Reactions of Main Group Homopolynuclear Cations with Transition-metal Carbonyls. Stabilisation of μ-$Se_2{}^{2+}$ and η^3-$Te_3{}^{2+}$ Dicationic Ligands and Crystal Structures of $[Mo(Te_3)(CO)_4][SbF_6]_2$ and $[FeW(Se_2)(CO)_8][SbF_6]_2$†

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Two tetrahedrane-like clusters, $[FeW(Se_2)(CO)_8][SbF_6]_2$ and $[Mo(Te_3)(CO)_4][SbF_6]_2$, have been prepared by reaction of the metal carbonyls $[Fe_2(CO)_9]$, $[W(CO)_6]$, and $[Mo(CO)_6]$ with the homonuclear cations $Se_4{}^{2+}$ and $Te_4{}^{2+}$. The compounds contain the entities $Se_2{}^{2+}$ and $Te_3{}^{2+}$ which are stabilised by the presence of metal carbonyl fragments. The selenium compound is monoclinic, $a = 15.251(4)$, $b = 12.267(3)$, $c = 12.047(3)$ Å, $\beta = 92.047(3)°$, space group $P2_1/c$; the tellurium compound is orthorhombic, $a = 15.177(5)$, $b = 8.367(4)$, $c = 14.590(4)$ Å, space group *Pnma*. The geometry of the two clusters, their formation, and bonding are described.

Cationic clusters of main-group elements have been known since the 1960s.[1] Their stabilisation and isolation as salts of $AsF_6{}^-$, $SbF_6{}^-$, $Sb_2F_{11}{}^-$,[2] $AlCl_4{}^-$, or $Al_2Cl_7{}^-$ [3] has been achieved by the systematic use of highly acidic or superacidic media, solutions and melts.

Such naked clusters, along with their anionic analogues (Zintl ions)[4] are generally considered as constituting a group distinct from 'classical' organometallic transition-metal clusters. In an attempt to establish a link, we have recently been investigating the possibility of incorporating transition-metal carbonyl fragments into main-group cationic clusters. This research, which has centred around selenium up to now, has produced a number of clusters including traditional neutral clusters such as $[Fe_3Se_2(CO)_9]$[5] as well as mixed charged species having an unusual bonding pattern such as $[W_2(Se_4)(CO)_{10}]^{2+}$.[6] This novel class of compounds is the cationic analogue of what have been termed 'Zintl metal carbonylates' for anionic mixed clusters.[7] In general, discussions relative to new mixed clusters have emphasised the transition-metal fragment aspect; our purpose is to concentrate on the chemistry and structural environment of the main-group element constituent. Recent discussions on the hypervalency of tellurium in a similar class of compounds[8] have further stimulated our efforts in this field.

This research has a two-fold objective: the development of synthetic methods using naked polycationic species for the preparation of mixed clusters and their systematic use to evaluate the limits of their applicability; and the structural determination of the polynuclear compounds thus prepared.

In a recent article we briefly reported the reaction of $Se_4{}^{2+}$ with Group 6 metal carbonyls and described the structure of the dimeric cation $[W_2(Se_4)(CO)_{10}]^{2+}$.[6] Normally, we would have included the complete structural details, together with other results pertaining to further mixed clusters; however, we note that the full information on the molybdenum analogue has just been published by another group working in a similar area.[9a] Therefore, we shall limit this report to the description of the synthesis and structure of two tetrahedrane-like dicationic clusters $[Mo(Te_3)(CO)_4]^{2+}$ and $[FeW(Se_2)(CO)_8]^{2+}$, obtained from the reaction of $Te_4{}^{2+}$ or $Se_4{}^{2+}$ with metal carbonyls.‡ A preliminary account of the mixed iron–tungsten–selenium compound has been published.[10]

Experimental

Materials.—Selenium (Merck) and tellurium (Merck) were dried under vacuum at 25 °C overnight. Sulphur dioxide (Fluka) was dried and stored over P_2O_5 for at least 48 h before use. Antimony pentafluoride (Allied Chemicals) was distilled under vacuum and stored in a dry-box. Metal carbonyls (Merck), $[W(CO)_6]$, $[Mo(CO)_6]$, and $[Fe(CO)_5]$, were used as received.

Preparations.—$Se_4(Sb_2F_{11})_2$. This was prepared according to the method first published by Gillespie and co-workers.[11] All manipulations of this and the following compounds were carried out in a dry-box under an argon atmosphere.

$Te_4Sb_9F_{35}$. The method used was that first published by Gillespie and co-workers[12] for the preparation of $Te_4(Sb_2F_{11})_2$. The product obtained is a red, air-sensitive mixture of amorphous and semi-crystalline material which analyses as $Te_4Sb_9F_{35}$.

$[Fe_2(CO)_9]$. This was prepared by irradiating iron pentacarbonyl according to the published method.[13]

$[FeW(Se_2)(CO)_8][SbF_6]_2$.—This salt was prepared on a vacuum line using a double-bulb glass vessel reactor equipped with a magnetic stirrer bar and a glass frit separating the two bulbs. The compounds $[W(CO)_6]$, $[Fe_2(CO)_9]$, and $Se_4(Sb_2F_{11})_2$ were used in a 1.8:1:1 mole ratio. The metal carbonyls were dissolved in SO_2 in one bulb and $Se_4(Sb_2F_{11})_2$ in the other. Upon mixing a red solution was formed, which was stirred for several hours. The solution was filtered, and allowed to stand for 3 d at room temperature when small, air-sensitive red crystals were observed. Qualitative analysis using electron dispersive spectroscopy indicated the presence of Se, Fe, W, and Sb. The stoicheiometric formula was obtained from the crystallographic result. I.r. (as Nujol mull between AgCl windows): 2 130, 2 115, 2 090, 2 070, 2 040, 1 980, and 1 920 cm^{-1} $\nu(C{=}O)$.

$[Mo(Te_3)(CO)_4][SbF_6]_2$.—Bright red crystals were deposited from a green solution obtained by mixing $Te_4Sb_9F_{35}$ with $[Mo(CO)_6]$, both dissolved in SO_2, following the method

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† 1,1,1,1-Tetracarbonyl-*tetrahedro*-tritelluriummolybdenum(2+) and 1,1,1,2,2,2,2,2-octacarbonyl-*tetrahedro*-diselenium-1-iron-2-tungsten-(2+) hexafluoroantimonate, respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ *Note added in proof.* Whilst this paper was in the press a preliminary report[9b] of the preparation and structure of $[W(Te_3)(CO)_4][SbF_6]_2$ was published, showing structural features almost identical to those reported here for the molybdenum analogue.

Table 1. Room-temperature crystal data and details of *X*-ray intensity measurements and structure refinement for $[FeW(Se_2)(CO)_8][SbF_6]_2$ and $[Mo(Te_3)(CO)_4][SbF_6]_2$

Compound	$[FeW(Se_2)(CO)_8][SbF_6]_2$	$[Mo(Te_3)(CO)_4][SbF_6]_2$
M	4 372.5	4 248.4
System	Monoclinic	Orthorhombic
$a \times b \times c$/Å	15.251(4) × 12.267(3) × 12.047(3)	15.177(5) × 8.367(4) × 14.590(4)
β/°	92.047(3)	
U/Å^3	2 251	1 853
Space group	$P2_1/c$	$Pnma$
D_c/g cm^{-3}	3.23	3.81
μ/cm^{-1}	107.3	77.2
2θ limits/°	4—56	4—60
Scan mode	ω—4/3θ	ω—1/3θ
Crystal volume/mm^3	5.948×10^{-3}	2.56×10^{-4}
F(000)	1 960	2 192
No. data collected	5 626	2 868
No. unique data	4 609	2 706
No. reflections $F > 3\sigma(F)$	2 770	1 382
R	0.050	0.029
R'	0.049	0.029
g	0.0047	0.0080

Details common to both structures: $Z = 4$; graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å; scan range, $1.20 + 0.35 \tan\theta$; standard reflections, 3 every 50; weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$.

Table 2. Fractional atomic co-ordinates for $[FeW(Se_2)(CO)_8][SbF_6]_2$ with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
W	0.7845	0.580 2(1)	0.220 6(1)	C(1)	0.630 0(13)	0.340 2(17)	0.419 9(18)
Sb(2)	0.608 6(1)	0.972 7(1)	0.303 8(1)	C(2)	0.750 0(14)	0.469 7(16)	0.512 8(17)
Sb(1)	0.053 2(1)	0.768 3(1)	0.480 7(1)	C(3)	0.601 7(11)	0.552 2(14)	0.415 2(13)
Se(1)	0.787 4(1)	0.372 5(1)	0.266 2(2)	C(4)	0.844 3(11)	0.734 8(16)	0.203 1(15)
Se(2)	0.659 3(1)	0.438 3(1)	0.186 8(1)	C(5)	0.676 4(10)	0.669 6(13)	0.155 6(15)
Fe	0.688 5(2)	0.460 8(2)	0.378 2(2)	C(6)	0.916 0(12)	0.544 1(13)	0.273 5(14)
F(1)	0.005 4(11)	0.832 4(11)	0.603 7(11)	C(7)	0.766 0(11)	0.644 2(15)	0.373 7(14)
F(2)	0.39 1(8)	0.899 5(9)	0.404 5(10)	C(8)	0.821 7(11)	0.555 4(13)	0.054 6(17)
F(3)	−0.059 7(6)	0.725 0(11)	0.437 3(11)	O(1)	0.598 8(15)	0.266 1(14)	0.450 2(17)
F(4)	0.168 1(8)	0.807 0(11)	0.523 0(12)	O(2)	0.791 5(11)	0.478 7(14)	0.590 7(12)
F(5)	0.070 5(8)	0.637 1(10)	0.556 4(12)	O(3)	0.548 3(8)	0.612 8(12)	0.433 0(11)
F(6)	0.099 2(10)	0.705 2(11)	0.352 6(12)	O(4)	0.876 4(8)	0.817 2(11)	0.199 7(12)
F(7)	0.705 9(8)	0.884 0(11)	0.284 4(11)	O(5)	0.621 8(8)	0.720 4(11)	0.118 2(12)
F(8)	0.504 6(8)	1.054 0(10)	0.324 1(11)	O(6)	0.985 0(8)	0.523 8(10)	0.298 5(11)
F(9)	0.586 9(11)	0.970 7(15)	0.150 3(11)	O(8)	0.837 7(9)	0.548 3(11)	−0.032 5(11)
F(10)	0.678 0(10)	1.095 0(13)	0.292 6(15)	O(7)	0.757 0(9)	0.701 8(10)	0.447 1(10)
F(11)	0.633 7(13)	0.973 0(15)	0.456 1(11)				
F(12)	0.539 4(13)	0.850 8(14)	0.312 3(18)				

described above. Electron dispersive spectroscopy showed the presence of Te, Mo(W), and Sb and the stoicheiometric formula was obtained from the crystallographic result. I.r. (Nujol mull between AgCl and polyethylene windows): 2 150 (sh), 2 100m, 2 075m, 2 020s [ν(C=O)], 640 (SbF_6^-), 560 (sh), 520m, 460, 440, and 275 cm^{-1} (SbF_6^-). Raman: between 600 and 20 cm^{-1} two intense bands (143 and 126 cm^{-1}) can be attributed to the Te_3 group.

X-Ray Crystallography.—Crystals of $[FeW(Se_2)(CO)_8][SbF_6]_2$ show two types of morphology: the needle-shaped crystals tested were, without exception, twinned, whereas those of approximately pyramidal shape were single crystals. The compound $[Mo(Te_3)(CO)_4][SbF_6]_2$ crystallises as very fine needles. Preliminary oscillation and Weissenberg photographs were used in both cases to check crystal quality and to obtain cell and space-group information. Further work was on an Enraf-Nonius CAD4 automatic diffractometer. The crystal data and conditions used for the data collection are given in Table 1. No systematic trends in the intensities of two standard reflections collected every 50 reflections were observed. Lorentz and polarisation corrections were applied to all data. Absorption corrections were made. The structures were solved by the location of heavy-atom positions using SHELX 76 direct methods.[14] Carbon, oxygen, and fluorine atoms could then be found from Fourier maps. Least-squares refinement converged to the residuals given in Table 1. The final atomic positions for $[FeW(Se_2)(CO)_8][SbF_6]_2$ and $[Mo(Te_3)(CO)_4][SbF_6]_2$ are given in Tables 2 and 3 respectively.

Results and Discussion

Description of the Structures.—The crystal of $[Mo(Te_3)(CO)_4][SbF_6]_2$ is made up of discrete $[Mo(Te_3)(CO)_4]^{2+}$ cations and SbF_6^- anions (Figure 1). Bond lengths and angles are given in Table 4. The cation may be viewed as a cyclic tritellurium(2+) ion, Te_3^{2+}, acting as a trihapto (η^3) ligand of approximately D_{3h} symmetry co-ordinated to a C_{4v} $Mo(CO)_4$ fragment. Apart from Te_6^{4+}, which may be considered as made up of two Te_3^{2+} cations interacting through rather long Te $\cdots$

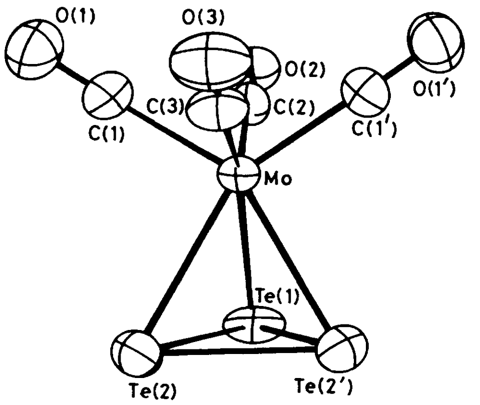

Figure 1. The $[Mo(Te_3)(CO)_4]^{2+}$ dication showing 50% thermal ellipsoids

Table 3. Fractional atomic co-ordinates for $[Mo(Te_3)(CO)_4][SbF_6]_2$

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.813 4(1)	0.7500	0.445 1(1)
Te(1)	0.628 5(1)	0.7500	0.444 5(1)
Te(2)	0.715 5(1)	0.587 0(1)	0.3121
Sb(2)	0.537 2(1)	0.7500	0.747 4(1)
Sb(1)	0.654 8(1)	0.2500	0.555 4(1)
C(1)	0.871 0(7)	0.543 9(14)	0.486 6(7)
O(1)	0.904 9(6)	0.430 7(11)	0.510 4(6)
C(2)	0.796 7(11)	0.7500	0.582 3(10)
O(2)	0.788 7(8)	0.7500	0.658 6(7)
C(3)	0.932 0(10)	0.7500	0.373 4(11)
O(3)	−0.002 4(7)	0.7500	0.339 1(8)
F(1)	0.717 2(7)	0.2500	0.447 1(6)
F(2)	0.581 7(6)	0.092 9(10)	0.508 2(6)
F(3)	0.594 6(9)	0.2500	0.664 7(8)
F(4)	0.729 1(6)	0.093 7(9)	0.602 6(5)
F(5)	0.492 1(8)	0.7500	0.864 9(8)
F(6)	0.584 3(8)	0.7500	0.631 1(7)
F(7)	0.619 8(7)	0.899 7(13)	0.781 8(7)
F(8)	0.456 7(7)	0.904 9(15)	0.715 4(9)

Te bonds,[15] this is the first time that a regular cyclic three-atom arrangement has been observed for a chalcogen. The tellurium triangle is almost equilateral, with distances 2.728(1) and two of 2.708(1) Å related by the mirror plane. A typical Te–Te single bond distance is that found in Ph_2Te_2, 2.712 Å.[16] However, in the tetrahedrane $[MoFe(Te_2Br)(CO)_5(C_5H_5)]$, where one of the tellurium atoms is described as being hypervalent, the Te–Te bond length is 2.807 Å.[8] For comparison, in dimeric $(Te_3{}^{2+})_2$ the bond distances within the two triangular units are distinctly shorter, averaging 2.681 Å, and correspond to an approximate bond order of 1.2.[15] Finally, it should be noted that the mean Te–Te bond length in $[Mo(Te_3)(CO)_4]^{2+}$ is the same as that in the asymmetric Te_3 ring in $[Te_3S_3]^{2+}$.[17] The Mo–Te distances are 2.799(1) (two) and 2.806(1) Å, which compare well with the average distance of 2.795(1) Å reported for $[Mo_2Fe(Te_2)(CO)_7(C_5H_5)]$[18] or 2.747(1) Å in $[MoFe(Te_2Br)(CO)_5(C_5H_5)]$.[8] The average C=O and Mo–C distances are 1.12(1) and 2.039(1) Å respectively.

Figure 2 shows the superposition of the C_4 symmetry of the carbonyl groups on the C_3 symmetry of the Te_3 base, and reveals nearly coincident axes. Viewed along this axis, the seven-co-ordination around molybdenum corresponds to one of the two C_s forms of the classical triangular-base square-cap arrangement,[19] or alternatively as a distorted monocapped octahedral geometry. Indeed, the structure approaches the staggered molecular configuration observed for $[Co(As_3)(CO)_3]$.[20] As described by Dahl and co-workers,[20] this conformation arises from the 'electron sink' function of the $Co(CO)_3$ group which removes electron density from the triarsenic fragment with dissipation of the resulting metal electron charge *via* the carbonyl π^* orbitals. The additional carbonyl group [CO(2)] in $[Mo(Te_3)(CO)_4]^{2+}$ may be considered to cap the Te(1),CO(1),CO(1′) face, whereas the Te(2),Te(2′),CO(3) face is non-capped. The distribution of all distances agrees exactly with that predicted from site-preference analysis using the scheme for seven-co-ordination of Hoffmann *et al.*[19] More specifically, CO(3) occupies a non-favourable site for a π acceptor, resulting in one particularly long Mo–CO(3) distance (2.081 Å) and a correspondingly short C(3)–O(3)

Table 4. Interatomic distances (Å) and selected bond angles (°) in $[Mo(Te_3)(CO)_4][SbF_6]_2$ with estimated standard deviations in parentheses*

Mo–Te(2)	2.799(1)	Mo–C(1)	2.026(11)	Sb(2)–F(5)	1.846(11)
Mo–Te(1)	2.806(1)	Mo–C(2)	2.018(14)	Sb(2)–F(6)	1.841(10)
Te(1)–Te(2)	2.708(1)	Mo–C(3)	2.081(15)	Sb(2)–F(7)	1.841(9)
Te(2)–Te(2′)	2.728(1)	C(1)–O(1)	1.132(12)	Sb(2)–F(8)	1.842(9)
		C(2)–O(2)	1.120(15)		
		C(3)–O(3)	1.115(18)		
Sb(1)–F(1)	1.842(9)	Te(1)–F(2)	3.519(9)	Te(2)–F(1)	3.440(5)
Sb(1)–F(2)	1.852(7)	Te(1)–F(2′)	3.098(8)	Te(2)–F(4)	3.171(7)
Sb(1)–F(3)	1.838(10)	Te(1)–F(6)	2.804(10)	Te(2)–F(7)	2.983(10)
Sb(1)–F(4)	1.859(7)			Te(2)–F(8)	3.052(11)
Te(2)–Mo–Te(2′)	58.33(4)	Te(2)–Mo–C(3)	96.3(4)	F(2)–Sb(1)–F(2′)	90.4(5)
Te(2)–Mo–Te(1)	57.79(4)	C(1)–Mo–C(1′)	116.7(4)	F(2)–Sb(1)–F(4)	90.1(4)
Te(2)–Te(1)–Mo	60.97(5)	C(1)–Mo–C(2)	76.0(4)	F(2)–Sb(1)–F(4′)	179.4(4)
Te(2)–Te(1)–Te(2′)	60.47(5)	C(1)–Mo–C(3)	77.1(3)	F(4)–Sb(1)–F(4′)	89.4(5)
Te(1)–Te(2)–Te(2′)	59.76(2)	C(2)–Mo–C(3)	127.4(6)	F(6)–Sb(2)–F(8)	91.4(5)
Te(1)–Te(2)–Mo	61.24(4)	Mo–C(1)–O(1)	178.4(9)	F(6)–Sb(2)–F(7)	89.2(4)
Te(2′)–Te(2)–Mo	60.83(2)	Mo–C(2)–O(2)	179.0(15)	F(6)–Sb(2)–F(5)	178.9(5)
Te(1)–Mo–C(1)	91.2(3)	Mo–C(3)–O(3)	176.5(13)	F(7)–Sb(2)–F(5)	90.0(4)
Te(1)–Mo–C(1′)	115.6(3)	F(3)–Sb(1)–F(1)	178.9(5)	F(7)–Sb(2)–F(7′)	85.7(7)
Te(1)–Mo–C(2)	82.9(5)	F(3)–Sb(1)–F(2)	91.4(4)	F(8)–Sb(2)–F(5)	89.4(5)
Te(1)–Mo–C(3)	149.6(4)	F(3)–Sb(1)–F(2)	88.9(4)	F(8)–Sb(2)–F(7)	92.4(5)
Te(2)–Mo–C(1)	91.2(3)	F(1)–Sb(1)–F(2)	89.4(3)	F(8)–Sb(2)–F(7′)	178.0(5)
Te(2)–Mo–C(1′)	148.3(3)	F(1)–Sb(1)–F(4)	90.3(3)	F(8)–Sb(2)–F(8′)	89.5(7)
Te(2)–Mo–C(2)	128.4(4)				

* Primes denote positions related by mirror symmetry in the ionic unit.

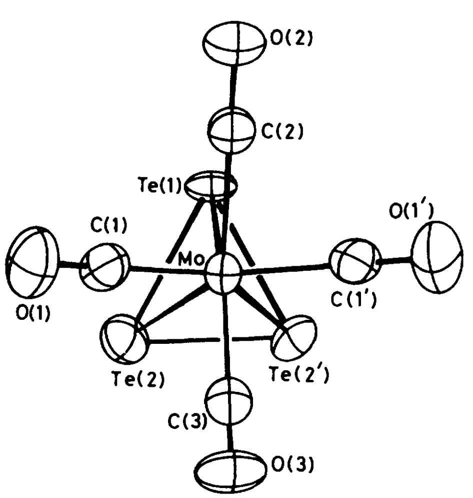

Figure 2. View of the $[Mo(Te_3)(CO)_4]^{2+}$ cation illustrating the superposition of the metal carbonyl fragment (C_{4v}) on to the Te_3 base (D_{3h})

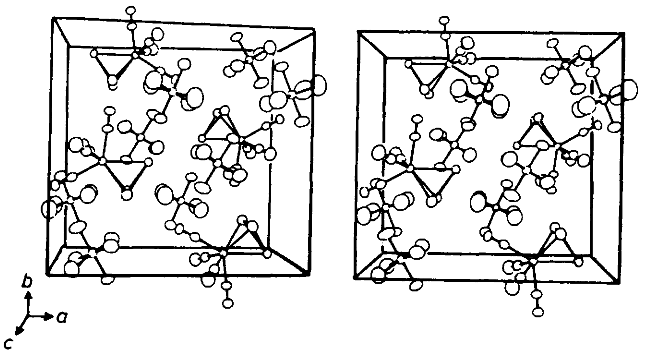

Figure 3. Stereoview of the unit cell of $[Mo(Te_3)(CO)_4][SbF_6]_2$ showing the packing arrangement

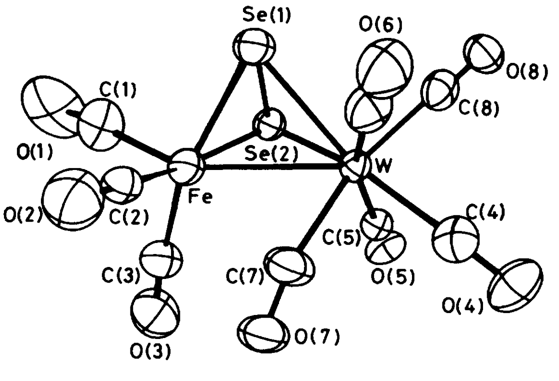

Figure 4. The $[FeW(Se_2)(CO)_8]^{2+}$ dication

distance (1.115 Å). Furthermore, the longest Te(1)–Mo distance can be rationalised in terms of its less favourable position for a π-donor ligand.

There is significant charge-transfer interaction of the main-group entity of the cation with the accompanying anions. The atoms Te(1) and Te(2) are surrounded by four and five fluorines respectively at less than 3.60 Å. The particularly short F(6)–Te(1) distance [2.80(1) Å] is of a similar length to that observed in $Te_4(SbF_6)_2$.[21] These interionic interactions do not appear significantly to affect distances within SbF_6^-, which are all approximately equal. A stereoscopic view of the unit cell is shown in Figure 3.

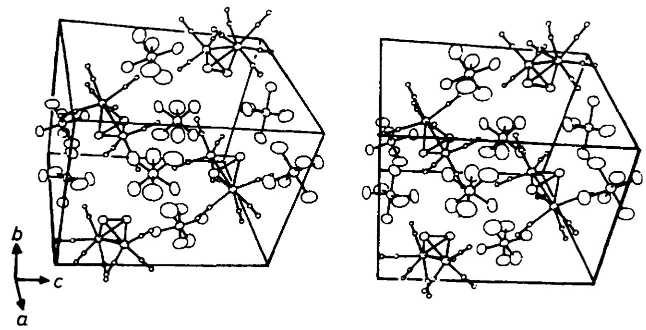

Figure 5. Stereoview of the unit cell of $[FeW(Se_2)(CO)_8][SbF_6]_2$. The positions of the carbonyl groups are indicated by arbitrary isotropic thermal parameters with 50% thermal ellipsoids for all other atoms

The structure of the $[FeW(Se_2)(CO)_8]^{2+}$ cation is shown in Figure 4, and bond lengths and angles in Table 5. The $FeW(Se_2)$ core adopts a distorted tetrahedral arrangement which is devoid of any space group-imposed symmetry, but which nevertheless has an approximate mirror plane which bisects the Se_2 group and contains atoms O(4), C(4), O(8), C(8), W, O(7), C(7), Fe, O(1), and C(1). The selenium fragment in the cluster may formally be considered as an Se_2^{2+} ion stabilised by organometallic groups. Obviously the triple bond of the free Se_2^{2+} is lengthened by interaction with the carbonyl fragment and the π-acceptor capacity of the Se_2 moiety. The Se–Se bond length, 2.281(3) Å, corresponds to an approximate Se–Se bond order of 1.5,[22] showing the presence of extensive delocalisation. This distance is longer than that found in the diselenium(2+) cation $[W_2(Se_4)(CO)_{10}]^{2+}$, 2.208 Å,[6] and closely approaches that in the mixed iron–selenium cluster $[Fe_2(Se_2)(CO)_6]$, 2.293 Å.[22] The Se–W distances, 2.601(2) and 2.606(2) Å, are also shorter than those in $[W_2(Se_4)(CO)_{10}]^{2+}$, 2.626(1) and 2.631(1) Å. The Fe–W bond length is 2.857(3) Å, significantly shorter than that observed recently for $[FeWH(CO)_9]^-$, 2.997(2) Å, $[FeWH(CO)_8\{P(OMe)_3\}]^-$, 2.974(5) Å, or $[FeW(AuPPh_3)(CO)_9]^-$, 3.012 Å.[23]

Around tungsten and iron the average metal–carbon and C=O distances are 2.12(1), 1.11(1) and 1.82(1), 1.11(1) Å respectively. One carbonyl on the W atom is slightly semi-bridging. The low-energy $\nu_{C=O}$ absorption is found at 1 920 cm^{-1}, 80 cm^{-1} lower than the corresponding absorption observed for the $W(CO)_5$ fragment in $[W_2(Se_4)(CO)_{10}][SbF_6]_2$.

The geometry of the W,C(7),O(7),Fe moiety [C(7)–Fe 2.54(2) Å, C(7)–W 2.04(2) (the shortest around W), C(7)–O(7) 1.14(2) Å, and O(7)–C(7)–Fe 117°] does not fit exactly into any of the categories of bridging carbonyls recently described by Crabtree and Lavin.[24] Short non-bonded interactions occur between selenium and fluorine, Table 5. Although the network of Se–F interactions is not as extensive as that found in $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$,[21] there are four Se–F distances less than 3.2 Å. These contacts distort the geometry of the hexafluoroantimonate ion; the longest Sb–F distance, 1.90(1) Å, involves the fluorine atom in strongest interaction with Se [2.87(1)Å]. Figure 5 is a stereoscopic view of the unit-cell contents.

Bonding and Formation of the Clusters.—From a valence-bond electron-counting viewpoint, the structure of Te_3^{2+} may be simply described in terms of localised electron-pair σ bonds and two delocalised π-electron pairs. The sum of valence

Table 5. Interatomic distances (Å) and selected bond angles (°) in $[FeW(Se_2)(CO)_8][SbF_6]_2$

Se(1)–W	2.606(2)	Sb(1)–F(1)	1.86(1)	Fe–C(1)	1.81(2)	C(7)–O(7)	1.14(2)
Se(2)–W	2.601(2)	Sb(1)–F(2)	1.86(1)	Fe–C(2)	1.84(2)	C(8)–O(8)	1.09(2)
Fe–W	2.857(3)	Sb(1)–F(3)	1.85(1)	Fe–C(3)	1.81(2)	Sb(2)–F(7)	1.86(1)
Se(1)–Fe	2.339(3)	Sb(1)–F(4)	1.86(1)	Fe–C(7)	2.54(2)	Sb(2)–F(8)	1.90(1)
Se(2)–Fe	2.343(3)	Sb(1)–F(5)	1.86(1)	W–C(4)	2.12(2)	Sb(2)–F(9)	1.86(1)
Se(1)–Se(2)	2.281(3)	Sb(1)–F(6)	1.89(1)	W–C(5)	2.10(1)	Sb(2)–F(10)	1.84(2)
C(1)–O(1)	1.10(2)	Se(1)–F(2)	3.44(1)	W–C(6)	2.12(2)	Sb(2)–F(11)	1.86(1)
C(2)–O(2)	1.11(2)	Se(1)–F(4)	3.40(1)	W–C(7)	2.04(2)	Sb(2)–F(12)	1.84(2)
C(3)–O(3)	1.13(2)	Se(1)–F(5)	2.97(1)	W–C(8)	2.13(2)	Se(2)–F(8)	2.87(1)
C(4)–O(4)	1.12(2)	Se(1)–F(6)	3.08(1)	C(5)–O(5)	1.12(2)	Se(2)–F(11)	2.99(1)
				C(6)–O(6)	1.11(2)	Se(2)–F(12)	3.21(2)
Se(1)–W–Se(2)	52.0(1)	F(1)–Sb(1)–F(3)	87.2(7)	Se(1)–W–C(6)	74.1(5)	C(7)–W–C(8)	164.0(7)
Se(1)–W–Fe	50.4(1)	F(1)–Sb(1)–F(4)	94.3(7)	Se(1)–W–C(7)	100.8(5)	W–C(4)–O(4)	176(2)
Se(2)–W–Fe	50.6(1)	F(1)–Sb(1)–F(5)	91.6(7)	Se(1)–W–C(8)	93.2(4)	W–C(5)–O(5)	176(1)
Se(1)–Fe–Se(2)	58.3(1)	F(1)–Sb(1)–F(6)	178.2(7)	Se(2)–W–C(4)	154.1(5)	W–C(6)–O(6)	178(1)
Se(1)–Fe–W	59.2(1)	F(2)–Sb(1)–F(3)	91.5(6)	Se(2)–W–C(5)	74.6(5)	W–C(7)–O(7)	165(1)
Se(2)–Fe–W	59.0(1)	F(2)–Sb(1)–F(4)	89.9(6)	Se(2)–W–C(6)	125.7(4)	W–C(8)–O(8)	175(1)
Se(1)–Fe–C(1)	97.0(7)	F(2)–Sb(1)–F(5)	178.5(6)	Se(2)–W–C(7)	105.5(5)	F(7)–Sb(2)–F(8)	176.0(6)
Se(1)–Fe–C(2)	102.7(7)	F(2)–Sb(1)–F(6)	89.4(6)	Se(2)–W–C(8)	89.1(5)	F(7)–Sb(2)–F(9)	88.4(6)
Se(1)–Fe–C(3)	158.6(6)	F(3)–Sb(1)–F(4)	178.0(6)	Fe–W–C(4)	139.6(5)	F(7)–Sb(2)–F(10)	90.2(7)
Se(2)–Fe–C(1)	96.0(7)	F(3)–Sb(1)–F(5)	89.8(6)	Fe–W–C(5)	95.6(5)	F(7)–Sb(2)–F(11)	89.9(7)
Se(2)–Fe–C(2)	160.1(7)	F(3)–Sb(1)–F(6)	91.6(5)	Fe–W–C(6)	101.6(5)	F(7)–Sb(2)–F(12)	89.7(8)
Se(2)–Fe–C(3)	102.1(5)	F(4)–Sb(1)–F(5)	88.7(6)	Fe–W–C(7)	59.9(5)	F(8)–Sb(2)–F(9)	91.5(6)
W–Fe–C(1)	151.4(7)	F(4)–Sb(1)–F(6)	86.9(7)	Fe–W–C(8)	136.1(5)	F(8)–Sb(2)–F(10)	93.9(7)
W–Fe–C(2)	107.5(7)	F(5)–Sb(1)–F(6)	89.8(7)	C(4)–W–C(5)	80.2(6)	F(8)–Sb(2)–F(11)	90.2(7)
W–Fe–C(3)	104.6(5)	Se(2)–Se(1)–W	63.9(1)	C(4)–W–C(6)	79.1(6)	F(8)–Sb(2)–F(12)	86.2(8)
C(1)–Fe–C(2)	92.3(10)	Fe–Se(1)–W	70.3(1)	C(4)–W–C(7)	79.9(7)	F(9)–Sb(2)–F(10)	90.7(9)
C(1)–Fe–C(3)	93.5(8)	Fe–Se(1)–Se(2)	60.9(1)	C(4)–W–C(8)	84.2(7)	F(9)–Sb(2)–F(11)	178.2(7)
C(2)–Fe–C(3)	95.4(8)	Se(1)–Se(2)–W	64.1(1)	C(5)–W–C(6)	159.2(6)	F(9)–Sb(2)–F(12)	88.3(9)
Fe–C(1)–O(1)	175(2)	Se(1)–Se(2)–Fe	60.8(1)	C(5)–W–C(7)	89.8(7)	F(10)–Sb(2)–F(11)	88.8(9)
Fe–C(2)–O(2)	175(2)	Fe–Se(2)–W	70.4(1)	C(5)–W–C(8)	87.9(7)	F(10)–Sb(2)–F(12)	179.0(10)
Fe–C(3)–O(3)	176(1)	Se(1)–W–C(4)	153.2(5)	C(6)–W–C(7)	88.8(7)	F(11)–Sb(2)–F(12)	92.1(10)
F(1)–Sb(1)–F(2)	89.3(6)	Se(1)–W–C(5)	126.5(5)	C(6)–W–C(8)	87.8(7)		

electrons at molybdenum from all the ligands amounts to 12, if we consider the ring Te_3^{2+} to be a four-π-electron donor. This enables molybdenum to attain the noble-gas configuration upon inclusion of the corresponding metal *d* orbitals.

Similarly, electron counting for the $[FeW(Se_2)(CO)_8]^{2+}$ cluster shows that tungsten and iron have 18- and 16-electron environments respectively. Completion of the iron environment occurs by the donation of two electrons from tungsten, which creates a formal charge distribution of $W^+ \longrightarrow Fe^-$. Thus the semi-bridging carbonyl CO(7) can be considered as serving to minimise the charge-separation effect by facilitating electron transfer from filled *d* orbitals on iron to empty carbonyl π^* orbitals.

Both cations $[Mo(Te_3)(CO)_4]^{2+}$ and $[FeW(Se_2)(CO)_8]^{2+}$ may be considered to originate from the tetrahedral molecules As_4 or P_4 by replacement of the phosphorus or arsenic atoms by electronically related substituent groups. Hoffmann,[25] Stone,[26] and others[20,27] have pointed out that the following isolobal relationships exist between main-group atoms or ions and transition-metal carbonyl fragments. Isolobal replacement in

$$Mo(CO)_4,\ W(CO)_4,\ Fe(CO)_3 \underset{\circ}{\longleftrightarrow} CH^+ \underset{\circ}{\longleftrightarrow} As^+$$

$$W(CO)_5 \underset{\circ}{\longleftrightarrow} CH_2 \underset{\circ}{\longleftrightarrow} Se,\ Te$$

either $[Mo(Te)_3(CO)_4][SbF_6]_2$ or $[FeW(Se_2)(CO)_8][SbF_6]_2$ leads to the naked cluster type AsE_3^{3+} (E = Se or Te), although this particular species has never been isolated, and it follows that these are similarly related to the tetrahedrane mixed clusters derived from $As_n[M(CO)_3]_{4-n}$, first isolated by Dahl and co-workers.[20,28] Although several tetrahedrane mixed clusters have been identified, $[Mo(Te_3)(CO)_4]^{2+}$ and $[FeW(Se_2)(CO)_8]^{2+}$ are, to the best of our knowledge, the first cationic examples, along with the recently published $MoFe(Te_2)^+$ core in $[MoFe(Te_2)(CO)_5(C_5H_5)][SbF_6]$.[8]

It is interesting to extend the isolobal concept to the case of $[W_2(Se_4)(CO)_{10}]^{2+}$. This cation is isovalent with cyclohexene, C_6H_{10}, as are the naked ions Se_6^{2+}, Te_6^{2+}, and As_6^{4-}.[29] The mixed $S_3Te_3^{2+}$ and $Se_2Te_4^{2+}$ both adopt a transannular bonded boat-like form,[17] whereas As_6^{4-} is a planar ring with delocalised π electrons, and $[W_2(Se_4)(CO)_{10}]^{2+}$ adopts a chair arrangement of the six heavy atoms.[6] The variety of geometrical conformations exhibited is rather surprising, but can be rationalised through the isolobal connection to unstable forms of cyclohexene.

When $[M(CO)_6]$ (M = Mo or W) is allowed to react with planar chalcogen cations E_4^{2+} (E = Se or Te) different types of compounds are formed depending on the nature of E [see equations (1) and (2)]. Considering for the moment the

$$2\,[M(CO)_6] + Se_4^{2+} \longrightarrow [M_2(Se_4)(CO)_{10}]^{2+} + 2\,CO \quad (1)$$

$$[M(CO)_6] + Te_4^{2+} \longrightarrow [M(Te_3)(CO)_4]^{2+} + 2\,CO + Te \quad (2)$$

chalcogen moiety of the cluster in isolation, the formal oxidation state per chalcogen atom is higher in the case of the tetrahedrane-like cations $[FeW(Se_2)(CO)_8]^{2+}$ and $[Mo(Te_3)(CO)_4]^{2+}$ than for the E_4^{2+} ring or for $[W_2(Se_4)(CO)_{10}]^{2+}$. In fact we reach the same conclusion if we consider the overall oxidation state of the cluster after isolobal replacement of the carbonyl fragment. This is not surprising, inasmuch as it is known that Te_4^{2+} is more oxidising than Se_4^{2+} and more efficiently causes carbonyl-group departure.[30] In a similar manner, partial transfer of a carbonyl group from $[W(CO)_5]$ to $[Fe(CO)_3]$ favours the isolation of $[FeW(Se_2)(CO)_8]^{2+}$.

Other factors probably come into play in determining the isolation of the more or less oxidised chalcogen species. For instance, the respective sizes of the chalcogen atoms and steric hindrance around the metal fragments both intervene. Schmid[31] has already reported that for the tetrahedral clusters Co_3E ($E = S$, Se, or Te) only elements E having a covalent radius less than 1.30 Å can be isolated in the *closo* form $[Co_3E(CO)_9]$. Correlation between the covalent radius of the main-group element and the metal–metal distance appears in the series *nido*-$[Fe_3E_2(CO)_9]$ (E = Se or Te) and in the differing thermal stability of the clusters $[Fe_2E_2(CO)_6]$.[32]

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Received 26*th August* 1986; *Paper* 6/1727