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Mixed chalcogen carbonyl compounds

III *. Construction of the new unsaturated mixed metal clusters $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$

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Abstract

Addition of $Ru(CO)_4(C_2H_4)$ to $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ and to $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ lead to a clean formation of the new unsaturated mixed metal, mixed chalcogen carbonyl clusters, $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ respectively. The Fe_3Ru cluster is also obtainable from the photolysis of a solution containing $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ and $Fe(CO)_5$.

Introduction

Cluster unsaturation is an important property for consideration of the cluster-surface analogy in studies related to catalysis. Although numerous examples exist of clusters which are electron deficient, in recent times, it has been the class of tetranuclear clusters of the form $M_4(CO)_{11}(\mu_4\text{-}X)_2$ (M = Fe, Ru; X = PR, AsR, S, Se, Te), whose synthesis, structure and property of electronic unsaturation has invoked considerable interest [2]. These compounds, in general, can be obtained in fair yields, using either mild thermolytic or photolytic reaction conditions. Theoretical studies to examine interaction between the (μ_4-X) groups in these clusters has further prompted investigation of their designed synthesis [2d,2g].

In continuation of our work on the use of group 16 elements as bridges in cluster growth reactions [3], we have attempted to design the composition of unsaturated tetranuclear clusters such that they have different transition metals as well as different group 16 elements as bridging ligands in the same molecule. Earlier, we have reported the synthesis of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (Fig. 1) from an atom transfer reaction of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$ [2b], and also the facile

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* For Part II see ref. 1.

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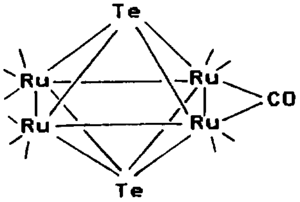


Fig. 1. $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$.

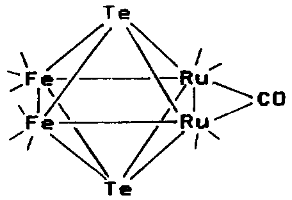
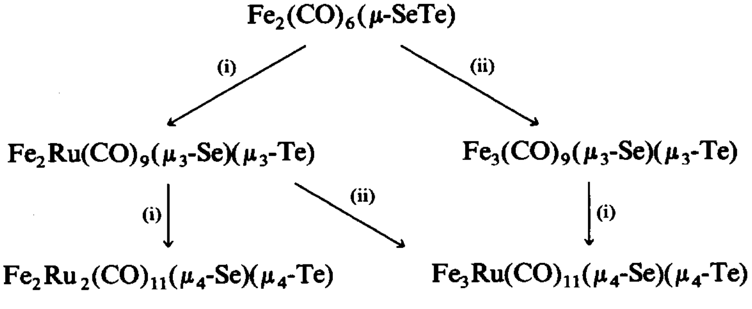


Fig. 2. $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$.

synthesis of mixed metal cluster, $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (Fig. 2) from the stepwise addition of ruthenium carbonyl units to $Fe_2(CO)_6(\mu\text{-}Te_2)$ [2c]. The second reaction appears to be a convenient prototype for obtaining unsaturated tetranuclear clusters under room temperature conditions and in reasonable yields. The tetra-ruthenium cluster, $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$, can be obtained in good yield from the room temperature reaction of $Ru_3(CO)_9(\mu_3\text{-}Te)_2$ with $Ru(CO)_4(C_2H_4)$ [4]. Recently, we have reported on a convenient method of obtaining the mixed chalcogen derivatives, $Fe_2(CO)_6(\mu\text{-}SeTe)$ and $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ in pure form [5]. Here, we report on the use of these mixed chalcogen compounds for the synthesis of the new unsaturated mixed metal, mixed chalcogen carbonyl clusters, $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ (Scheme 1).

Results and discussion

The new mixed metal cluster $Fe_2Ru_2(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ (I) was obtained from the room temperature stirring of a hexane solution containing $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ and $Ru(CO)_4(C_2H_4)$. Cluster I was characterised by IR spectroscopy,



Scheme 1. (i) $Ru(CO)_4(C_2H_4)$; (ii) $Fe(CO)_5$, *hν*.

Table 1

Comparison of the carbonyl stretching frequencies of $(\mu\text{-Se})_2$, $(\mu\text{-Te})_2$ and $(\mu\text{-Se})(\mu\text{-Te})$ compounds

Compound	Solvent [a]	CO (cm^{-1})
$Fe_3(CO)_9(\mu_3\text{-Se})_2$	a	2057(vs), 2038(s), 2017(s)
$Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$	a	2052(vs), 2033(s), 2011(s)
$Fe_3(CO)_9(\mu_3\text{-Te})_2$	a	2047(vs), 2028(s), 2007(s)
$Fe_2Ru_2(CO)_{11}(\mu_4\text{-Se})_2$	b	2090(w), 2046(vs), 2011(m), 1841(w), 1828(vw)
$Fe_2Ru_2(CO)_{11}(\mu_4\text{-Se})(\mu_4\text{-Te})$	b	2087(w), 2041(vs), 2007(m), 1836(w), 1826(vw)
$Fe_2Ru_2(CO)_{11}(\mu_4\text{-Te})_2$	b	2085(w), 2037(vs), 2001(m), 1833(w), 1827(vw)
$Fe_3Ru(CO)_{11}(\mu_4\text{-Se})_2$	b	2087(w), 2046(vs), 2034(m), 2014(m), 1841(w), 1828(w)
$Fe_3Ru(CO)_{11}(\mu_4\text{-Se})(\mu_4\text{-Te})$	b	2086(w), 2042(vs), 2031(m), 2010(m), 1837(w), 1827(w)
$Fe_3Ru(CO)_{11}(\mu_4\text{-Te})_2$	b	2085(w), 2037(vs), 2027(m), 2005(m), 1995(m), 1834(w), 1822(w)

[a] a, hexane solvent; b, dichloromethane solvent.

mass spectrometry and microanalytical data. The infrared spectrum of I in dichloromethane solvent shows carbonyl stretching frequencies at 2087w, 2041vs, 2007m, 1836w and 1826vw cm^{-1}, in a pattern typical of clusters of the form $M_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-E})_2$, where M = Fe or Ru and E = S, Se or Te. X-Ray structural characterisation of $Fe_4(CO)_{11}(\mu_4\text{-S})_2$ [2d], $Ru_4(CO)_{11}(\mu_4\text{-Te})_2$ [2b] and $Fe_2Ru_2(CO)_{11}(\mu_4\text{-Te})_2$ [2c] suggests that all the clusters of the form $M_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-E})_2$ should have identical structural features, i.e., a trapezoidal arrangement of the metal atoms with both sides of the M_4 plane quadruply bridged by the group 16 elements to give a distorted octahedral $M_4(\mu_4\text{-E})_2$ core. The presence of a bridging carbonyl group is also a characteristic feature of these clusters; the bridged metal–metal bond being the shortest in length in the cases which have been structurally characterised. Infrared spectroscopy has proved particularly useful in the identification of clusters containing different group 16 elements as bridging ligands in the same molecule. For instance, we observe that the carbonyl stretching frequencies of I are an almost exact mean of the corresponding frequencies of $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-Se})_2$ [6] and $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-Te})_2$. A similar relationship has been observed when the frequencies of other mixed chalcogen carbonyl derivatives are compared with the corresponding $(\mu\text{-Se})_2$ and $(\mu\text{-Te})_2$ compounds (Table 1). The FAB mass spectrum of I showed molecular ion peaks centred at *m/e* 828, with an isotopic distribution pattern which matches well with that obtained by computer simulation (Fig. 3(i)). The molecular formula of I was also confirmed by elemental analysis (found: C, 16.2. $C_{11}Fe_2O_{11}Ru_2SeTe$ calc.: C, 15.9%).

Room temperature stirring of a hexane solution containing $Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ and $Ru(CO)_4(C_2H_4)$ yielded the mixed metal cluster $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-Se})(\mu_4\text{-Te})$ (II). Infrared spectrum of II in dichloromethane solvent shows carbonyl stretching frequencies at 2086w, 2042vs, 2031m, 2010m, 1837w and 1827vw cm^{-1}. As was observed in cluster I, the carbonyl stretching frequencies of II also are a

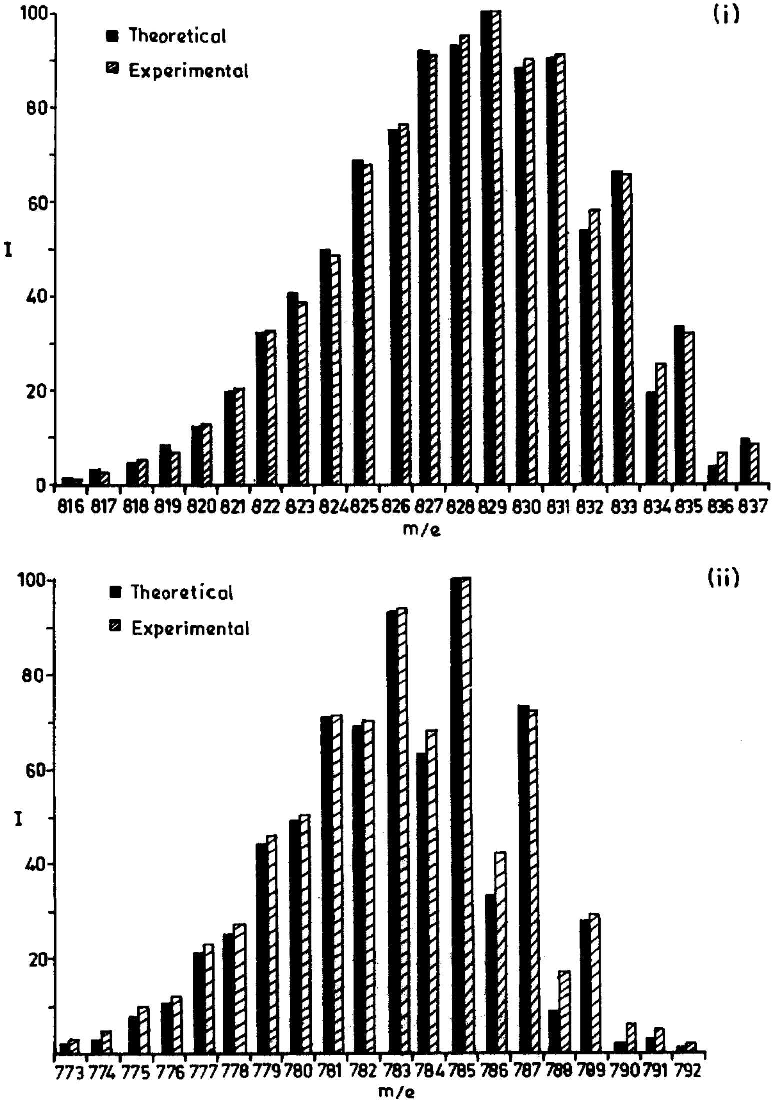
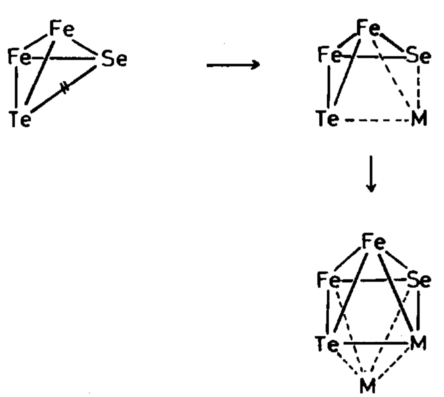


Fig. 3. Comparison of experimentally observed and computer simulated isotopic distribution pattern of the molecular ions of (i) $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ and (ii) $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)(\mu_4\text{-}Te)$.

mean of the corresponding frequencies in $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ [6] and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (Table 1). FAB mass spectrum of II showed peaks centred at *m/e* 783 due to the molecular ion. There is good match between the observed and computer simulated isotopic distribution patterns for the molecular ion (Fig. 3(ii)). Elemental analysis confirmed the molecular formula of II (found: C, 16.5. $C_{11}Fe_3O_{11}RuSeTe$ calc.: C, 16.9%). Cluster II was also found to form when hexane solution containing $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ and $Fe(CO)_5$ was photolysed with visible light.

Formation of the mixed metal mixed chalcogenide clusters, I and II, at room temperature, once again demonstrates the potential of the bridging main group



Scheme 2. Structural and bonding changes on addition of metal carbonyl groups to the bridging Se and Te atoms. Carbonyl groups have been omitted for clarity. || bond cleavage, — — — bond formation.

ligands in influencing cluster growth reactions. Scheme 2 shows the versatility of the Se and the Te ligands to change their mode of bonding during the metal addition process. Although the electrophilicity of the μ-E_2 moiety and the string inherent in the FeEEFe ring in complexes $Fe_2(CO)_6(\mu$-$E_2)$ are recognised to favour metal addition leading to the stepwise synthesis of trinuclear and tetranuclear clusters, the formation of I and II shows that when the mixed chalcogenide complexes, $Fe_2(CO)_6(\mu$-$EE')$ and $Fe_3(CO)_9(\mu_3$-$E)(\mu_3$-$E')$ are used it is possible to design the cluster construction. Thus, trinuclear and tetranuclear clusters containing different metal atoms and different group 16 elements can be obtained under facile reaction conditions using this approach. Cluster I represents the first example of a cluster consisting of Fe_2 and Ru_2 units connected by a selenium and a tellurium atoms.

The cluster $Fe_3Ru(CO)_{10}(\mu$-$CO)(\mu_4$-$Te)_2$ is known to form from the room temperature reaction of $Fe_3(CO)_9(\mu_3$-$Te)_2$ and $Ru(CO)_4(C_2H_4)$, and also from that of $Fe_2Ru(CO)_9(\mu_3$-$Te)_2$ with $Fe(CO)_5$ on visible light irradiation. In solution, $Fe_3Ru(CO)_{10}(\mu$-$CO)(\mu_4$-$Te)_2$ slowly converts into the trinuclear cluster $Fe_3(CO)_9$-$(\mu_3$-$Te)_2$. Cluster II, which can be thought of as being derived from $Fe_3Ru(CO)_{10}(\mu$-$CO)(\mu_4$-$Te)_2$ by substitution of one μ_4-Te by a μ_4-Se bridge, is found to behave similarly, and convert gradually in solution to the mixed chalcogen trinuclear compound $Fe_3(CO)_9(\mu_3$-$Se)(\mu_3$-$Te)$ over a period of days.

Experimental

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents were thoroughly dried and distilled immediately before use. $Fe_2Ru(CO)_9(\mu_3$-$Se)(\mu_3$-$Te)$ [1] and $Fe_3(CO)_9(\mu_3$-$Se)(\mu_3$-$Te)$ [5] were prepared as reported earlier. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in CH_2Cl_2 in NaCl cells. Elemental analyses were performed on a Carlo Erba automatic analyser.

Preparation of $Fe_2Ru_2(CO)_{11}(\mu_4$-$Se)(\mu_4$-$Te)$ (I)

A hexane solution (90 ml) containing $Ru_3(CO)_{12}$ (0.021 g, 0.033 mmol) was photolysed under a constant ethylene purge in an ultraviolet photochemical reactor for 10 min. The colourless solution of $Ru(CO)_4(C_2H_4)$ thus formed was added to a hexane solution (100 ml) of $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (0.067 g, 0.1 mmol). The mixture was stirred for 3 h. The solvent was removed *in vacuo* and the residue was subjected to chromatographic work up using a silica gel column. Elution with a hexane/dichloromethane (70 : 30 v/v) mixture separated trace amounts of $Ru_3(CO)_{12}$ and $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ from the major green band of $Fe_2Ru_2(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)$. Yield: 0.021 g, 25%.

Preparation of $Fe_3Ru(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)$ (II)

Method (a). To a hexane solution (100 ml) of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (0.063 g, 0.1 mmol) was added 90 ml of hexane containing 0.1 mmol of $Ru(CO)_4(C_2H_4)$, prepared as described before. The reaction mixture was stirred at room temperature for 3 h. Chromatography of the mixture on a silica gel column using hexane/dichloromethane (70:30 v/v) mixture as eluant afforded the green $Fe_3Ru(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)$, as the sole product. Yield: 0.023 g, 30%.

Method (b). A hexane solution (90 ml) containing $Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (0.067 g, 0.1 mmol) and Fe(CO)5 (0.13 ml, 0.1 mmol) was irradiated with visible light (40 W) for 0.5 h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column. Elution with hexane/dichloromethane (70 : 30 v/v) mixture yielded $Fe_3Ru(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)$. Yield: 0.019 g, 24%.

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