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## Mixed chalcogen carbonyl compounds

### II \*. Synthesis and characterization of $\text{Fe}_2\text{Ru}(\mu_3\text{-Se})\text{-}(\mu_3\text{-Te})(\text{CO})_9$ and $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\mu_3\text{-Se})(\mu_3\text{-Te})(\text{CO})_6$

Debojit Chakrabarty, Md. Munkir Hossain, R. Krishna Kumar  
 and Pradeep Mathur \*

*Chemistry Department, Indian Institute of Technology, Powai, Bombay 400076 (India)*  
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#### Abstract

The new mixed metal complexes, each containing bridging selenium and tellurium ligands in the same molecule,  $\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_6(\mu_3\text{-Se})(\mu_3\text{-Te})$  have been prepared from the room temperature reactions of  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  with  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  and  $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ , respectively. Reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_6(\mu_3\text{-Se})(\mu_3\text{-Te})$  with  $\text{Pt}(\text{PPh}_3)_4$  forms the previously known  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})(\mu_3\text{-Te})\text{Pt}(\text{PPh}_3)_2$  and on treatment with NaOMe, followed by acidification,  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  is formed.

#### Introduction

Transition metal carbonyl compounds containing certain main group elements as bridging ligands have been receiving increasing attention [2]. Compounds containing bonds between the transition metal and group 16 elements (S, Se, Te) have been studied due to the potential usefulness of these Main Group elements as bridges between different metal atoms in clusters and as stabilizing ligands to prevent their fragmentation [3,4]. Of the three group 16 elements, S has been the most extensively used for the purpose of cluster growth reactions, and there are numerous examples of clusters in which the S ligand exhibits diverse bonding modes [5]. Clusters containing Se or Te in different bonding modes have also been reported [5], and it is expected that there will be a contrast in clusters containing the different group 16 elements, in particular between the S or Se containing clusters from the Te containing ones [5].

In general, the dinuclear compounds  $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$  and the trinuclear compounds  $(\text{CO})_9\text{M}_3(\mu_3\text{-E})_2$ , (M = Fe, Ru or Os; E = S, Se or Te) have been employed

\* For Part I see ref. 1.

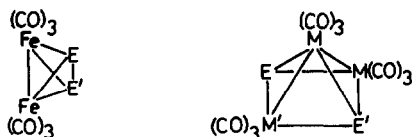
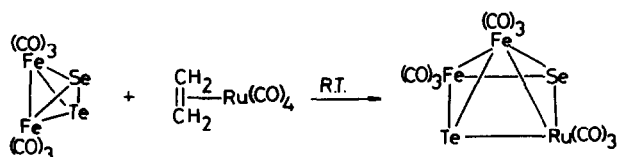


Fig. 1.

as starting materials for cluster growth reactions [6]. Whereas in the dinuclear compound addition across the E–E bond occurs readily, in the trinuclear starting material it is the lone pairs of electrons on the  $\mu_3$ -E ligands which act as the initial points of contact with coordinatively unsaturated species, the availability of the lone pairs being greatest for S and least for Te. The different reactivities of the chalcogen ligands is seen in the greater thermal stability of  $(CO)_6Fe_2(\mu-S_2)$  relative to  $(CO)_2Fe_2(\mu-Te_2)$ . In the case of the trinuclear compounds the different metal atoms and the different chalcogen ligands introduce contrasting reactivity features in the molecules. Little is known of the chemical reactivity of compounds of the form  $(CO)_6Fe_2(\mu-EE')$  and the mixed metal derivatives  $M_2M'(CO)_9(\mu_3-E)(\mu_3-E')$  (Fig. 1). This has been due to the difficulties associated with isolating pure mixed chalcogen derivatives. In a previous report we described a modified method by which pure  $(CO)_6Fe_2(\mu-SeTe)$  and  $(CO)_9Fe_3(\mu_3-Se)(\mu_3-Te)$  could be obtained [1]. Here, we describe the synthesis and characterization of the new mixed metal mixed chalcogen compounds  $Fe_2Ru(CO)_9(\mu_3-Se)(\mu_3-Te)$  and  $(\eta^5-C_5H_5)Co(\mu_3-Se)(\mu_3-Te)Fe_2(CO)_6$ .

## Results and discussion

Room temperature stirring of hexane solution containing  $(CO)_6Fe_2(\mu-SeTe)$  and  $Ru(CO)_4(C_2H_4)$  led to the formation of  $Fe_2Ru(CO)_9(\mu_3-Se)(\mu_3-Te)$  (I) in good yield (Scheme 1). Compound I was characterized by infrared spectroscopy, mass spectrometry and microanalytical data. The infrared spectrum of I in hexane solvent displays in the carbonyl stretching region bands at 2092w, 2061vs, 2055s, 2047m, 2032vs and 2009s in a pattern typical of the  $M_3(CO)_9(\mu_3-E)_2$  type of molecule (Fig. 2). The mass spectrum shows the molecular ion peaks centred at  $m/e = 670$  and peaks centred at  $m/e = 670 - n28$  ( $n = 1-9$ ), corresponding to fragments arising from the successive loss of nine carbonyl groups. There are also weak peaks at



Scheme 1.

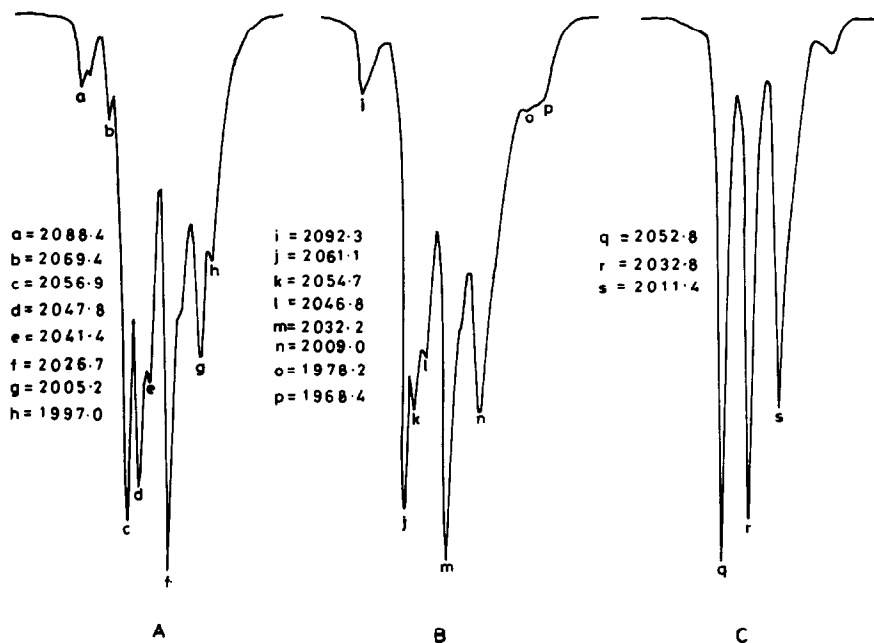
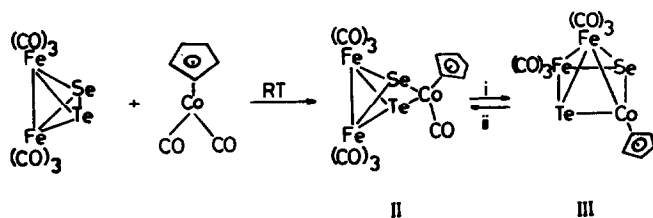


Fig. 2. Infrared spectra in the carbonyl region, in hexane solvent ( $\nu$  in  $\text{cm}^{-1}$ ) of A.  $\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Te})_2$ , B.  $\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$  and C.  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ .

$m/e = 321$ , due to the  $\text{Fe}_2\text{SeTe}^+$  ion and at  $m/e = 213$ , due to the  $\text{Fe}_2\text{Ru}^+$  ion. Microanalytical data confirm the molecular formula of I (found: C, 16.49.  $\text{C}_9\text{O}_9\text{Fe}_2\text{RuSeTe}$  calc.: C, 16.11%).

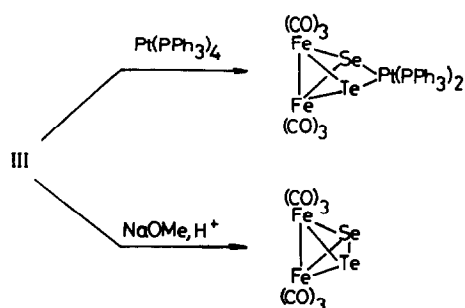
The formation of I involves a straightforward addition of the coordinatively unsaturated ' $\text{Ru}(\text{CO})_4$ ' fragment across the Se-Te bond in  $(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$ , followed by decarbonylation and formation of a Fe-Ru bond. In the related reaction of  $(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$  with  $\text{Fe}(\text{CO})_5$ ,  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Fe}(\text{CO})_4$  is formed initially, which loses one CO group and rearranges to form  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})_2$  [7]. A similar mechanism for the formation of I would require the ruthenium atom to occupy one of the basal sites in the square pyramidal  $\text{Fe}_2\text{RuSeTe}$  core, and the Fe-Fe bond to remain intact.

When a hexane solution containing  $(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  was stirred at room temperature for 10 hours, a mixture of red  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_7(\mu_3\text{-Se})(\mu_3\text{-Te})$  (II) and green  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_6(\mu_3\text{-Se})(\mu_3\text{-Te})$  (III) was obtained (Scheme 2). Characterization of II is based on comparison of its infrared spectrum in the carbonyl region (in hexane solvent,  $\nu(\text{CO})$ : 2054m, 2031vs,



Scheme 2. (i) heat; (ii) CO bubbling.

2014w, 1989s, 1977s and 1954w  $\text{cm}^{-1}$ ) with that of the related compound,  $(\eta^5\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_7(\mu_3\text{-Te})_2$ , which was sufficiently stable to have been isolated in pure form and characterized [8]. Trimethylamine *N*-oxide effects decarbonylation of  $(\eta^5\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_7(\mu_3\text{-Te})_2$  to form the *nido* hexacarbonyl derivative  $(\eta^5\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_6(\mu_3\text{-Te})_2$ . Not surprisingly, in the formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_6(\mu_3\text{-S})_2$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_6(\mu_3\text{-Se})_2$  the open heptacarbonyl compound could not be isolated, demonstrating the tendency of the  $\mu_3\text{-Te}$  moiety to stabilize more open clusters than has been found for smaller tethering atoms. In solution, although the formation of the heptacarbonyl derivative, II, was observed, it was found to convert readily to the *nido*-hexacarbonyl compound III. Compound II therefore could not be isolated in pure form. Compound III was also obtained from II when one equivalent of trimethylamine *N*-oxide was added to a dichloromethane solution of II and the solution stirred for 10 minutes. When CO was bubbled through a solution containing III, there was an almost quantitative formation of II. Compound III has been characterised by infrared spectroscopy, mass spectrometry,  $^1\text{H}$  NMR spectroscopy and microanalytical data. The infrared spectrum of III in the carbonyl region in hexane solvent displays stretching frequencies at 2053m, 2031vs, 1989s and 1977s  $\text{cm}^{-1}$ . The mass spectrum shows the molecular ion at  $m/e = 609$  and peaks centred at  $m/e = 609 - n \cdot 28$  ( $n = 1-6$ ) corresponding to fragments formed by the successive loss of six carbonyl groups.  $^1\text{H}$  NMR spectrum of III in  $\text{CDCl}_3$  shows a single peak at  $\delta$  5.83 due to the  $\text{C}_5\text{H}_5$  protons. Microanalytical data confirm the molecular formula of III (found: C, 21.65; H, 2.18.  $\text{C}_{11}\text{H}_5\text{CoFe}_2\text{SeTe}$  calc.: C, 21.60; H, 0.82%). The rhodium derivative has been reported to form in two interconverting isomeric forms, which differ from each other in the location of the  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)$  moiety; in one the Rh atom occupies a basal site in the  $\text{Fe}_2\text{RhTe}_2$  square pyramidal core, while in the other it is situated at the apical site. Simple 2e oxidative addition of 'M( $\text{PPh}_3$ ) $_2$ ' (M = Ni, Pd, Pt) across the E-E bond of  $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$  has been observed. To cover the possibility that III also exists in two isomeric forms which are chromatographically inseparable, we reacted III with  $\text{Pt}(\text{PPh}_3)_4$  (Scheme 3) with the expectation that a mixture of  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})(\mu_3\text{-Te})\text{Pt}(\text{PPh}_3)_2$  (IV) and the new  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}(\text{CO})_6(\mu_3\text{-Se})(\mu_3\text{-Te})\text{Pt}(\text{PPh}_3)_2$  (V) would be formed. However, compound IV was identified as the sole product of the



Scheme 3.

reaction. Also, NaOMe treatment of III followed by acidification afforded a single product,  $(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})^*$ .

## Experimental

All reactions were carried out under an argon atmosphere with use of standard Schlenk techniques. The solvents were purified and dried prior to use. Elemental analyses were carried out on a Carlo Erba automatic analyser,  $^1\text{H}$  NMR spectrum as  $\text{CDCl}_3$  solution on a Varian XL-300 spectrometer, infrared spectra were obtained using a Nicolet 5-DXB FT IR spectrometer and mass spectra on a Shimadzu QP1100 mass spectrometer.  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  was prepared as described before [1].  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  was prepared as described in the literature [9].

### 1. Preparation of $\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$

To a hexane solution of  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  (prepared from 0.16 g, 0.25 mmol of  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ , and assuming 40% conversion, 0.1 mmol of  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  was used) was added  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  (freshly prepared by photolyzing a hexane solution of  $\text{Ru}_3(\text{CO})_{12}$  (0.021 g, 0.033 mmol) under constant purge of ethylene gas). The reaction mixture was allowed to stir at room temperature for 2h, during which period there was a distinct colour change from orange to violet. The solvent volume was reduced and the reaction mixture was chromatographed on a silica gel column. Elution with hexane afforded  $\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Se})(\mu_3\text{-Te})$  as the sole fraction. Yield: 0.053 g (80%).

### 2. Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$ with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$

A hexane solution (150 mL) containing  $\text{Fe}_2(\text{CO})_6(\mu\text{-SeTe})$  (0.5 g, 1.02 mmol) and  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  (0.8 mL) was stirred for 10 h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column. Elution with hexane separated two bands; in order of elution, a trace of green coloured  $(\eta^5\text{-C}_5\text{H}_5)\text{-CoFe}_2(\text{CO})_6(\mu\text{-Se})(\mu_3\text{-Te})$  (III) and red  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_7(\mu_3\text{-Se})(\mu_3\text{-Te})$  (II) as the major product (0.3 g, 60%).

### 3. Decarbonylation of $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_7(\mu_3\text{-Se})(\mu_3\text{-Te})$

To a solution of  $\text{Me}_3\text{NO}$  (0.008 g, 0.1 mmol) in 100mL of dichloromethane was added  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_7(\mu_3\text{-Se})(\mu_3\text{-Te})$  (0.063 g, 0.1 mmol) and the mixture was stirred at room temperature for 10 min. Chromatographic work-up on silica gel plates using hexane as eluant separated the green coloured  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_6(\mu\text{-Se})(\mu_3\text{-Te})$  (III) (0.024 g, 35%) from the unreacted  $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_7(\mu_3\text{-Se})(\mu_3\text{-Te})$  (II).

\* Note added in proof: We have recently prepared and structurally characterised  $\text{Fe}_2\text{W}(\text{CO})_{10}(\mu_3\text{-Te})_2$ . It consists of a square pyramidal  $\text{Fe}_2\text{WTe}_2$  core with no Fe-Fe bond. However, its reaction with NaOMe,  $\text{H}^+$  yields  $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ . Therefore, formation of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$  after reaction with NaOMe,  $\text{H}^+$  does not provide a reliable indication on the presence of Fe-Fe bond in the starting material.

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