warming to room temperature the mixture was allowed to stand for 30 min. Solvent was removed under reduced pressure (20 °C, 10 mmHg) and the resulting red solid was pumped (30 min at 25 °C, 0.01 mmHg). The residue was dissolved in hexane (40 °C), the solution filtered, and the product crystallized at −20 °C as nonacarbonylbis(μ_3-ethoxy)(μ_2-chloro)trimanganese (0.16 g, 80%), red crystals (Table 1).

TABLE 1

The nonacarbonylbis(μ_3-ethoxy)(μ_2-halogeno)trimanganese complexes

	Analysis (%)							
	Found			Calc.				
Complex	C	H	Halogen	C	H	Halogen	ν(CO) bands * (cm^{-1})	^{1}H N.m.r. δ/p.p.m.
$[Mn_3(CO)_9(OEt)_2F]$	29.2	1.85	3.3	29.6	1.90	3.6	2 069 (1.3) 2 043 (7.8) 2 037 (10) 1 992 (6.3) 1 963 (7.2) 1 957 (8.3) 1 951 (sh) 1 931 (6.6) 1 911 (2.3)	1.60 (t) Me 3.95 (q) CH_2
$[Mn_3(CO)_9(OEt)_2Cl]$	28.3	1.75	6.4	28.7	1.85	6.5	2 071 (1.1) 2 047 (9.1) 2 040 (10) 2 997 (7.5) 1 970 (7.2) 1 963 (10) 1 959 (sh) 1 937 (7) 1 907 (2.8)	1.48 (t) Me 3.38 (q) CH_2
$[Mn_3(CO)_9(OEt)_2Br]$	26.1	1.60	13.4	26.5	1.70	13.6	2 079 (0.5) 2 045 (9.6) 2 031 (10) 1 994 (6.2) 1 961 (5.4) 1 953 (10) 1 949 (sh) 1 935 (6) 1 905 (1.7)	1.47 (t) Me 3.36 (q) CH_2
$[Mn_3(CO)_9(OEt)_2I]$	24.1	1.45	19.7	24.6	1.55	20.0	2 065 (1.5) 2 040 (10) 2 034 (9.3) 1 991 (7.4) 1 969 (5.1) 1 961 (7.9) 1 953 (2.8) 1 936 (4.5) 1 901 (2)	1.44 (t) Me 3.25 (q) CH_2

* Relative peak heights are given in parentheses.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 2

Atomic parameters

Atom	x/a	y/b	z/c
(*a*) Compound (1): $\times 10^4$ for Mn, $\times 10^3$ for C, F, and O			
Mn(1)	2 041(7)	4 063(3)	2 194(6)
Mn(2)	3 063(7)	2 628(2)	3 169(5)
Mn(3)	2 648(8)	3 821(2)	4 632(6)
F	328(2)	289(1)	497(2)
O(1)	367(3)	360(1)	300(2)
O(2)	150(3)	332(1)	340(2)
C(1)	514(5)	379(2)	282(4)
C(2)	568(5)	364(2)	139(4)
C(3)	15(5)	318(2)	364(4)
C(4)	−70(6)	281(2)	249(5)
C(11)	191(3)	380(2)	72(3)
O(11)	163(4)	359(2)	−38(4)
C(12)	43(5)	443(3)	205(4)
O(12)	−64(5)	470(1)	179(4)
C(13)	305(5)	486(2)	145(4)
O(13)	363(4)	525(2)	96(4)
C(21)	289(3)	241(2)	169(3)
O(21)	281(3)	220(1)	55(3)
C(22)	468(5)	219(2)	317(4)
O(22)	571(4)	187(1)	315(3)
C(23)	217(4)	184(2)	370(3)
O(23)	154(3)	139(1)	397(3)
C(31)	189(4)	478(3)	428(3)
O(31)	175(4)	527(1)	433(4)
C(32)	170(7)	388(2)	585(3)
O(32)	80(5)	390(1)	668(4)
C(33)	396(6)	424(2)	557(3)
O(33)	484(4)	439(1)	617(3)
(*b*) Compound (2): $\times 10^4$ for Mn and I, $\times 10^3$ for C and O			
Mn(1)	4 239(5)	1 265(3)	2 288(6)
Mn(2)	1 076(5)	1 395(3)	2 972(6)
Mn(3)	2 612(3)	144(3)	2 173(6)
1	−76(2)	17(1)	2 687(3)
O(1)	227(2)	116(1)	157(3)
O(2)	286(2)	88(1)	355(2)
C(1)	195(4)	130(2)	26(4)
C(2)	216(5)	211(3)	4(4)
C(3)	317(5)	70(3)	475(5)
C(4)	344(4)	140(2)	554(4)
C(11)	455(5)	213(2)	260(4)
O(11)	493(3)	277(2)	283(3)
C(12)	575(3)	112(2)	310(3)
O(12)	679(3)	97(2)	358(3)
C(13)	518(4)	148(2)	102(4)
O(13)	590(3)	163(2)	12(3)
C(21)	162(3)	230(2)	323(3)
O(21)	180(3)	285(2)	343(3)
C(22)	−37(4)	176(2)	230(4)
O(22)	−136(3)	196(1)	186(3)
C(23)	10(4)	145(2)	425(4)
O(23)	−34(3)	144(1)	523(3)
C(31)	443(4)	6(2)	174(4)
O(31)	540(3)	−19(2)	139(3)
C(32)	283(4)	−61(2)	301(4)
O(32)	306(3)	−117(2)	350(3)
C(33)	215(5)	−29(3)	77(5)
O(33)	185(3)	−63(2)	9(3)
(*c*) Compound (3): $\times 10^4$ for Mn and P, $\times 10^3$ for C and O			
Mn(1)	6 710(2)	5 221(1)	1 652(3)
Mn(2)	8 478(1)	6 084(1)	3 872(3)
Mn(3)	6 956(1)	4 448(1)	3 430(1)
P	7 181(3)	3 516(3)	2 968(6)
O(1)	701(1)	543(1)	378(1)
O(2)	791(1)	535(1)	206(1)
O(3)	808(1)	504(1)	469(1)
C(1)	644(1)	545(1)	485(1)
C(2)	651(1)	620(1)	466(2)
C(3)	853(1)	536(1)	102(1)
C(4)	907(1)	614(1)	11(2)
C(5)	813(1)	492(1)	617(2)
C(6)	916(1)	527(1)	663(2)
C(11)	709(1)	613(1)	83(2)
O(11)	731(1)	668(1)	30(2)

TABLE 2 (*Continued*)

Atom	x/a	y/b	z/c
C(12)	650(1)	483(1)	−113(2)
O(12)	633(1)	456(1)	−112(2)
C(13)	558(1)	495(1)	171(2)
O(13)	476(1)	473(1)	172(2)
C(21)	879(1)	700(1)	297(2)
O(21)	902(1)	757(1)	256(2)
C(22)	870(1)	658(1)	554(2)
O(22)	886(1)	250(1)	344(2)
C(23)	965(2)	645(1)	380(2)
O(23)	1 051(1)	674(1)	381(2)
C(31)	592(1)	385(1)	235(2)
O(31)	522(1)	366(1)	179(2)
C(33)	617(1)	387(1)	488(2)
O(33)	555(1)	347(1)	572(2)
C(41)	614(1)	250(1)	344(2)
C(42)	816(1)	364(1)	401(2)
C(43)	747(2)	342(1)	107(2)
C(44)	834(1)	358(1)	73(3)
C(45)	847(2)	346(1)	−67(3)
C(46)	780(2)	316(1)	−171(3)
C(47)	689(2)	297(1)	−133(2)
C(48)	671(1)	310(1)	2(2)

The corresponding bromo- and iodo-complexes were prepared in 80 and 77% yield respectively by the analogous reactions of boron tribromide and boron tri-iodide (Table 1).

With hydrogen chloride. Through a solution of the carbonyl (0.2 g) in hexane (20 cm³) was bubbled dry hydrogen chloride for 15 min. Solvent was then removed under reduced pressure (20 °C, 15 mmHg) and the red solid pumped (25 °C, 0.01 mmHg) for 15 min. The residue was dissolved in warm hexane, the solution filtered, and the product left to crystallize at −20 °C as nonacarbonylbis-(μ_3-ethoxy)(μ_2-chloro)trimanganese (0.15 g, 78%), red crystals. The corresponding bromo-complex was prepared in an analogous manner (70% yield), but $[Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)]$ was recovered unchanged after treatment with an excess of hydrogen fluoride.

X-*Ray Crystallography*.—*Crystal data*. $C_{13}H_{10}FMn_3O_{11}$, (1), $M = 526.02$, Monoclinic, $a = 9.34(1)$, $b = 19.88(2)$, $c = 10.23(1)$ Å, $\gamma = 89.65(6)°$, $U = 1\,902.04$ Å³, $Z = 4$, $D_c = 1.836$ g cm^{-3}, $F(000) = 1\,040$, space group $P2_1/b$ (C^5_{2h}, no. 14), Cu-K_α radiation, $\lambda = 1.540\,51$ Å, $\mu(\text{Cu-}K_{\alpha_1}) = 64.95$ cm^{-1}.

$C_{13}H_{10}IMn_3O_{11}$, (2), $M = 633.93$, Monoclinic, $a = 9.67(1)$, $b = 18.70(1)$, $c = 11.26(1)$ Å, $\gamma = 86.25(5)°$, $U = 2\,031.78$ Å³, $Z = 4$, $D_c = 2.072$ g cm^{-3}, $F(000) = 1\,216$, space group $P2_1/b$, Cu-K_α radiation, $\lambda = 1.540\,51$ Å, $\mu(\text{Cu-}K_\alpha) = 176.72$ cm^{-1}.

$C_{22}H_{26}Mn_3O_{11}P$, (3), $M = 662.23$, Monoclinic, $a = 17.609$ (2), $b = 21.319$ (3), $c = 9.220(2)$ Å, $\alpha = 127.16(1)°$, $U = 2\,758.44$ Å³, $Z = 4$, $D_c = 1\,594$ g cm^{-3}, $F(000) = 1\,344$, space group $P2_1/b$, Cu-K_α radiation, $\lambda = 1.540\,51$ Å, $\mu(\text{Cu-}K_\alpha) = 50.59$ cm^{-1}.

All three compounds had very deep red crystals which decompose in the *X*-ray beam. Therefore small crystals were sealed in Lindemann glass capillaries and the data were collected on a conventional Picker FACS-1 four-circle diffractometer [compounds (1) and (2)] with the fastest scan speed (2° min^{-1}), and on a CAD3 diffractometer [compound (3)] attached to a Rigaku 6-kW rotating-anode *X*-ray generator with a scan speed of 4° min^{-1}. Totals of 1 332, 1 757, and 2 734 independent reflections were measured respectively for the three compounds. Of these 973, 1 315, and 1 606 had $I > 3\sigma(I)$. Lorentz and polarization corrections were applied to all three compounds, and absorption and primary extinction corrections to (2). The

TABLE 3

Interatomic distances (Å) and angles (°)

	Compound		
	(1; X = F)	(2; X = I)	[3; X = O(3)]
Mn(1) · · · Mn(2)	3.165(7)	3.148(7)	3.216(3)
Mn(1) · · · Mn(3)	2.602(8)	2.705(8)	2.539(4)
Mn(2) · · · Mn(3)	2.829(7)	2.835(8)	2.867(3)
Mn(1)–O(1)	1.95(2)	2.09(2)	2.01(1)
Mn(1)–O(2)	1.99(2)	2.10(2)	2.00(1)
Mn(1)–C(11)	1.61(4)	1.70(4)	1.78(2)
Mn(1)–C(12)	1.68(4)	1.73(3)	1.76(2)
Mn(1)–C(13)	2.00(4)	1.76(4)	1.70(2)
Mn(2)–O(1)	2.02(2)	1.99(2)	2.07(1)
Mn(2)–O(2)	2.01(2)	2.03(2)	2.09(1)
Mn(2)–X	1.93(2)	2.892(6)	2.03(1)
Mn(2)–C(21)	1.58(3)	1.83(4)	1.87(2)
Mn(2)–C(22)	1.74(4)	1.69(4)	1.77(2)
Mn(2)–C(23)	1.86(3)	1.72(5)	1.71(3)
Mn(3)–O(1)	1.99(2)	2.03(2)	2.06(2)
Mn(3)–O(2)	1.94(2)	2.10(2)	2.05(1)
Mn(3)–X	1.97(2)	2.689(6)	1.96(1)
Mn(3)–C(31)	2.06(5)	1.82(4)	1.77(2)
Mn(3)–C(32)	1.53(5)	1.70(4)	
Mn(3)–C(33)	1.77(4)	1.85(6)	1.78(2)
O(1)–C(1)	1.44(5)	1.53(5)	1.43(3)
O(2)–C(3)	1.32(6)	1.43(6)	1.43(3)
O(3)–C(5)			1.41(2)
C(1)–C(2)	1.57(6)	1.56(6)	1.54(3)
C(3)–C(4)	1.61(6)	1.62(6)	1.56(3)
C(5)–C(6)			1.53(3)
C(11)–O(11)	1.22(5)	1.29(5)	1.10(3)
C(12)–O(12)	1.17(6)	1.16(5)	1.12(3)
C(13)–O(13)	1.06(6)	1.27(6)	1.22(3)
C(21)–O(21)	1.24(4)	1.09(4)	1.10(3)
C(22)–O(22)	1.15(5)	1.12(5)	1.16(3)
C(23)–O(23)	1.10(4)	1.18(6)	1.24(3)
C(31)–O(31)	0.99(6)	1.09(5)	1.16(2)
C(32)–O(32)	1.20(7)	1.19(5)	
C(33)–O(33)	1.07(6)	1.04(6)	1.18(2)
Mn(3)–P			2.29(1)
P–C(41)			1.86(2)
P–C(42)			1.85(2)
P–C(43)			1.87(2)
C(43)–C(44)			1.38(4)
C(43)–C(48)			1.45(3)
C(44)–C(45)			1.36(4)
C(45)–C(46)			1.36(4)
C(46)–C(47)			1.45(4)
C(47)–C(48)			1.35(3)
Mn(2)–Mn(1)–Mn(3)	57.8(2)	57.3(2)	58.4(1)
Mn(2)–Mn(1)–O(1)	38(1)	38(1)	38.5(3)
Mn(2)–Mn(1)–O(2)	38(1)	39(1)	39.1(3)
Mn(2)–Mn(1)–C(11)	92(2)	96(2)	92.9(6)
Mn(2)–Mn(1)–C(12)	133(2)	134(1)	135.7(8)
Mn(2)–Mn(1)–C(13)	134(1)	134(1)	134.7(6)
Mn(3)–Mn(1)–O(1)	49(1)	48(1)	52.3(5)
Mn(3)–Mn(1)–O(2)	48(1)	50(1)	52.1(3)
Mn(3)–Mn(1)–C(11)	149(2)	154(2)	151.1(6)
Mn(3)–Mn(1)–C(12)	111(1)	116(1)	111.3(9)
Mn(3)–Mn(1)–C(13)	114(1)	119(1)	112.3(7)
O(1)–Mn(1)–O(2)	66(1)	68(1)	70.7(5)
O(1)–Mn(1)–C(11)	107(2)	113(2)	107.4(7)
O(1)–Mn(1)–C(12)	160(2)	163(2)	163.5(11)
O(1)–Mn(1)–C(13)	99(1)	102(2)	98.3(7)
O(2)–Mn(1)–C(11)	109(2)	110(2)	105.0(8)
O(2)–Mn(1)–C(12)	98(2)	98(1)	98.4(10)
O(2)–Mn(1)–C(13)	161(1)	168(2)	164.2(7)
C(11)–Mn(1)–C(12)	89(2)	81(2)	87.2(9)
C(11)–Mn(1)–C(13)	86(2)	80(2)	88.9(10)
C(12)–Mn(1)–C(13)	93(2)	91(2)	89.6(1)
Mn(1)–Mn(2)–Mn(3)	51.1(2)	53.4(2)	48.9(1)
Mn(1)–Mn(2)–O(1)	36(1)	41(1)	37.2(3)
Mn(1)–Mn(2)–O(2)	38(1)	41(1)	37.3(4)
Mn(1)–Mn(2)–X	95(1)	109.5(2)	91.9(3)
Mn(1)–Mn(2)–C(21)	85(1)	77(1)	83.4(5)
Mn(1)–Mn(2)–C(22)	135(1)	134(2)	132.9(8)
Mn(1)–Mn(2)–C(23)	136(1)	137(1)	136.1(6)
Mn(3)–Mn(2)–O(1)	45(1)	46(1)	45.9(4)
Mn(3)–Mn(2)–O(2)	43(1)	48(1)	45.6(2)
Mn(3)–Mn(2)–X	44(1)	56.0(2)	43.0(3)
Mn(3)–Mn(2)–C(21)	136(1)	130(1)	132.3(5)
Mn(3)–Mn(2)–C(22)	122(1)	124(1)	123.7(5)
Mn(3)–Mn(2)–C(23)	119(1)	125(1)	122.1(9)
O(1)–Mn(2)–O(2)	64(1)	72(1)	68.0(5)
O(1)–Mn(2)–X	79(1)	88(1)	79.0(5)
O(1)–Mn(2)–C(21)	102(2)	98(1)	98.2(7)
O(1)–Mn(2)–C(22)	103(2)	101(2)	99.9(8)
O(1)–Mn(2)–C(23)	164(1)	170(1)	167.7(9)
O(2)–Mn(2)–X	78(1)	89(1)	77.4(5)
O(2)–Mn(2)–C(21)	103(1)	96(1)	97.7(6)
O(2)–Mn(2)–C(22)	165(2)	172(2)	167.5(6)
O(2)–Mn(2)–C(23)	102(1)	102(2)	101.9(7)
X–Mn(2)–C(21)	180(1)	174(1)	174.9(6)
X–Mn(2)–C(22)	93(1)	87(1)	97.7(8)
X–Mn(2)–C(23)	90(1)	84(1)	92.2(9)
C(21)–Mn(2)–C(22)	87(2)	89(2)	86.9(9)
C(21)–Mn(2)–C(23)	89(1)	90(2)	89.9(10)
C(22)–Mn(2)–C(23)	87(1)	85(2)	89.6(10)
Mn(1)–Mn(3)–Mn(2)	71.1(2)	69.2(2)	72.7(1)
Mn(1)–Mn(3)–O(1)	48(1)	50(1)	50.5(3)
Mn(1)–Mn(3)–O(2)	49(1)	50(1)	50.4(4)
Mn(1)–Mn(3)–X	114(1)	132.3(3)	117.6(4)
Mn(1)–Mn(3)–C(31)	66(1)	59(1)	66.5(7)
Mn(1)–Mn(3)–C(32)	130(2)	125(1)	
Mn(1)–Mn(3)–C(33)	126(1)	124(2)	124.5(9)
Mn(2)–Mn(3)–O(1)	46(1)	45(1)	46.0(3)
Mn(2)–Mn(3)–O(2)	45(1)	46(1)	46.7(3)
Mn(2)–Mn(3)–X	43(1)	63.1(2)	44.9(5)
Mn(2)–Mn(3)–C(31)	137(1)	128(1)	120.1(6)
Mn(2)–Mn(3)–C(32)	125(2)	123(1)	
Mn(2)–Mn(3)–C(33)	126(2)	121(2)	139.1(7)
O(1)–Mn(3)–O(2)	66(1)	69(1)	68.8(5)
O(1)–Mn(3)–X	79(1)	93(1)	80.7(5)
O(1)–Mn(3)–C(31)	103(1)	95(1)	102.6(9)
O(1)–Mn(3)–C(32)	169(2)	166(2)	
O(1)–Mn(3)–C(33)	104(2)	96(2)	97.3(9)
O(2)–Mn(3)–X	78(1)	93(1)	79.8(4)
O(2)–Mn(3)–C(31)	100(1)	96(1)	103.6(6)
O(2)–Mn(3)–C(32)	104(2)	97(2)	
O(2)–Mn(3)–C(33)	170(2)	164(2)	165.3(8)
X–Mn(3)–C(31)	177(1)	169(1)	175.9(8)
X–Mn(3)–C(32)	95(2)	83(1)	
X–Mn(3)–C(33)	98(2)	83(1)	93.6(7)
C(31)–Mn(3)–C(32)	83(2)	90(2)	
C(31)–Mn(3)–C(33)	84(2)	90(2)	83.6(8)
C(32)–Mn(3)–C(33)	86(3)	97(2)	
Mn(1)–O(1)–Mn(2)	106(1)	101(1)	104.3(5)
Mn(1)–O(1)–Mn(3)	83(1)	82(1)	77.3(5)
Mn(1)–O(1)–C(1)	125(2)	122(2)	126.0(12)
Mn(2)–O(1)–Mn(3)	90(1)	90(1)	88.1(7)
Mn(2)–O(1)–C(1)	122(2)	128(2)	124.3(9)
Mn(3)–O(1)–C(1)	120(2)	120(2)	122.2(10)
Mn(1)–O(2)–Mn(2)	105(1)	100(1)	103.6(6)
Mn(1)–O(2)–Mn(3)	83(1)	80(1)	77.5(4)
Mn(1)–O(2)–C(3)	121(2)	127(2)	126.9(10)
Mn(2)–O(2)–Mn(3)	91(1)	87(1)	87.7(4)
Mn(2)–O(2)–C(3)	125(2)	125(2)	120.8(8)
Mn(3)–O(2)–C(3)	121(2)	124(2)	127.9(12)
O(1)–C(1)–C(2)	112(3)	106(3)	109.5(14)
O(2)–C(3)–C(4)	116(3)	111(4)	110.7(19)
Mn(2)–X–Mn(3)	93(1)	60.9(2)	92.1(6)
Mn(2)–O(3)–C(5)			123.6(11)
Mn(3)–O(3)–C(5)			127.8(8)
O(3)–C(5)–C(6)			111.7(14)
Mn(1)–C(11)–O(11)	172(3)	174(4)	178.4(18)
Mn(1)–C(12)–O(12)	172(4)	174(3)	177.3(15)
Mn(1)–C(13)–O(13)	175(4)	178(3)	177.9(18)
Mn(2)–C(21)–O(21)	176(3)	172(3)	172.9(15)
Mn(2)–C(22)–O(22)	177(4)	176(4)	177.9(26)
Mn(2)–C(23)–O(23)	174(3)	168(4)	176.8(19)
Mn(3)–C(31)–O(31)	162(4)	159(3)	168.8(19)
Mn(3)–C(32)–O(32)	170(5)	173(4)	

TABLE 3 (*Continued*)

	Compound		
	(1; X = F)	(2; X = I)	[3; X = O(3)]
Mn(3)–C(33)–O(33)	168(4)	168(5)	171.0(20)
Mn(1)–Mn(3)–P			129.0(3)
Mn(2)–Mn(3)–P			123.9(2)
O(1)–Mn(3)–P			169.6(3)
O(2)–Mn(3)–P			102.7(4)
O(3)–Mn(3)–P			92.2(5)
C(31)–Mn(3)–P			84.9(9)
C(33)–Mn(3)–P			90.6(9)
Mn(3)–P–C(41)			113.7(9)
Mn(3)–P–C(42)			114.7(8)
Mn(3)–P–C(43)			118.3(9)
C(41)–P–C(42)			103.0(10)
C(41)–P–C(43)			103.4(9)
C(42)–P–C(43)			101.8(11)
P–C(43)–C(44)			121.4(17)
P–C(43)–C(48)			116.0(18)
C(44)–C(43)–C(48)			122.4(20)
C(43)–C(44)–C(45)			117.2(22)
C(44)–C(45)–C(46)			124.2(28)
C(45)–C(46)–C(47)			117.9(24)
C(46)–C(47)–C(48)			121.4(21)
C(47)–C(48)–C(43)			116.7(22)

crystals of compounds (1) and (3) were small and effectively spherical, so no absorption correction was thought to be necessary. In each case three standard reflections were measured after every 58 reflections and their intensities fell rapidly. A new crystal was mounted when the intensities of these standards had fallen to half their original value. Two crystals were required for compounds (1) and (2); three were needed for compound (3). The data for each crystal were reduced to a common scale by a least-squares fitting of the intensities of the standards to a first-order decay. Average values of σ for the least squares fits for the three structures were 0.021, 0.060, and 0.058 respectively, which compare with 0.012, 0.023, and 0.018 for the average estimated standard deviation (e.s.d.) of the counting statistics.

The structures were solved using the Sheldrick '*X*-RAY '76' system,[10] with a multi-solution application of the tangent formula.[11] The manganese atoms, and the iodine [compound (2)] and phosphorus [compound (3)] atoms, were located in the corresponding E map with the lowest Karle R factor.[12] The remaining atoms were located on successive Fourier syntheses. The structures were refined by full-matrix least squares (minimum $w\Delta F^2$) with isotropic temperature factors on all atoms, and by 'large-block' least squares when anisotropic temperature factors were subsequently introduced. These 'large blocks' contained all the matrix cross terms from the atom parameters in chemically distinct units. The refinements converged at $R = 0.10$, 0.09, and 0.08 respectively for the three compounds, but the final positions, particularly of carbons of the ethoxy-groups, and in some instances the carbonyl groups, are not well defined; presumably this is a consequence of the decomposition of the crystals during irradiation. The final atomic co-ordinates are given in Table 2, observed structure amplitudes, calculated structure factors, and anisotropic temperature factors, where appropriate are listed in Supplementary Publication No. SUP 22615 (35 pp.).* The atomic scattering factors were those recorded in ref. 13, and were corrected for the real part of the anomalous dispersion effect. The interatomic distances and bond angles are given in Table 3. Figure 1 shows the single molecule of the fluoride [compound (1)] and Figure 2 shows a comparison of both the configuration and the manganese cluster for the three compounds. Figures 3—5 illustrate the unit-cell packing.

The crystals of all three compounds are constructed from isolated molecules and each of these molecules contains three manganese atoms arranged on the corners of a scalene triangle. Above and below the plane defined by these three manganese atoms are the oxygen atoms of two ethoxy-groups. The oxygen atoms are bonded with equivalent bonds to all three manganese atoms. The X group (F, I, or OEt) is in the plane of the triangle and is bonded to just two of the manganese atoms, and the pendant carbonyl and phosphine groups are arranged symmetrically around this plane.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.