[{$Fe_2(CO)_6(\mu_3\text{-Se})(\mu_3\text{-Te})$}$_2Mo(CO)_2$]: a novel mixed-metal, mixed-chalcogenide cluster with an unusual structure

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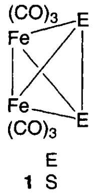
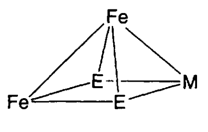
The room-temperature reaction of [$Fe_2(CO)_6(\mu\text{-SeTe})$] with two equiv. of [$Mo(CO)_5(thf)$] yields the mixed-metal, mixed-chalcogenide cluster [$Fe_4Mo(CO)_{14}(\mu_3\text{-Se}_2)(\mu_3\text{-Te})_2$], which has an unusual structure as established by single-crystal X-ray diffraction.

The class of compounds [$Fe_2(CO)_6(\mu\text{-E}_2)$] (E = S **1**, Se **2**, Te **3**), have served as useful starting materials for numerous types of cluster-growth reactions.[1] Under facile conditions, addition of mono- and poly-nuclear metal carbonyl species occurs across the E–E bond to yield mixed-metal clusters.[1c,1e,2] Mostly, the addition of mononuclear metal carbonyl species across the E–E bond is accompanied by formation of one new bond between an iron atom and the adding metal atom to give clusters (structure **4**) with a square-pyramidal core of the three metal atoms and the two chalcogens, in which one of the iron atoms occupies the apical site.[1–3] However, a few instances are recorded where the addition of the heterometal atom across the E–E bond is accompanied by Fe–Fe bond cleavage and two new Fe–heterometal atom bond formations, resulting in a square-pyramidal core in which the heterometal atom occupies the apical site (structure **5**).[1c,4] We have recently developed synthesis of the mixed-chalcogenide compounds [$Fe_2(CO)_6(\mu\text{-EE}')$] and have reported the reaction of organic and inorganic species across the very reactive E–E′ bond.[5] In continuation of our interest in mixed-metal clusters of form **5**, we have investigated the reaction of the mixed-chalcogenide compound [$Fe_2(CO)_6(\mu\text{-SeTe})$] with [$Mo(CO)_5(thf)$].

When equimolar amounts of [$Fe_2(CO)_6(\mu\text{-SeTe})$] and [$Mo(CO)_5(thf)$] were stirred in hexane solvent at room temperature, the reaction mixture changed from orange to maroon and IR spectroscopy indicated some new bands in the CO region with a pattern and stretching frequencies comparable with those of the previously reported compounds [$Fe_2M(CO)_{10}(\mu_3\text{-E})_2$], (M = W, E = Te; M = Mo, W, E = Se).[4a] During chromatographic work-up, in addition to the unreacted [$Fe_2(CO)_6(\mu\text{-SeTe})$] and [$Mo(CO)_5(thf)$], two new bands were observed: a major maroon band (**6**) and a much smaller amount of a green band (**7**). The maroon band was found to gradually convert to the green compound **7** during the chromatography. The reaction of 2 equiv. of [$Fe_2(CO)_6(\mu\text{-SeTe})$] and [$Mo(CO)_5(thf)$] yielded a much better yield of **7** (Scheme 1).[†] The molecular structure of **7** was established by a single-crystal X-ray structure analysis (Fig. 1).[‡] The Mo atom occupies the common apical site of two distorted square-pyramidal cores in each of which the two Fe atoms, one Se atom and one Te atom occupy the basal sites. Two terminally bonded carbonyl ligands on the Mo atom give it an overall coordination number of ten. Three of the four Mo–Fe bond distances [2.867(5)–2.889(5) Å] are comparable with the Mo–Fe bond lengths reported for other Mo/Fe mixed-metal



E
1 S
2 Se
3 Te



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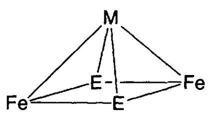

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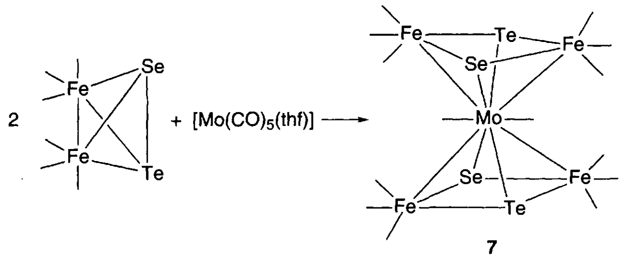

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Scheme 1 *Reagents and conditions*: room temp., 3 h, hexane

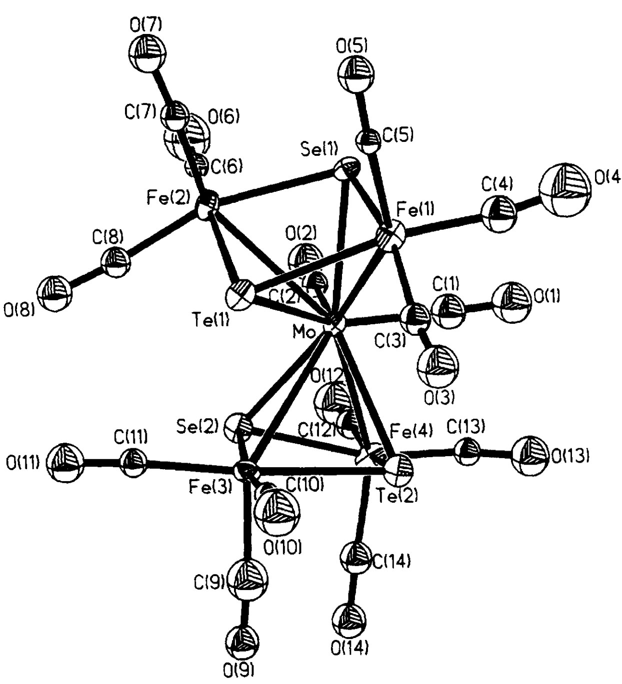

Fig. 1 Crystal structure of **7**. Selected bond lengths (Å) and angles (°): Mo–Fe(1) 2.886(2), Mo–Fe(2) 2.889(5), Mo–Fe(3) 3.083(5), Mo–Fe(4) 2.867(5), Mo–Se(1) 2.567(4), Mo–Se(2) 2.622(4), Mo–Te(1) 2.792(4), Mo–Te(2) 2.701(4), Fe(1)–Se(1) 2.381(7), Fe(2)–Se(1) 2.398(6), Fe(3)–Se(2) 2.465(6), Fe(4)–Se(2) 2.444(5), Fe(1)–Te(1) 2.529(5), Fe(2)–Te(1) 2.531(6), Fe(3)–Te(2) 2.532(5), Fe(4)–Te(2) 2.503(6); Fe(1)–Mo–Fe(2) 78.3(2), Fe(1)–Mo–Se(1) 51.4(1), Fe(1)–Mo–Te(1) 52.9(1), Fe(2)–Mo–Se(1) 51.7(1), Fe(2)–Mo–Te(1) 52.9(1), Fe(3)–Mo–Fe(4) 76.1(1), Fe(3)–Mo–Se(2) 50.4(1), Fe(3)–Mo–Te(2) 51.4(1), Fe(4)–Mo–Se(2) 52.7(1), Fe(4)–Mo–Te(2) 53.3(1), Fe(1)–Mo–Fe(3) 96.9(2), Fe(1)–Mo–Fe(4) 140.9(2), Fe(1)–Mo–Se(2) 145.1(2), Fe(1)–Mo–Te(2) 92.0(1), Fe(2)–Mo–Fe(3) 96.2(1), Fe(2)–Mo–Fe(4) 140.2(2), Fe(2)–Mo–Se(2) 92.1(1), Fe(2)–Mo–Te(2) 145.2(2), Fe(3)–Mo–Se(1) 135.2(2), Fe(3)–Mo–Te(1) 59.6(1), Fe(4)–Mo–Se(1) 148.7(2), Fe(4)–Mo–Te(1) 135.7(2), Se(1)–Mo–Te(1) 75.6(1), Se(2)–Mo–Te(2) 76.9(1), Se(1)–Mo–Se(2) 141.1(2), Se(1)–Mo–Te(2) 140.5(1), Te(1)–Mo–Te(2) 94.6(1), Se(2)–Mo–Te(1) 94.6(1).

clusters stabilized by chalcogen ligands,[6] whereas the fourth bond is somewhat long [Mo–Fe(3), 3.083(5) Å], making one of the square pyramids more distorted than the other. While the two Mo–Se distances are similar [2.567(4), 2.622(4) Å], there is a slightly greater difference in the two Mo–Te bond lengths [2.792(4), 2.701(4) Å].

A contrast in the influence of the chalcogens in the cluster expansion is seen in the reactions of $[\mathrm{Fe_2(CO)_6(\mu\text{-}Se)_2}]$ and $[\mathrm{Fe_2(CO)_6(\mu\text{-}Te)_2}]$. The former readily reacts with $[\mathrm{M(CO)_5(thf)}]$ (M = Mo or W) to form $[\mathrm{Fe_2M(CO)_{10}(\mu_3\text{-}Se)_2}]$; on the other hand, $[\mathrm{Fe_2(CO)_6(\mu\text{-}Te)_2}]$ reacts with the tungsten compound only to form $[\mathrm{Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2}]$; formation of $[\mathrm{Fe_2Mo(CO)_{10}(\mu_3\text{-}Te)_2}]$ is not observed.[4a] The use of the mixed-chalcogenide starting compound $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$, therefore, leads to an intermediate situation with respect to its reaction with $[\mathrm{Mo(CO)_5(thf)}]$. The formation of $[\mathrm{Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)(\mu_3\text{-}Te)}]$ **6** is observed; however, it quickly converts to the unusual compound $[\mathrm{Fe_4Mo(CO)_{14}(\mu_3\text{-}Se)_2(\mu_3\text{-}Te)_2}]$. Such a transformation appears to be unique to the mixed-chalcogenide precursor because attempts to add $\mathrm{Fe_2(CO)_6(\mu\text{-}E_2)}$ groups to $[\mathrm{Fe_2Mo(CO)_{10}(\mu_3\text{-}E)_2}]$ (E = Se, Te) or to $[\mathrm{Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2}]$ have so far been unsuccessful. We are currently investigating the possibility of adding coordinatively unsaturated metal carbonyl species to the two open FeSeFeTe faces of **7**.

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Footnotes

† *Synthesis* of **6** and **7**: a thf solution (120 ml) of $[\mathrm{Mo(CO)_6}]$ (0.068 g, 0.26 mmol) was irradiated with 366 nm UV light in an immersion type photolysis instrument for 10 min under a constant argon purge. The yellow–green solution of $[\mathrm{Mo(CO)_5(thf)}]$ was added to a hexane solution (50 ml) containing $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ (0.125 g, 0.26 mmol). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue was subjected to chromatographic work-up on a silica gel chromatography column. Elution with hexane yielded a trace amount of $[\mathrm{Mo(CO)_6}]$, maroon band **6** {0.025 g, 23%, based on $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ consumed; IR [hexane, ν(CO)/cm^{-1}]: 2086w, 2052vs, 2010s, 1969w} and $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ (0.050 g, 40%) followed by a green band **7** {0.035 g, 11%, based on $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ consumed; mp 174–176 °C (decomp.) IR [hexane, ν(CO)/cm^{-1}]: 2083w, 2057vs, 2050vs, 2043vs, 2019w, 2009s, 1996w, 1989w, 1982w. Anal. Calc. for $\mathrm{C_{14}O_{14}Fe_4MoSe_2Te_2}$: C, 14.95. Found: C, 15.3}. When the reaction was carried out with an excess of $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ (0.25 g, 0.51 mmol) and $[\mathrm{Mo(CO)_5(thf)}]$ [prepared from 0.068 g, 0.26 mmol of $\mathrm{Mo(CO)_6}$], in addition to the unreacted $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ (0.1 g, 40%) compound **7** was obtained in a higher yield {0.105 g, 30%, based on $[\mathrm{Fe_2(CO)_6(\mu\text{-}SeTe)}]$ consumed}.

‡ *Crystal data* for **7**: $\mathrm{C_{14}Fe_4MoO_{14}Se_2Te_2}$, M = 1124.6; dark-greenish plate, crystal size 0.05 × 0.15 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 15.454(3), b = 11.565(2), c = 14.509(3) Å, β = 98.75(2)°, U = 2563(2) Å^3, Z = 4, D_c = 2.915 Mg m^{-3}, $\mu_{\text{calc.}}$ = 7.823 mm^{-1}. Of 3265 data collected on a Siemens R3 m/V diffractometer (Mo-Kα, $3.5 \leqslant 2\theta \leqslant 44.0°$, 220 K) 1639 reflections were observed [$F > 6.0\,\sigma(F)$]. Data were corrected for Lorentz and polarization effects. Semi-empirical absorption study was applied with min./max. transmission 0.930/0.606, respectively. The structure was solved by heavy-atom methods on PC computers using SHELXTL-PLUS (G. M. Sheldrick, Structure Determination Software Program Package, Siemens analytical X-ray Instruments, Inc., Madison, WI, 1990). The Se and Te atoms were disordered at the positions of Se(2) and Te(2) with Se/Te 0.70/0.30 at the Se(2) position, and Se/Te 0.30/0.70 at Te(2). Fe, Mo, Se, and Te atoms were anisotropically refined, while C and O atoms were treated isotropically. Final cycles of refinement converged at $R = 0.072, R_w = 0.082$ ($w = [\sigma^2(F_o) + 0.001\,(F_o)^2]^{-1}$) with a GOF = 1.63; 194 parameters for observed reflections. The maximum and minimum residual electron density were +2.05 and −1.99 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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