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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS{μ-[(TRIFLUOROMETHYL)SELENO]MANGANESE TETRACARBONYL}

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SUMMARY

The crystal structure of $[(CF_3Se)Mn(CO)_4]_2$ has been determined by single crystal X-ray diffraction. The crystals are monoclinic, $P2_1/c$, $a=6.32$, $b=15.35$, $c=9.75$ Å, $\beta=108.9°$, $Z=2$. The molecule possesses a crystallographic centre of symmetry, and is based on a planar $[MnSe]_2$ unit with four almost equal Mn–Se bonds (2.50 Å). The principal bond lengths and angles are Mn–Mn 3.74, Se–Se 3.31 Å; Se–Mn–Se 83.1°, Mn–Se–Mn 96.9°; Mn–C (mean) 1.83, C–O (mean) 1.16, Se–C 1.97, C–F (mean) 1.31 Å.

INTRODUCTION

A remarkable variety of structural types have been reported[1] for polynuclear transition metal carbonyl derivatives in which sulphur atoms or *S*-alkyl groups act as bridging ligands. The infrared spectra[2,3] of complexes of the type $[(R_FE)Mn(CO)_4]_2$ ($E=S, Se$) suggest that the two $Mn(CO)_4$ moieties are bridged by the two R_FE-ligands, where R_F is a perfluoroalkyl group. There appear to be no crystallographic data on any polynuclear carbonyl derivatives involving R_FS- or R_FSe-groups. We report here the determination of the crystal structure of bis{μ-[(trifluoromethyl)seleno]manganese tetracarbonyl}.

EXPERIMENTAL

The sample was prepared as described in ref. 3. Crystals were obtained by slow cooling of a solution in toluene, and sealed into Lindemann glass capillary tubes. Preliminary X-ray photographs revealed fairly rapid decomposition of the crystals in the X-ray beam when they were maintained at room temperature. The rate of decomposition was considerably reduced by cooling the crystals to −20°, and so all the data were collected at this temperature. Photographs were taken for crystals mounted about [100] and [001], but the [100] data were of much higher quality and so were used exclusively in the structure refinement. Intensities were determined visually from equi-inclination Weissenberg photographs taken with Ni-filtered Cu-K_α radiation (layers *0kl* to *5kl* inclusive) and a crystal of approximate dimensions 0.25 × 0.056 × 0.23 mm. Lorentz, polarisation and absorption corrections were applied. 833 unique non-zero reflections were obtained, but 15 of these were omitted from the refinements, either because they were strongly absorbed, or because their intensities were difficult to estimate. Unit cell dimensions were obtained from the single crystal photographs taken at −20°.

TABLE 1

ANALYSIS OF VARIANCE[a]

(a). As a function of sin θ

	sin θ				
	0.00–0.40	0.40–0.50	0.50–0.56	0.56–0.62	0.62–0.67
N	87	88	71	82	81
V	555	383	385	352	337

	sin θ				
	0.67–0.73	0.73–0.78	0.78–0.84	0.84–0.90	0.90–1.00
N	100	69	80	83	77
V	394	367	356	314	444

(b). As a function of $|F_{obs}|$

	$(F_{obs}/F_{max})^{\frac{1}{2}}$				
	0.00–0.25	0.25–0.29	0.29–0.32	0.32–0.35	0.35–0.37
N	82	106	75	98	58
V	411	292	334	335	359

	$(F_{obs}/F_{max})^{\frac{1}{2}}$				
	0.37–0.40	0.40–0.44	0.44–0.49	0.49–0.56	0.56–1.00
N	84	83	74	77	81
V	371	379	446	437	559

(c). As a function of parity group, etc.

	ggg	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*
N	112	124	57	120	60	118	109	118
V	391	414	365	385	356	400	370	439

	0kl	*h0l*	*hk0*	*all*
N	64	40	54	818
V	336	417	506	396

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[a] *N* is the number of F_{obs}. *V* is 100 times the root-mean-square deviation of a reflection of unit weight on an absolute scale of *F*.

Crystal data

$C_{10}F_6Mn_2O_8Se_2$, mol.wt., 629.9, monoclinic, $a=6.32(2)$[*], $b=15.35(2)$, $c=9.75(1)$ Å, $\beta=108.9(4)°$, $U=895$ Å^3, $d_c=2.34$ for $Z=2$, confirmed by approximate density measurements by flotation. $F(000)=592$, $\lambda=1.5418$ Å, $\mu(\text{Cu-}K_\alpha)=184$ cm^{-1}. Systematic absences: $h0l$, $l=2n$; $0k0$, $k=2n$. These uniquely determine the space group as $P2_1/c$.

Structure solution and refinement

The selenium and manganese atoms were located by interpretation of an unsharpened Patterson function. The remaining atoms were found from successive difference Fourier syntheses. The molecule possesses a crystallographic centre of symmetry, the asymmetric unit consisting of one half of one molecule. The structure was refined by full-matrix least-squares, initially with isotropic temperature factors for all the atoms. Allowing the selenium and manganese atoms, and then subsequently the fluorine atoms, to refine anisotropically resulted in improvements in the generalised R index which were significant at the 99.5% confidence level[4]. Since the interlayer scale factors were also refined, the anisotropic temperature factor components U_{11} are not as well determined as the other parameters; however the values obtained appear to be physically reasonable. The weighting scheme adopted was $w=1/(12.27+|F_o|+0.0106\ F_o^2)$, which gives a satisfactory distribution of residuals with the magnitudes of sin (θ) and of F_0 (Table 1).

In the final cycles of refinement, a total of 88 parameters were varied simultaneously, including 5 inter-layer scale factors, anisotropic temperature factors for the manganese, selenium and fluorine atoms only, and the Zachariasen secondary extinction coefficient[5] which refined to the value $r^*=(12\pm3)\times10^{-4}$. Complex neu-

TABLE 2

ATOM CO-ORDINATES AND ISOTROPIC VIBRATIONAL AMPLITUDES (Å$^2\times10^3$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	*U*
Se	0.2108(4)	0.0634(2)	0.9975(3)	
Mn	0.1021(7)	0.0012(3)	0.2027(4)	
C(1)	0.3278(54)	0.0586(22)	0.3328(33)	64(7)
C(2)	0.0201(51)	0.9438(20)	0.3420(31)	56(7)
C(3)	0.3110(59)	0.9173(24)	0.2065(36)	69(9)
C(4)	0.9005(55)	0.0861(21)	0.2076(34)	65(8)
C(5)	0.1645(46)	0.1902(17)	0.9959(28)	47(6)
O(1)	0.4599(37)	0.0934(15)	0.4210(24)	73(6)
O(2)	0.9676(37)	0.9061(16)	0.4252(24)	73(6)
O(3)	0.4418(48)	0.8603(20)	0.2137(30)	99(8)
O(4)	0.7756(44)	0.1414(18)	0.2170(29)	88(7)
F(1)	0.9610(44)	0.2142(13)	0.0033(34)	
F(2)	0.1658(59)	0.2227(15)	0.8745(29)	
F(3)	0.3086(47)	0.2259(15)	0.1054(30)	

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[*] Estimated standard deviations (in parentheses) are given in units of the least significant digit of the quantity to which they refer.

TABLE 3

ANISOTROPIC VIBRATIONAL AMPLITUDES (Å x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Se	41(6)	57(2)	33(1)	−1(1)	13(1)	−3(1)
Mn	45(7)	61(2)	33(2)	2(2)	11(2)	3(2)
F(1)	135(21)	64(11)	140(19)	3(14)	66(16)	12(13)
F(2)	223(29)	73(14)	115(19)	28(13)	96(20)	10(17)
F(3)	154(22)	73(15)	118(20)	−29(13)	−50(17)	−20(15)

The anistropic temperature factor takes the form: $\exp[-2\pi^2(U^{11}\cdot h^2\cdot a^{*2}+U^{22}\cdot k^2\cdot b^{*2}+U^{33}\cdot l^2\cdot c^{*2}+2\,U^{23}\cdot k\cdot l\cdot b^*\cdot c^*+2\,U^{31}\cdot l\cdot h\cdot c^*\cdot a^*+2\,U^{12}\cdot h\cdot k\cdot a^*\cdot b^*)]$.

tral-atom scattering factors were employed for all atoms[6,7]. The final value of $R=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o$ ($\Delta=|F_o-F_c|$) was 0.120; the corresponding unweighted index,0.115. A final difference Fourier revealed no pronounced features. The results from the final full-matrix least-squares cycle are given in Tables 2 and 3. These results together with the full covariance matrix and estimated standard deviations in the unit-cell dimensions were used to calculate the bond lengths and angles given in Table 4; no corrections have been applied for libration. Fig. 1. shows a perspective view of one molecule,

TABLE 4

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEGREES)

(*a*). *Distances*

Se–Mn	2.505(6)	2.498[a]	C(1)–O(1)	1.12(3)	1.16[a]
Se–Mn′	2.490(6)		C(2)–O(2)	1.13(3)	
Mn–C(1)	1.80(3)	1.83[a]	C(3)–O(3)	1.19(4)	
Mn–C(2)	1.83(3)		C(4)–O(4)	1.18(4)	
Mn–C(3)	1.84(4)		C(5)–F(1)	1.36(4)	1.31[a]
Mn–C(4)	1.83(3)		C(5)–F(2)	1.29(3)	
Se–C(5)	1.97(3)		C(5)–F(3)	1.28(3)	

(*b*). *Angles*

Se–Mn–Se′	83.1(3)		C(1)–Mn–Se′	171.7(10)	
Mn–Se–Mn′	96.9(3)		C(2)–Mn–Se	173.5(10)	
C(5)–Se–Mn	107.8(8)		C(3)–Mn–C(4)	177.4(14)	
C(5)–Se–Mn′	108.0(9)		Mn–C(1)–O(1)	174.8(29)	176.5[a]
C(1)–Mn–Se	90.9(10)	90.3[a]	Mn–C(2)–O(2)	177.7(27)	
C(2)–Mn–Se′	92.6(10)		Mn–C(3)–O(3)	176.4(30)	
C(3)–Mn–Se	84.4(10)		Mn–C(4)–O(4)	177.1(29)	
C(3)–Mn–Se′	97.0(11)		Se–C(5)–F(1)	114.1(18)	111.7[a]
C(4)–Mn–Se	97.0(10)		Se–C(5)–F(2)	110.2(19)	
C(4)–Mn–Se′	85.5(12)		Se–C(5)–F(3)	110.7(20)	
C(1)–Mn–C(2)	93.6(13)		F(1)–C(5)–F(2)	103.4(25)	107.2[a]
C(1)–Mn–C(3)	85.9(15)		F(1)–C(5)–F(3)	105.6(24)	
C(1)–Mn–C(4)	87.5(13)		F(2)–C(5)–F(3)	112.7(28)	
C(2)–Mn–C(3)	91.3(14)				
C(2)–Mn–C(4)	87.5(13)				

[a] Mean value.

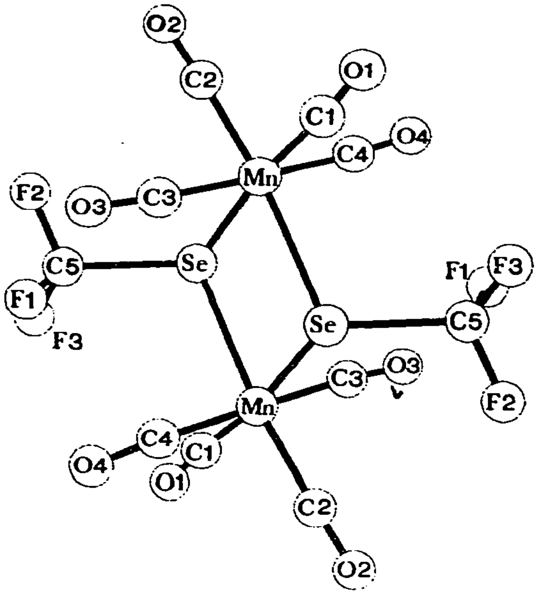

Fig. 1. A perspective view of the molecule.

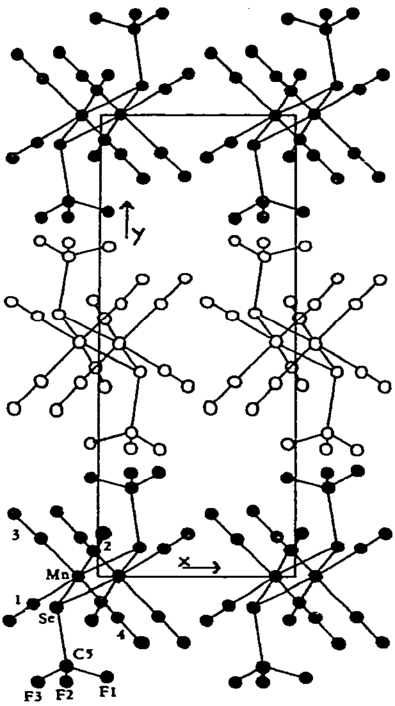

Fig. 2. The crystal structure seen in projection down the z axis.

and Fig. 2 illustrates the packing of the molecules. Tables of observed and calculated structure factors may be obtained from the authors.

DISCUSSION

The molecule possesses an exact crystallographic centre of symmetry, at the centre of the $[MnSe]_2$ rhombus. The plane through the manganese and selenium atoms is described by the equation:

$$-3.694\,(x/a)+12.456\,(y/b)+1.795\,(z/c)=0.000$$

where (x/a) etc. are the crystallographic fractional coordinates. Two of the carbonyl groups on each manganese atom lie close to this plane, but each is deflected away from the respective neighbouring $-CF_3$ group. The deviations from the plane are C(1) 0.12, O(1) 0.22, C(2) −0.16, O(2) −0.29 Å.

The two carbonyl groups approximately perpendicular to the plane are also bent away from their neighbouring CF_3 groups, resulting in two C–Mn–C angles of less than 90°. Three of the C–Mn–C angles are slightly greater than 90°, as normally found in compounds of the type $XMn(CO)_5$. ($X=H$, $Mn(CO)_5$, $HgMn(CO)_5$, $SnPh_3$, $SnMe_3$ and $SiMe_3$). The Se–C(5) bond makes an angle of 62.7° with the $[MnSe]_2$ plane. The C(5)–Se–Mn angles are identical within experimental error. The conformation adopted by the CF_3 groups appears to minimise the repulsions from the two carbonyl groups on the same side of the $[MnSe]_2$ plane; F(1) is almost

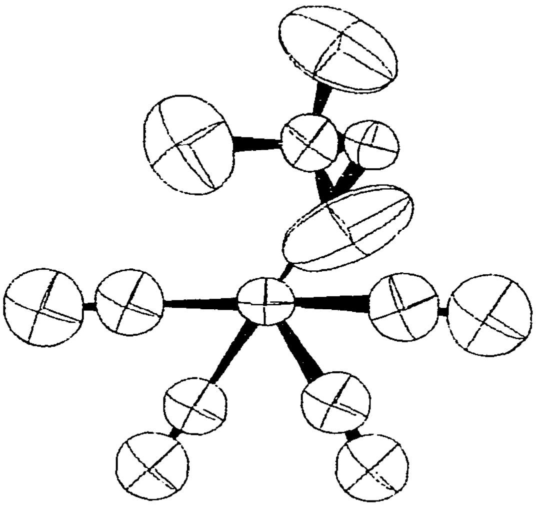

Fig. 3. The thermal motion of the atoms in the asymmetric unit, showing 50% probability ellipsoids with principal axes.

equidistant from C(3'), O(3'), C(4) and O(4). Fig. 3 illustrates the thermal motion of the atoms, and indicates appreciable torsional motion of the CF_3 group about the Se–C bond.

The two Mn–Se bond lengths are not significantly different; no other covalent Mn–Se bond lengths appear to have been determined. The mean Mn–Se bond length of 2.50 Å is shorter than the mean of the Mn–Mn and Se–Se distances in $Mn_2(CO)_{10}$[8,9] and $(CF_3Se)_2$[10] (2.61 or 2.63 Å). Applying the 18-electron rule for manganese, the CF_3Se-groups can be regarded as 3-electron ligands. The Mn–Mn and Se–Se distances across the molecule do not indicate any further direct bonding interactions; the Se–Se distance is longer than the shortest intermolecular Se–Se contact in P_4Se_5[11]. The structure of $[(CF_3Se)Mn(CO)_4]_2$ is related to that found[12] for $[BrMn(CO)_4]_2$, where the $[MnBr]_2$ unit is almost planar and has four approximately equal Mn–Br bond lengths. On the other hand the $[FeS]_2$ units in $[SFe(CO)_3]_2$[13] and $[EtSFe(CO)_3]_2$[14] are nonplanar; both possess short Fe–Fe interactions (ca. 2.54 Å), and the former also has an S–S bond (2.01 Å). The Mn–C and C–O bond lengths in $[CF_3SeMn(CO)_4]_2$ fall within the ranges normally found in manganese carbonyl derivatives. There is no significant difference between the axial and equatorial Mn–C bond lengths, in contrast to the surprisingly large difference of 0.11 Å found[12] in $[BrMn(CO)_4]_2$. The Se–C and C–F distances are a little shorter than those found in recent electron diffraction studies[10,15] of CF_3Se-derivatives, but the differences are of the order of magnitude expected for libration.

The molecules are arranged in layers perpendicular to [010], consistent with the crystal habit of laminae with principal faces (010). The shortest intermolecular contacts (Table 5) are between fluorine and oxygen or carbon atoms. After exposure to X-rays, the spot shapes on the equi-inclination Weissenberg photographs became elongated parallel to y^*; this occurred more rapidly at higher temperature. It appears that radiation damage causes a stacking disorder of the weakly bound layers of molecules, causing a reduction in the effective mosaic dimension perpendicular to

TABLE 5

SELECTED NON-BONDED DISTANCES (Å)

Intramolecular, across the four-membered ring	
Se-Se' 3.314(8)	Mn-Mn' 3.739(8)
Intramolecular, through more than one angle[a]	
F(1)-C(4) 2.91	F(2)-O(3') 3.15
F(1)-O(4) 2.92	F(2)-C(2') 3.28
F(1)-O(3') 2.96	F(3)-C(1) 3.37
F(1)-C(3') 2.99	F(2)-O(2') 3.40
F(3)-O(4) 3.08	
Intermolecular, within a layer[a]	
O(3)-F(3') 2.84	O(2)-C(2') 3.22
O(2)-O(2') 3.20	O(1)-C(1') 3.31
O(1)-O(1') 3.22	O(4)-O(1) 3.32
Intermolecular, between layers[a]	
O(2)-F(1') 3.03	O(4)-F(2) 3.22
F(2)-F(3) 3.14	O(2)-F(3') 3.23
	O(1)-F(2) 3.33

[a] Distances of this type greater than 3.40 Å are omitted.

the layers. The reflections could also have been indexed using a monoclinic *B* face centred cell with β close to 90°, by defining $c' = 2c - a$ and retaining the original x and y axes. The intensities of reflections with h even exhibit approximate orthorhombic Laue symmetry. This may be related to the presence of an approximate molecular diad axis, which lies close to the new z axis.

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