Synthesis and spectroscopic characterization of new mixed-metal, mixed-chalcogenide clusters [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)(μ$_3$-E)] (E = Te or S). Structures of [Fe$_2$M(CO)$_{10}$(μ$_3$-Se)(μ$_3$-E)] (M = W, E = Se or Te; M = Mo, E = Se)

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The room-temperature reaction of [Fe$_2$(CO)$_6$(μ-SeTe)] and [Fe$_2$(CO)$_6$(μ-SSe)] with freshly prepared [W(CO)$_5$(thf)] (thf = tetrahydrofuran) yielded the new mixed-metal, mixed-chalcogenide clusters [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)(μ$_3$-E)] (E = Te **1** or S **2**). Compounds **1** and **2** were characterized by IR and ^{13}C, ^{77}Se and [125]Te NMR spectroscopy. The crystal structure of **1** was elucidated by X-ray diffraction methods. The previously reported compounds [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)$_2$] **3** and [Fe$_2$Mo(CO)$_{10}$(μ$_3$-Se)$_2$] **4** were further characterized by ^{77}Se NMR spectroscopy and single-crystal X-ray analysis. Clusters **1**, **3** and **4** are isostructural and isomorphous (in the solid state). The structure consists of square-pyramidal Fe$_2$WSeTe, Fe$_2$WSe$_2$ and Fe$_2$MoSe$_2$ cores respectively, and in each case the heterometal atom (W for **1** and **3** and Mo for **4**) occupies the apical site.
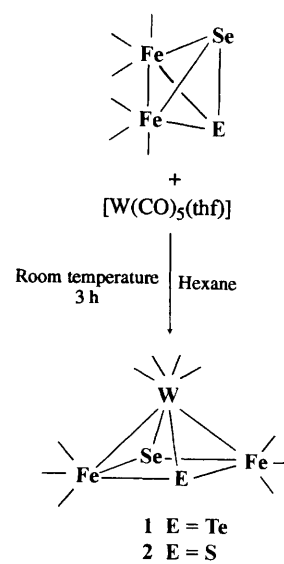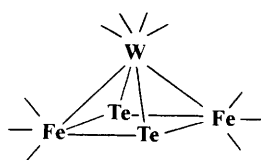
The chemistry of chalcogen-stabilized carbonyl cluster compounds continues to attract interest. While the earlier attention was concentrated largely on the use of sulfide as a bridging ligand,[1] in recent times the use of selenium and tellurium has also been explored quite extensively.[2] In the course of our investigations directed towards the preparation and structural characterization of mixed-metal clusters stabilized by the heavier chalcogen ligands we have reported the facile synthesis of [Fe$_2$W(CO)$_{10}$(μ$_3$-Te)$_2$] and [Fe$_2$M-(CO)$_{10}$(μ$_3$-Se)$_2$] (M = Mo or W).[3] Structural characterization of [Fe$_2$W(CO)$_{10}$(μ$_3$-Te)$_2$] by X-ray diffraction reveals it to consist of a heavy-atom square pyramid in which the apical site is occupied by the W atom. Attempts to synthesize the molybdenum analogue were unsuccessful; however. when Se was used as the bridging chalcogen ligand both [Fe$_2$M(CO)$_{10}$(μ$_3$-Se)$_2$] (M = Mo or W) were isolated and characterized on the basis of a comparison of their IR spectra in the CO region with that of [Fe$_2$W(CO)$_{10}$(μ$_3$-Te)$_2$] and by mass spectral analysis. Adams *et al.*[4] reported the preparation of [Fe$_2$W(CO)$_9$(PMe$_2$Ph)(μ$_3$-S)$_2$], which has a core structure similar to our [Fe$_2$W(CO)$_{10}$(μ$_3$-Te)$_2$]. The phosphine ligand in [Fe$_2$W(CO)$_9$(PMe$_2$Ph)(μ$_3$-S)$_2$] plays an important stabilizing role because we have been unable to obtain [Fe$_2$W(CO)$_{10}$(μ$_3$-S)$_2$]. In recent years we have been interested in the reactivities of the mixed-chalcogenide compound [Fe$_2$(CO)$_6$(μ-EE′)] for cluster-growth purposes and in continuation of our studies to explore the effect of different chalcogen ligands on the synthesis and relative stabilities of mixed-metal clusters we have studied the reaction of [Fe$_2$(CO)$_6$(μ-SeTe)] and [Fe$_2$(CO)$_6$(μ-SSe)] towards [W(CO)$_5$(thf)] (thf = tetrahydrofuran). For purposes of completion of earlier reported work,[3] and for comparison with the new clusters reported in this study, we have also carried out the structural characterization, by X-ray methods, of [Fe$_2$M(CO)$_{10}$(μ$_3$-Se)$_2$] (M = Mo or W).

Results and Discussion

Synthesis and characterization of [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)(μ$_3$-E)] (E = Te **1** or S **2**)

Room-temperature stirring of [Fe$_2$(CO)$_6$(μ-SeTe)] and [W-(CO)$_5$(thf)] in hexane afforded the new mixed-metal, mixed-chalcogen cluster [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)(μ$_3$-Te)] **1** in 55% yield (Scheme 1). Under similar conditions [Fe$_2$W(CO)$_{10}$(μ$_3$-S)-(μ$_3$-Se)] **2** was obtained in 40% yield from the reaction of [Fe$_2$(CO)$_6$(μ-SSe)] and [W(CO)$_5$(thf)]. While cluster **1** is stable in the solid state and in solution, **2** slowly decomposes in solution and traces of the cluster [Fe$_2$W(CO)$_{10}$(μ$_3$-Se)$_2$] **3** are formed. Clusters **1** and **2** were characterized by comparison of their infrared spectra in the carbonyl-stretching region with

Scheme 1

Table 1 Spectroscopic data for compounds 1–4

Compound	IR ($\bar{v}_{CO}$/cm⁻¹, hexane)	⁷⁷Se	¹²⁵Te	J/Hz
1 [Fe₂W(CO)₁₀(μ₃-Se)(μ₃-Te)]	2086w, 2049vs, 2039vs, 2007s, 1966w	442.8	355.8	60.3 (Se–W)
				156.4 (Te–W)
2 [Fe₂W(CO)₁₀(μ₃-S)(μ₃-Se)]	2092w, 2054vs, 2047vs, 2011s, 1970w	301.9		57.6 (Se–W)
3 [Fe₂W(CO)₁₀(μ₃-Se)₂]	2090w, 2053vs, 2044vs, 2010s, 1969w	372.2		58.8 (Se–W)
4 [Fe₂Mo(CO)₁₀(μ₃-Se)₂]	2090w, 2055vs, 2041vs, 2012s, 1972w	540		
[Fe₂W(CO)₁₀(μ₃-Te)₂]	2081w, 2044vs, 2034vs, 2002s, 1964w		467.4	160.2 (Te–W)

those of the previously reported clusters [Fe₂M(CO)₁₀(μ₃-E)₂] (M = W, E = Se or Te; M = Mo, E = Se).[3] The spectra of these compounds typically show terminal CO stretching bands and there is a shift of the corresponding bands to lower frequencies for [Fe₂W(CO)₁₀(μ₃-EE')] along the following series of EE' combinations: SeS > Se₂ > SeTe > Te₂. The ¹³C NMR spectrum shows two peaks each for the terminally bonded carbonyl groups of **1** and **2**. The ⁷⁷Se NMR spectra each show a single peak with satellites due to ⁷⁷Se–¹⁸³W coupling where the signal for **1** appears 140.9 ppm downfield of that for **2**. For the compounds [Fe₂W(CO)₁₀(μ₃-Se)(μ₃-E)] (E = S, Se or Te) there is a downfield shift of the ⁷⁷Se NMR signal along the series. A similar trend is observed in the ⁷⁷Se NMR spectra of [Fe₃(CO)₉(μ₃-Se)(μ₃-E)]: E = S, δ 679.7; Se, δ 778.4; Te, δ 867.1. Comparison of the spectra of [Fe₂W(CO)₁₀(μ₃-Se)₂] **3** and [Fe₂Mo(CO)₁₀(μ₃-Se)₂] **4** shows the signal for **4** to be 167.8 ppm downfield of that for **3**. There is a marginal increase in the Se–W couplings for the compounds [Fe₂W(CO)₁₀(μ₃-Se)(μ₃-E)] along the series E = S > Se > Te. The ¹²⁵Te NMR spectra show similar trends, with the chemical shifts and the Te–W couplings increasing along the series E = S > Se > Te. Table 1 lists the spectroscopic data for **1–4** and [Fe₂W(CO)₁₀(μ₃-Te)₂].

Molecular structures of compounds 1, 3 and 4

The molecular structures of [Fe₂W(CO)₁₀(μ₃-Se)(μ₃-Te)] **1**, and of the previously reported [Fe₂W(CO)₁₀(μ₃-Se)₂] **3** and [Fe₂Mo(CO)₁₀(μ₃-Se)₂] **4**, are depicted in Fig. 1. Relevant structural parameters are compared in Tables 2 and 3. The three clusters have the same heavy-atom skeleton which consists of an Fe₂ME(E') square pyramid in which the heterometal atom M is located at the apical site. There are four carbonyl groups associated with the heterometal atom, while the two iron atoms have three each. The structures are similar to those of the previously reported [Fe₂W(CO)₁₀(μ₃-Te)₂][3] and [Fe₂W(CO)₉(PMe₂Ph)(μ₃-S)₂].[4] The average Fe–W bond length of **1** (2.854 Å) is slightly longer than that of **3** (2.815 Å), and both of these are shorter than that reported for [Fe₂W(CO)₁₀(μ₃-Te)₂] (2.911 Å). The sulfido clusters [Fe₂W(CO)₉(PMe₂Ph)(μ₃-S)₂] (2.766 Å) and [CoFeW(CO)₇-(PMe₂Ph)(μ₃-S)][5] (2.759 Å) have still shorter Fe–W bond lengths. In the latter complexes the presence of phosphine groups, which are not as effective as carbonyl groups in withdrawing electron density from metal atoms, should favour stronger metal–metal interactions. The average Se–W bond distance in **1** (2.616 Å) is slightly longer than the Se–W bond distance of 2.554 Å observed in **3**. In addition, the Te–W bond distance of 2.674 Å in **1** is slightly shorter than that of 2.736 Å in [Fe₂W(CO)₁₀(μ₃-Te)₂]. However, the average Fe–Mo bond distance of **4** (2.809 Å) is similar to that of [Fe₂Mo₂-(η-C₅H₅)₂(CO)₇(μ₃-Se)₂][6] (2.816 Å), but slightly shorter than those of [FeMo₂(η-C₅H₅)₂(CO)₇(μ₃-Se)₂][6] (2.835 Å) and of [Fe₂Mo₂(η-C₅H₅)₂(CO)₆(μ₃-Se)₂(μ₄-Se)][7] (2.847 Å), and significantly shorter than that (2.853 Å) reported for [Fe₂Mo₂(η-C₅H₄Me)₂(CO)₆S₄].[8] The average Se–Mo bond distance in **4** (2.546 Å) is slightly longer than the Se–Mo bond
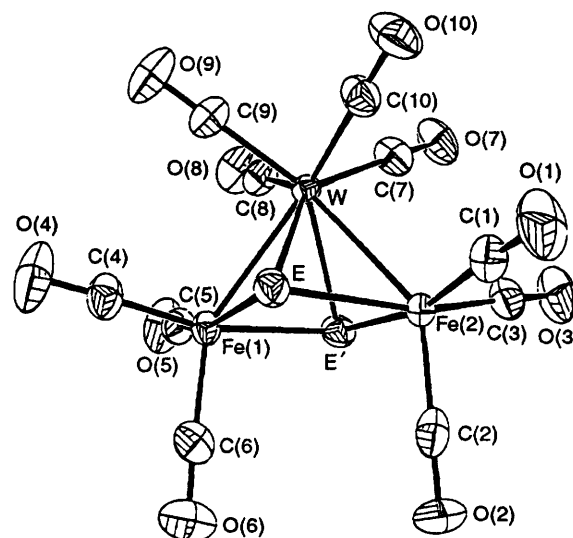
Fig. 1 Molecular structures of [Fe₂M(CO)₁₀(μ₃-E)(μ₃-E') [M = W, E = Te(1)/Se(1') (66/34), E' = Se(1)/Te(1') (66/34) **1**; M = W, E = Se(1), E' = Se(2) **3**, M = Mo, E = Se(1), E' = Se(2) **4**]

distances in [Fe₂Mo₂(η-C₅H₅)₂(CO)₇(μ₃-Se)₂][6] (2.502 Å) and [FeMo₂(η-C₅H₅)₂(CO)₇(μ₃-Se)][6] (2.509 Å).

In compounds **1–4** the selenium and tellurium ligands adopt the μ₃ bridging mode and so function as four-electron donors to the cluster. In terms of electron-counting rules, these are 50-electron clusters, and the formal application of the 18-electron rule would predict two metal–metal bonds as is observed. Application of the polyhedral skeletal electron pair theory also predicts correctly the *nido* octahedral structure due to the presence of seven skeletal electron pairs.

Experimental

Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified argon. Solvents were purified, dried and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path length NaCl cells. NMR (¹³C, ⁷⁷Se and ¹²⁵Te) spectra on a Varian VXR-300S spectrometer in CDCl₃. The ⁷⁷Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time, and referenced to Me₂Se (δ 0). The ¹²⁵Te NMR measurements were made similarly at an operating frequency of 94.75 MHz and referenced to Me₂Te (δ 0). Elemental analyses were performed on a Carlo-Erba automatic analyser. The compounds [Fe₂(CO)₆(μ-SeTe)],[9] [Fe₂(CO)₆(μ-SSe)],[10] [W(CO)₅(thf)][11] and [Fe₂M(CO)₁₀-(μ₃-Se)₂] (M = W or Mo)[3] were prepared by established procedures. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel having a 125 W immersion-type mercury lamp manufactured by Applied Photophysics Ltd.

Table 2 Crystal data and details of measurements for compounds **1**, **3** and **4***

	1	3	4
Formula	$C_{10}Fe_2O_{10}SeTeW$	$C_{10}Fe_2O_{10}Se_2W$	$C_{10}Fe_2O_{10}MoSe_2$
M	782.2	733.4	645.6
Crystal size/mm	$0.1 \times 0.2 \times 0.15$	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.2$
$a/Å$	6.885(2)	6.771(2)	6.788(1)
$b/Å$	9.470(3)	9.360(3)	9.401(2)
$c/Å$	13.670(4)	13.624(4)	13.646(2)
$\alpha/°$	81.38(3)	81.73(3)	81.81(2)
$\beta/°$	82.42(2)	82.01(2)	82.24(2)
$\gamma/°$	85.26(2)	85.23(2)	85.37(2)
$U/Å^3$	871.7	844.4	852.4
$D_c/g\ cm^{-3}$	2.98	2.88	2.52
$F(000)$	704	668	604
$\mu(Mo\text{-}K\alpha)/cm^{-1}$	115.9	124.8	66.6
Unique observed reflections	2997	2663	1638
Unique observed reflections with $I \geqslant 2\sigma(I)$	2404	2520	1228
Maximum, minimum residual electron density/e $Å^{-3}$	0.66, -0.66	1.11, -0.98	0.30, -0.34
Maximum, minimum absorption corrections	1.207, 0.881	1.441, 0.815	1.214, 0.774
Weighting scheme, w	$1.7830/[\sigma^2(F) + 0.000\ 239F^2]$	$2.2011/[\sigma^2(F) + 0.001\ 082F^2]$	$2.0048/[\sigma^2(F) + 0.000\ 316F^2]$
R	0.0209	0.0314	0.0298
R'	0.0222	0.0326	0.0294

* Details in common: triclinic, space group $P\bar{1}$; $Z = 2$.

Table 3 Selected bond lengths (Å) and bond angles (°) for compounds **1**, **3** and **4**

	1 M = W	3 M = W	4 M = Mo		1 M = W	3 M = W	4 M = Mo
Fe(1)–M	2.869(1)	2.829(4)	2.823(4)	C(7)–M	2.026(9)	2.055(11)	2.024(12)
Fe(2)–M	2.840(1)	2.802(4)	2.794(4)	C(8)–M	2.032(9)	2.031(12)	2.073(22)
Fe(1)–Se(1)	2.428(3)	2.374(3)	2.367(3)	C(9)–M	2.022(9)	2.028(11)	2.014(12)
Fe(1)–Te(1)	2.484(3)			C(10)–M	2.017(9)	2.023(10)	2.008(16)
Fe(1)–Se(2)		2.364(3)	2.361(4)	C(1)–Fe(1)	1.814(8)	1.784(11)	1.812(17)
Fe(2)–Se(1)	2.431(3)	2.370(3)	2.369(4)	C(2)–Fe(1)	1.783(9)	1.767(10)	1.782(10)
Fe(2)–Te(1)	2.486(3)			C(3)–Fe(1)	1.804(9)	1.811(11)	1.803(11)
Fe(2)–Se(2)		2.375(3)	2.369(3)	C(4)–Fe(2)	1.770(9)	1.793(12)	1.791(11)
Se(1)–M	2.616(4)			C(5)–Fe(2)	1.809(9)	1.807(11)	1.799(21)
Te(1)–M	2.674(4)			C(6)–Fe(2)	1.777(9)	1.782(10)	1.788(12)
Se(2)–M		2.554(4)	2.546(4)				
Fe(1)–M–Se(1)	52.4(0)	52.0(0)	52.0(0)	C(7)–M–Se(2)		87.9(3)	87.0(5)
Fe(1)–M–Te(1)	53.1(0)			C(8)–M–Fe(1)	138.5(2)	138.7(2)	138.1(5)
Fe(1)–M–Se(2)		51.8(0)	51.9(0)	C(8)–M–Fe(2)	84.2(2)	85.7(4)	83.9(5)
Fe(2)–M–Se(1)	52.8(0)	52.3(0)	52.4(0)	C(8)–M–Se(1)	87.5(2)	136.3(3)	134.7(4)
Fe(2)–M–Te(1)	53.5(0)			C(8)–M–Te(1)	135.8(2)		
Fe(2)–M–Se(2)		52.4(0)	52.4(0)	C(8)–M–Se(2)		88.3(4)	87.2(6)
Fe(2)–M–Fe(1)	79.4(0)	77.8(0)	77.8(0)	C(9)–M–Fe(1)	138.6(2)	138.2(2)	138.9(4)
Se(1)–M–Te(1)	77.0(0)			C(9)–M–Fe(2)	88.3(2)	88.2(4)	88.7(4)
Se(2)–M–Se(1)		75.9(0)	76.0(0)	C(9)–M–Se(1)	139.9(2)	88.3(4)	89.0(5)
Fe(2)–Se(1)–Fe(1)	96.7(0)	96.3(0)	96.3(0)	C(9)–M–Te(1)	88.0(2)		
Fe(2)–Te(1)–Fe(1)	94.1(0)			C(9)–M–Se(2)		139.2(3)	139.6(4)
Fe(2)–Se(2)–Fe(1)		96.5(0)	96.5(2)	C(10)–M–Se(1)	136.2(2)	89.1(3)	88.8(5)
Se(1)–Fe(1)–Te(1)	84.4(0)			C(10)–M–Te(1)	88.0(3)		
Se(1)–Fe(2)–Te(1)	84.3(0)			C(10)–M–Se(2)		136.4(2)	135.8(3)
Se(2)–Fe(1)–Se(1)		83.0(0)	83.0(0)	C(8)–M–C(7)	79.5(3)	78.6(5)	78.7(7)
Se(2)–Fe(2)–Se(1)		82.9(0)	82.8(0)	C(9)–M–C(7)	125.4(2)	125.2(5)	124.8(6)
C(7)–M–Fe(1)	87.4(2)	88.7(4)	89.2(5)	C(9)–M–C(8)	77.8(3)	77.6(4)	77.0(7)
C(7)–M–Fe(2)	137.4(2)	137.8(2)	136.5(4)	C(10)–M–C(7)	77.8(4)	77.4(4)	78.8(6)
C(7)–M–Se(1)	87.1(2)	139.4(3)	140.2(4)	C(10)–M–C(8)	128.5(4)	127.3(5)	129.3(7)
C(7)–M–Te(1)	139.1(2)			C(10)–M–C(9)	79.0(4)	79.3(5)	79.7(6)

Preparation of [Fe₂W(CO)₁₀(μ₃-Se)(μ₃-E)] (E = Te 1 or S 2)

In a typical preparation a thf solution (120 cm³) of [W(CO)₆] (0.145 g, 0.41 mmol, for **1**; 0.135 g, 0.38 mmol, for **2**) was irradiated with 366 nm UV light for 15 min under a constant argon purge. The lemon-yellow solution of [W(CO)₅(thf)] was added to a hexane solution (50 cm³) containing [Fe₂(CO)₆(μ-SeTe)] (0.2 g, 0.41 mmol) or [Fe₂(CO)₆(μ-SSe)] (0.15 g, 0.41 mmol). The reaction mixture was stirred at room temperature for 3 h. The solvent was then removed *in vacuo*, and the residue subjected to chromatographic work-up on a silica gel column. Elution with hexane yielded trace amounts of [W(CO)₆] and

[Fe₂(CO)₆(μ-SeE)], followed by a major maroon band of compound **1** (0.11 g, 55%) or **2** (0.06 g, 40%). Compound **1**: m.p. 148–150 °C (decomp.) (Found: C, 15.7. C₁₀Fe₂O₁₀SeTeW requires C, 15.4%); δ_C(CDCl₃) 206.4 (4 C, s, WCO) and 208.6 (6 C, s, FeCO). Compound **2**: m.p. 138–140 °C (decomp.) (Found: C, 17.6. C₁₀Fe₂O₁₀SSeW requires C, 17.5%); δ_C(CDCl₃) 208.8 (4 C, s, WCO) and 208.9 (6 C, s, FeCO).

Crystallography

Crystals of compounds **1**, **3** and **4** suitable for X-ray diffraction analysis were grown from hexane and dichloromethane solvent

mixtures by slow evaporation of the solvents at $-5\,^{\circ}C$. Crystallographic data (summarized in Table 2) were measured at 298 K on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$, using Mo-K$\alpha$ radiation ($\lambda = 0.710\,69$ Å). Data were corrected for Lorentz polarization and also for absorption.[12] The structures were solved by Patterson methods and refined on F^2 using the SHELX suite of programs.[13] Early refinement revealed that the selenium and tellurium positions were mutually disordered for **1**. In particular, Se(1) and Te(1) share their sites with Te(1′) and Se(1′) respectively, in the occupancy ratio of 66:34. In the final least-squares cycles all atoms were allowed to vibrate anisotropically.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/2.

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