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The synthesis and characterisation of the novel cluster, $Ru_4Te_2(CO)_{12}$

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Abstract

Reflux of solution of $Fe_3Te_2(CO)_9$ and $Ru_3(CO)_{12}$ in benzene yields the cluster, $Ru_4Te_2(CO)_{12}$, which is the first example of a tetraruthenium cluster containing tellurium ligands. The cluster has been characterised by infrared spectroscopy, mass spectrometry, and microanalysis. The transmetallation reaction leading to the formation of $Ru_4Te_2(CO)_{12}$ is similar to that yielding the related molecule $Co_4Te_2(CO)_{11}$ from the reaction of $Fe_3Te_2(CO)_9$ and $Co_2(CO)_8$. The $Ru_4Te_2(CO)_{12}$ cluster may be compared to the pentaruthenium cluster $Ru_5S(CO)_{15}$ if it is visualised as $Ru_5S(CO)_{15}$ with the sulfido and the $Ru(CO)_3$ *trans* to it replaced by tellurium ligands.

Introduction

Transition metal cluster chemistry is attracting increasingly more attention owing to its usefulness in catalytic processes [1]. The synthesis of novel cluster complexes [2] has become much more predictable, eliminating most of the serendipity previously associated with it. One of the best routes involves the use of single atom ligands derived from certain main group elements of the Periodic Table (eq. 1) [3]. Adams

$$M_xE: + M'_y \rightarrow M_x(\mu - E)M'_y \quad (1)$$

has exploited this method most elegantly to synthesise, stepwise, a large number of novel sulfido-osmium and sulfido-mixed metal clusters [4]. The sulfido ligands act as the initial points of contact for the incoming metal carbonyl units as a preliminary step in the cluster growth reactions. Although several cluster compounds containing transition metals and selenium within the cluster framework have been reported [5], those containing tellurium have not attracted as much attention because of the relative paucity of tellurium-containing complexes. Rauchfuss et al. [6] have reported a convenient route to $Fe_3Te_2(CO)_9$ and have described its

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conversion to the more reactive $Fe_2Te_2(CO)_6$. Comparison of the syntheses and reactivity of analogous sulfur- and tellurium-containing clusters demonstrates that there is a marked contrast in the reactivity of the two types of clusters [7]. We have explored the utility of $Fe_3Te_2(CO)_9$ in the synthesis of several tellurium containing complexes [8], and here, we report the use of the same cluster for the synthesis of the novel cluster, $Ru_4Te_2(CO)_{12}$.

Results and discussions

Equimolar amounts of $Ru_3(CO)_{12}$ and $Fe_3Te_2(CO)_9$, when refluxed in benzene solvent for 5 h, yield the novel cluster $Ru_4Te_2(CO)_{12}$ (I) as identified on the basis of infrared spectroscopy, mass spectrometry, and microanalysis. In the carbonyl region, the infrared spectrum shows bands at 2087(w), 2044(s), 2026(m), 1989(m), and 1827(w) cm^{-1}, corresponding to terminal as well as bridging carbonyls. The electron impact mass spectrum shows peaks at $m/z = 972$, 944, 916, 888, 860, 832, 804, 776, 748, 720, 692, 664, corresponding to $[Ru_4Te_2(CO)_{11}]^+$ and the fragments obtained after the successive losses of the carbonyl groups. There is good agreement between the observed and the computer simulated isotopic pattern for the $Ru_4Te_2^+$ fragment (Fig. 1). The elemental analysis, however, suggests that the molecular formula should be $Ru_4Te_2(CO)_{12}$ (Found: C, 14.3. $C_{12}O_{12}Ru_4Te_2$ calcd.: C, 14.4%). If each tellurium ligand acts as a four electron donor, $Ru_4Te_2(CO)_{12}$ will be a 64 electron cluster containing four metal–metal bonds. On the other hand, the electron count for $Ru_4Te_2(CO)_{11}$ predicts the existence of five metal–metal bonds in its structure, i.e. a butterfly arrangement of the metal atoms.

In the related molecule $Os_4S_2(CO)_{12}$, a 64 electron cluster, instead of the expected four metal–metal bonds in its structure, there are five metal–metal bonds; a butterfly arrangement of four metal atoms, with the sulfido ligands triply bridging

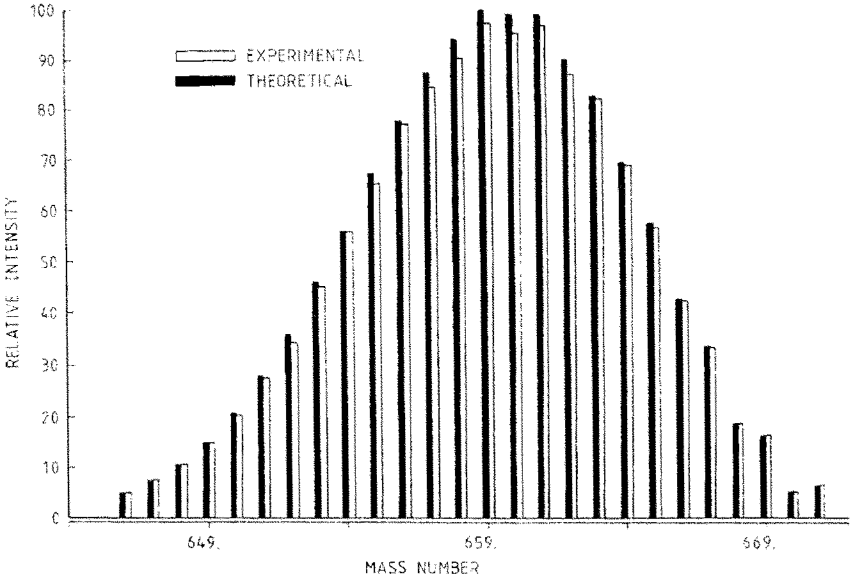

Fig. 1. Comparison of calculated and observed isotopic pattern for the $Ru_4Te_2^+$ ion.

a

b

Fig. 2. Structural similarities between $Ru_5S(CO)_{15}$ and $Ru_4Te_2(CO)_{12}$.

the two wing tip and one each of the two hinge metal atoms [9]. That the infrared spectrum of complex I is completely different from that of $Os_4S_2(CO)_{12}$ excludes the butterfly structure in I. The pentaruthenium cluster, $Ru_5S(CO)_{15}$ has recently been prepared by the photolysis of $Ru(CO)_5$ and $Ru_3S(CO)_{10}$, and has been structurally characterised [10]. The molecule consists of an octahedron of five ruthenium atoms and one quadruply bridging sulfido ligand. There are two terminally bonded carbonyls on each ruthenium atom; in addition, there are doubly bridging carbonyl groups along four metal–metal bonds (Fig. 2a). The similarity in the infrared spectra of I and $Ru_5S(CO)_{15}$ indicates that there may be some resemblance in the structures of the two clusters. In $Ru_5S(CO)_{15}$, if the sulfur and the ruthenium carbonyl fragment *trans* to it are replaced by tellurium ligands, the cluster $Ru_4Te_2(CO)_{12}$ (Fig. 2b) results. Complex I is the first example of a tellurium-containing tetraruthenium cluster. The type of overall transmetallation process by which I is formed, is not without precedence, because $Fe_3Te_2(CO)_9$ reacts with $Co_2(CO)_8$ to give $Co_4Te_2(CO)_{11}$ under carbon monoxide pressure at elevated temperatures [6]. The mechanism by which $Ru_4Te_2(CO)_{12}$ is formed is currently under investigation.

Experimental

All reactions were carried out under dry nitrogen or argon using standard Schlenk techniques. The solvents were purified and dried before use. $Fe_2(CO)_9$ (Aldrich) and $Ru_3(CO)_{12}$ (Strem) were used as received. $Fe_3Te_2(CO)_9$ was prepared by the method of Lesch and Rauchfuss [6b].

A mixture of $Fe_3Te_2(CO)_9$ (0.10 g, 0.148 mmol) and $Ru_3(CO)_{12}$ (0.094 g, 0.148 mmol) in benzene (120 cm^3) was refluxed for 5 h. After cooling the solution, it was filtered through celite and the solvent was removed in vacuo. Chromatography of the residue on a silica gel column with neat hexane as eluant separated trace amounts of the unchanged starting materials, $Fe_3Te_2(CO)_9$ and $Ru_3(CO)_{12}$. Further elution with hexane/dichloromethane (3/1 v/v) gave the deep red band of $Ru_4Te_2(CO)_{12}$. Recrystallisation of the crude product from hexane/dichloromethane mixture gave reddish black crystals of pure $Ru_4Te_2(CO)_{12}$, in 37% yield (based on $Fe_3Te_2(CO)_9$).

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