

# Synthesis, Structural Characterization, Electrochemistry, and Reactivities of Heptaosmium Carbonyl Clusters Bearing Thioxane Ligands – Crystal and Molecular Structures of $[\text{Os}_7(\text{CO})_{16}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2\}_2]$ , $[\text{Os}_7(\text{CO})_{17}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2\}\{\text{S}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2\}]$ , and $[\text{Os}_7(\text{CO})_{18}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2\}]$

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Reaction of the activated heptaosmium cluster  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$  with 1,4-thioxane in  $\text{CH}_2\text{Cl}_2$  at ambient temperature led to the isolation of three air-stable clusters  $[\text{Os}_7(\text{CO})_{16}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}_2]$  (**1**),  $[\text{Os}_7(\text{CO})_{17}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}\{\text{S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**2**) and  $[\text{Os}_7(\text{CO})_{18}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**3**). The metal skeletons of these clusters are in the form of a winding helix

made up of four tetrahedra sharing three common faces. From electrochemical studies, the extent of the cathodic shifts of the reduction waves of these clusters were found to differ from that of the parent cluster  $[\text{Os}_7(\text{CO})_{21}]$ . Treatment of **2** with carbon monoxide produced an isomer of **3**, namely compound **4**, which has the same molecular formula as **3**, but a different ligand arrangement.

## Introduction

The chemistry of heptaosmium carbonyl clusters is not well explored, probably because reliable synthetic routes are unavailable, unlike the case for the hexaosmium system.<sup>[1]</sup> Pyrolysis of  $[\text{Os}_3(\text{CO})_{12}]$  at 210°C leads to a small amount of  $[\text{Os}_7(\text{CO})_{21}]$  (< 10%) after repeated TLC purification.<sup>[2]</sup> A more rational synthesis of a heptaosmium cluster is by nucleophilic attack of a mononuclear osmium fragment at a  $\text{Os}_6$  cluster core that contains a labile ligand such as MeCN. The heptaosmium dihydrido clusters  $[\text{H}_2\text{Os}_7(\text{CO})_{20}]$ ,  $[\text{H}_2\text{Os}_7(\text{CO})_{21}]$ , and  $[\text{H}_2\text{Os}_7(\text{CO})_{22}]$  have been obtained by this strategy.<sup>[3]</sup> Subsequent reactions of  $[\text{H}_2\text{Os}_7(\text{CO})_{20}]$  with diphenylacetylene is reported to give  $[\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4]$  and  $[\text{Os}_7(\text{CO})_{18}(\mu_3\text{-CPh})_2]$ .<sup>[4]</sup> A similar reaction with dimethylacetylene as the ligand afforded  $[\text{Os}_7(\text{CO})_{19}(\mu_3\text{-}\eta^2\text{-C}_2\text{Me}_2)]$ .<sup>[5]</sup> Lewis and Braga have shown that treatment of the parent cluster  $[\text{Os}_7(\text{CO})_{21}]$  with trimethoxyphosphane in the presence of  $\text{Me}_3\text{NO}$  yields the red-brown cluster  $[\text{Os}_7(\text{CO})_{20}\text{P}(\text{OMe})_3]$ .<sup>[6]</sup> Hoping to develop a more accessible synthetic route for higher-nuclearity cluster systems, we previously used the preformed labile species  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$  to synthesize a number of hexaosmium cluster derivatives bearing donor ligands.<sup>[7]</sup> We extended this approach to the heptanuclear system and prepared the title compounds and studied their reactions. Their molecular structures were determined by single-crystal X-ray crystallography.

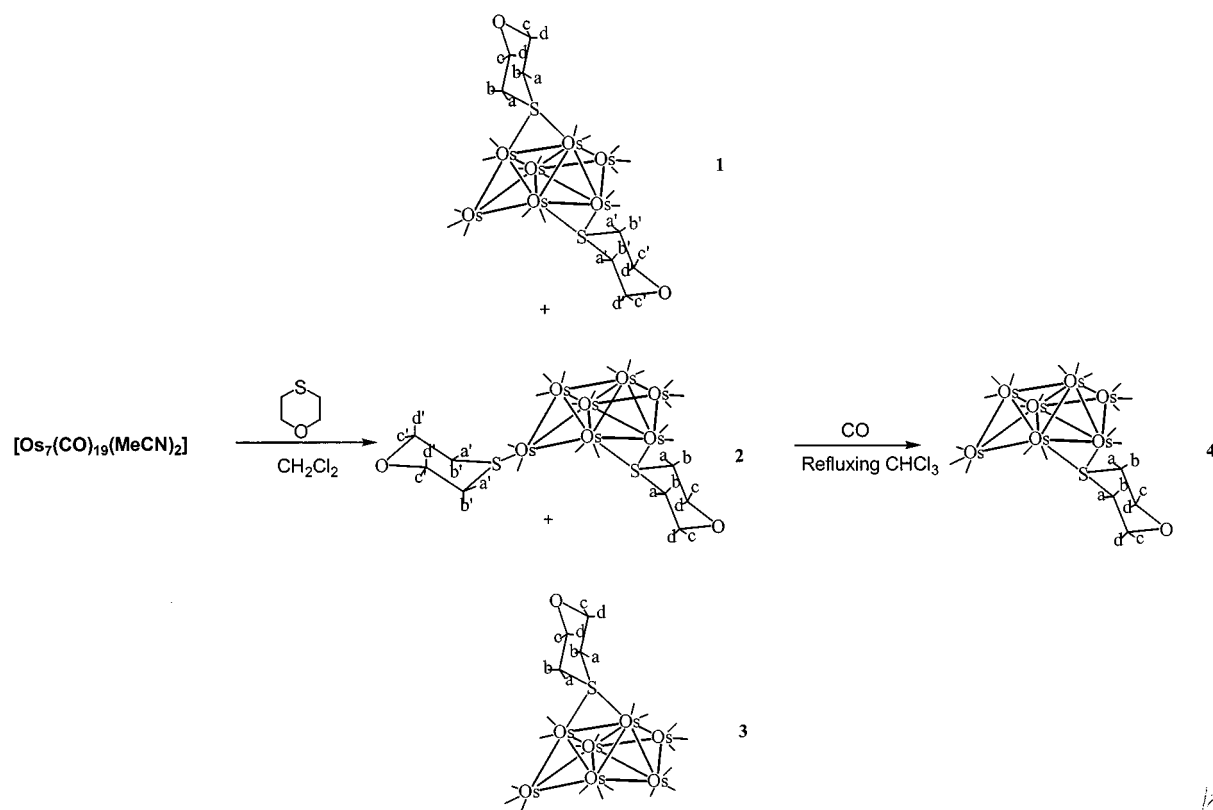
## Results and Discussion

Synthesizing a cluster derivative by nucleophilic displacement of a donor ligand with a preformed labile parent carbonyl cluster is a general and effective way to generate new clusters in low-nuclearity systems.<sup>[8]</sup> The advantage of using such a strategy is not only the mild reaction conditions needed, but also that the reaction is more selective. However, there have been only very few reports of cluster syntheses with this approach in hexa- and heptanuclear systems, such as the preparation of hexanuclear clusters from the reactions with pyridine<sup>[7a]</sup> and 7-azaindole.<sup>[7b]</sup> In this article we report the use of  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$ , which is generated from the parent cluster  $[\text{Os}_7(\text{CO})_{21}]$ , to synthesize a new family of heptanuclear cluster compounds containing thioxane ligands.

Treatment of the heptanuclear carbonyl cluster  $[\text{Os}_7(\text{CO})_{21}]$  with 2 equiv.  $\text{Me}_3\text{NO}$ , in acetonitrile at  $-78^\circ\text{C}$ , led to the formation of an activated cluster precursor  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$ . Subsequent reaction of this labile cluster with 1,4-thioxane in  $\text{CH}_2\text{Cl}_2$ , at ambient temperature for 6 h, followed by TLC purification, gave three air-stable clusters  $[\text{Os}_7(\text{CO})_{16}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}_2]$  (**1**),  $[\text{Os}_7(\text{CO})_{17}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}\{\text{S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**2**), and  $[\text{Os}_7(\text{CO})_{18}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**3**) (Scheme 1). Their formulae were first established by FAB MS and  $^1\text{H}$ -NMR spectroscopy, and were eventually confirmed by X-ray crystallography. All the spectroscopic data are summarized in Table 1.

The metal frameworks of clusters **1**, **2**, and **3** may be described as four fused tetrahedra sharing three common faces, or two fused bicapped trigonal bipyramids sharing a

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Scheme 1. Reaction of  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$  with 1,4-thioxane in  $\text{CH}_2\text{Cl}_2$  at ambient conditionsTable 1. Spectroscopic data for  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$  and clusters **1** to **4**

	IR $\tilde{\nu}(\text{CO})^{[a]}$ [ $\text{cm}^{-1}$ ]	$^1\text{H}$ NMR $\delta$ ( $J$ [Hz]) $^{[b]}$	Mass spectrum $m/z^{[c]}$
$[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$	2069(w), 2042(s), 2008(s)	2.86 (s, 6 H)	—
<b>1</b>	2080(w), 2059(s), 2005(vs)	3.87–4.48 (m, 8 H, $\text{H}_a$ , $\text{H}_b$ , $\text{H}_{a'}$ , $\text{H}_{b'}$ ), 3.31–3.79 (m, 8 H, $\text{H}_c$ , $\text{H}_d$ , $\text{H}_{c'}$ , $\text{H}_{d'}$ )	1988(1988)
<b>2</b>	2078(s), 2051(vs), 2020(vs), 2010(vs), 1964(w), 1943(w)	4.21–4.53 (m, 8 H, $\text{H}_a$ , $\text{H}_b$ , $\text{H}_{a'}$ , $\text{H}_{b'}$ ), 3.82–3.97 (m, 8 H, $\text{H}_c$ , $\text{H}_d$ , $\text{H}_{c'}$ , $\text{H}_{d'}$ )	2108 (2108)
<b>3</b>	2085(vw), 2070(s), 2065(s), 2058(vs), 2037(s), 2011(ms)	4.57–4.69 (m, 4 H, $\text{H}_a$ , $\text{H}_b$ ), 3.81–3.94 (m, 4 H, $\text{H}_c$ , $\text{H}_d$ )	1940 (1940)
<b>4</b>	2095(w), 2070(vs), 2055(vs), 2018(vs)	4.23–4.47 (m, 4 H, $\text{H}_a$ , $\text{H}_b$ ), 3.52–3.94 (m, 4 H, $\text{H}_c$ , $\text{H}_d$ )	1940 (1940)

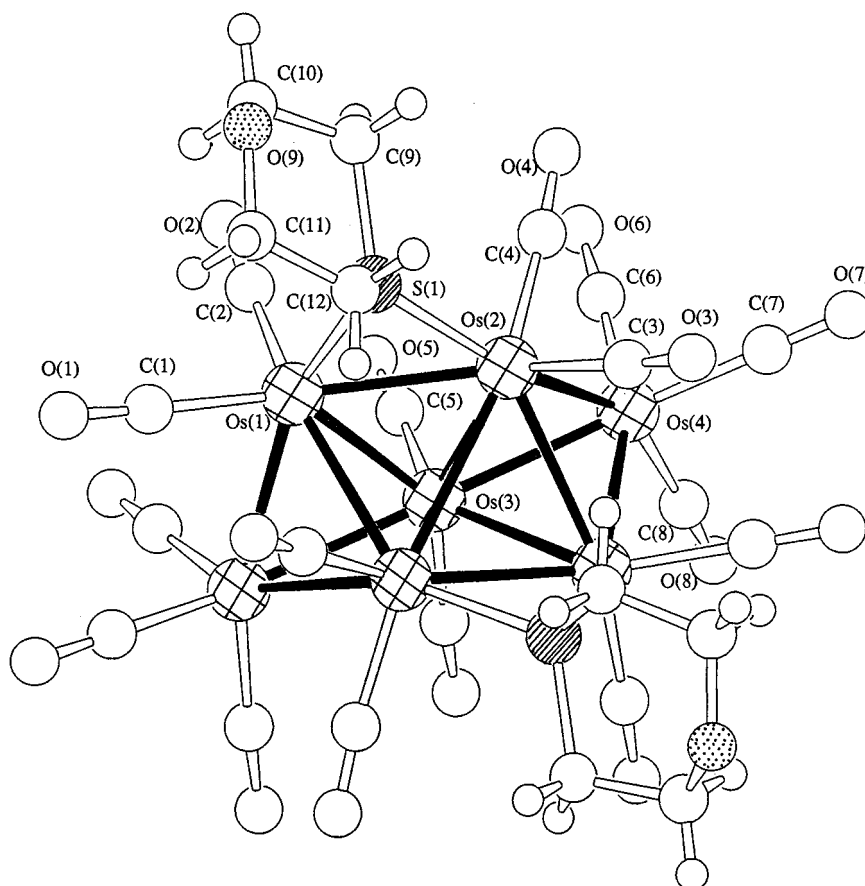
$^{[a]}$   $\text{CH}_2\text{Cl}_2$ . —  $^{[b]}$   $\text{CD}_2\text{Cl}_2$ . —  $^{[c]}$  Simulated values given in parentheses.

common triangular face. This kind of  $\text{Os}_7$  architecture differs widely from the parent cluster  $[\text{Os}_7(\text{CO})_{21}]$ , which is a monocapped octahedron. $^{[9]}$  The compound  $[\text{Os}_7(\text{CO})_{17}(\eta^6\text{-C}_6\text{H}_6)]^{[10]}$ , prepared by Lewis and co-workers, is so far the only structurally characterized homometallic example with this type of metal skeleton. Although the metal framework of some heterometallic clusters such as  $[\text{Cp}_3\text{W}_3\text{Ir}_4(\mu\text{-H})(\text{CO})_{12}]^{[11]}$  is similar, complexes  $[\text{Fe}_4(\text{CO})_{12}\{\text{Au}(\text{L})_2\text{BH}\}]$  ( $\text{L} = \text{AsPh}_3$  or  $\text{PPh}_3$ ), $^{[12]}$   $[\text{Fe}_3(\text{CO})_9\{\text{Au}(\text{PPh}_3)_3\}_3]$ , $^{[13]}$  and  $[\text{Fe}_4(\text{CO})_{12}\text{Au}_2\{\text{P}(p\text{-MeC}_6\text{H}_4)_3\}_2\text{BH}]^{[14]}$  could be considered similar only if the edge-bridging, rather than face-capping, heteroatoms are regarded as one of the vertices.

The molecular geometry of complex **1** and its atomic labelling scheme is depicted in Figure 1. Some selected interatomic bond lengths and angles are given in Table 2.

Compound **1** crystallizes in the monoclinic space group  $C2/c$  with half a molecule per asymmetric unit. All the internuclear  $\text{Os}-\text{Os}$  distances are within 2.703(9) to 2.994(4) Å which is comparable to those found in other high-nuclearity clusters. Thioxane ligands bridge the  $\text{Os}(1)-\text{Os}(2)$  and  $\text{Os}(1)^*-\text{Os}(2)^*$  edges of the metal skeleton. As predicted by the Effective Atomic Number (EAN) rule, there are fifteen metal–metal bonds. $^{[15]}$  The structure of this 96 CVE cluster can be rationalized by the condensed polyhedral approach, $^{[16]}$  but it is not possible to assign 18 electrons to each osmium atom. This is not uncommon for high-nuclearity system, as was suggested by Adams, $^{[17]}$  Kaesz, $^{[18]}$  and Lewis. $^{[19]}$

The redox properties of cluster **1** were studied by cyclic voltammetry (CV) and controlled potential electrolysis

Figure 1. Molecular structure of cluster **1** with atom labels for non-hydrogen atomsTable 2. Selected bond lengths [Å] and angles [°] for cluster **1**

Os(1)–Os(2)	2.737(1)	Os(3)–Os(4)	2.722(1)
Os(1)–Os(2)*	2.830(1)	Os(1)–S(1)	2.292(4)
Os(1)–Os(3)	2.705(1)	Os(2)–S(1)	2.288(4)
Os(1)–Os(4)*	2.744(1)		
Os(2)–Os(2)*	2.994(1)	Os(1)–S(1)–Os(2)	73.4(1)
Os(2)–Os(3)	2.703(1)	S(1)–Os(1)–Os(2)	53.2(1)
Os(2)–Os(4)	2.877(1)	Os(1)–Os(2)–S(1)	53.4(1)

(CPE) at a platinum disc electrode. The parent cluster  $[\text{Os}_7(\text{CO})_{21}]$  undergoes a single, irreversible two-electron transfer step with  $E_p = -0.10$  V vs Ag/AgCl, to yield the corresponding dianion  $[\text{Os}_7(\text{CO})_{20}]^{2-}$ . We believe that the incorporation of a sulfur heteroatom in the cluster framework should lead to changes in redox behaviour. The cyclic voltammograms of compound **1** in acetonitrile solution contained an irreversible cathodic wave at ca.  $E_p = -0.22$  V vs Ag/AgCl. Cyclic voltammetric measurements were obtained at scan rates varying from 50 mV to 10,000 mV s<sup>-1</sup>, but the  $\Delta E_p$  values remained virtually unchanged. This observation, together with the findings in CPE, are characteristic of an irreversible two-electron transfer process involving reduction of **1** into its corresponding dianion  $[\mathbf{1}]^{2-}$ . Because the thioxane groups are better  $\sigma$ -donors than carbonyl ligands are, coordination of such a good  $\sigma$ -donor in **1** would raise the LUMO energy; this in turn would make reduction more difficult, and would therefore lead to a

more cathodic potential. For **1**, an additional irreversible anodic wave is located at ca.  $E_p = +0.37$  V vs Ag/AgCl. It is likely that this oxidation process, which is absent in the parent cluster, is the consequence of oxidation of the thioxane ligands. Ferrocene was added as an internal reference, and its half-wave potential  $E_{1/2} = +0.10$  V vs Ag/AgCl remained practically constant throughout the measurement. The electrochemical data are collected in Table 3.

Table 3. Cyclic voltammetric data for  $[\text{Os}_7(\text{CO})_{21}]$  and compounds **1**, **2**, and **3** in MeCN (0.1 mol dm<sup>-3</sup>  $n\text{Bu}_4\text{NPF}_6$ ) at 298 K

Compound	$E_{pa}$ [V] <sup>[a]</sup> vs Ag/AgNO <sub>3</sub>	$E_{pc}$ [V] <sup>[a]</sup> vs Ag/AgNO <sub>3</sub>
$[\text{Os}_7(\text{CO})_{21}]$	–	–0.10
<b>1</b>	+0.37	–0.22
<b>2</b>	+0.37	–0.24
<b>4</b>	+0.38	–0.17

<sup>[a]</sup>  $E_{pa}$  and  $E_{pc}$  are the anodic and cathodic potentials respectively.

The heptametallic cluster **2** is analogous to **1**, except that one bridging thioxane group is replaced by a terminally bonded ligand. In the solid state, both ligand forms are in the chair conformation, with all the C–C bonds staggered. A perspective drawing of cluster **2** with its atomic numbering is shown in Figure 2. Some important bond parameters are given in Table 4. Compared with their counterparts in compound **1**, all the metal–metal bond lengths are within

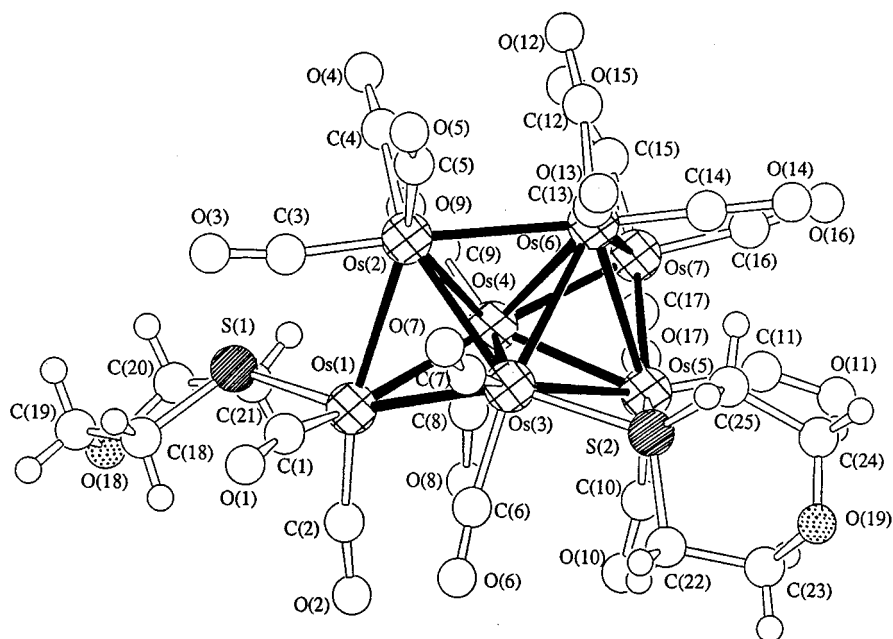


Figure 2. Molecular structure of cluster 2

the expected ranges. The redox properties of complex **2** were also studied, and all the electrochemical data are presented in Table 3. The cyclic voltammograms of **2** are very

similar to those of **1**, with one irreversible reduction wave at ca.  $E_p = -0.24$  V and one irreversible oxidation peak at ca.  $E_p = +0.37$  V vs Ag/AgCl. The assignment of these two

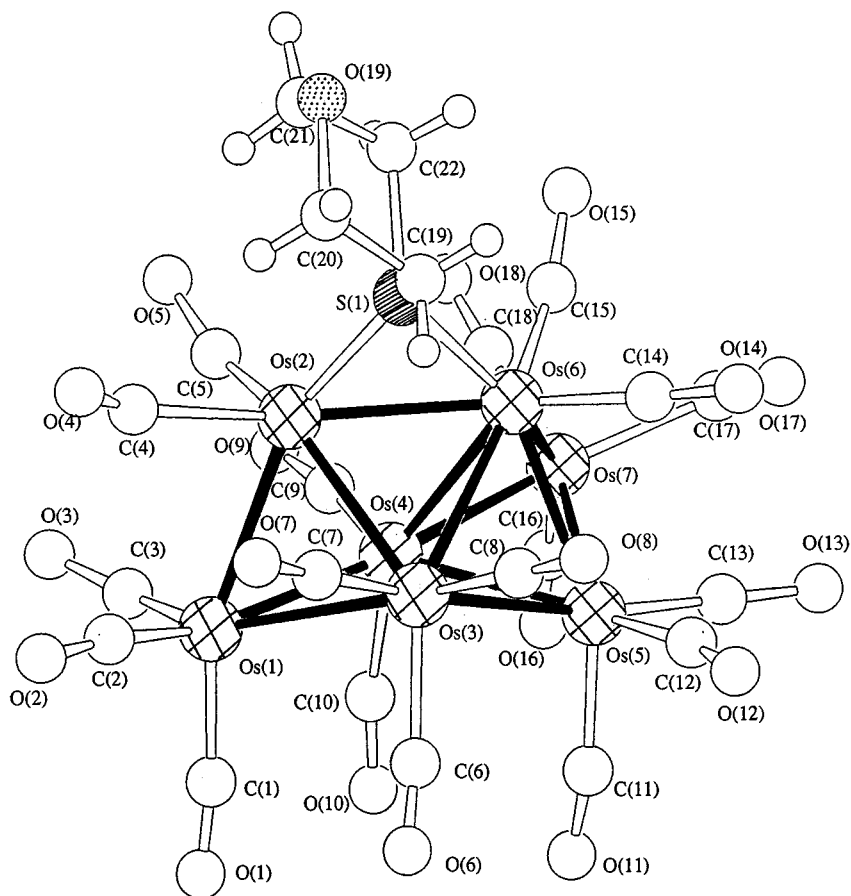


Figure 3. Molecular structure of cluster 3

Table 4. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for cluster **2**

Os(1)–Os(2)	2.830(3)	Os(4)–Os(7)	2.676(3)
Os(1)–Os(3)	2.860(3)	Os(5)–Os(6)	2.853(3)
Os(1)–Os(4)	2.727(3)	Os(5)–Os(7)	2.789(4)
Os(2)–Os(3)	2.812(3)	Os(6)–Os(7)	2.938(3)
Os(2)–Os(4)	2.707(3)	Os(1)–S(1)	2.34(1)
Os(2)–Os(6)	2.875(3)	Os(3)–S(2)	2.32(1)
Os(3)–Os(4)	2.726(3)	Os(5)–S(2)	2.30(1)
Os(3)–Os(5)	2.763(3)		
Os(3)–Os(6)	2.885(3)	Os(3)–S(2)–Os(5)	73.5(5)
Os(4)–Os(5)	2.675(3)	S(2)–Os(5)–Os(3)	53.5(3)
Os(4)–Os(6)	2.780(3)	Os(5)–Os(3)–S(2)	52.9(3)

peaks follow that of **1**, since **1** and **2** are structurally similar.

Carboxylation of **2** in refluxing  $\text{CHCl}_3$  led to the formation of  $[\text{Os}_7(\text{CO})_{18}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**4**) which is an isomer of **3**. Spectroscopic data of **4** (FAB MS,  $^1\text{H}$ -NMR, and IR spectra) suggested that a CO molecule replaced the terminally bonded thioxane ligand. However, prolonged carboxylation of **2** did not recover the starting cluster  $[\text{Os}_7(\text{CO})_{21}]$ . This contrasts with the facile replacement of both thioxane ligands observed for the analogous compound  $[\text{Os}_6(\text{CO})_{15}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$ .<sup>[20]</sup> Under similar conditions, **2** did not react with molecular hydrogen.

The metal skeleton of **3** is identical to that of **1** and **2**, with eighteen terminally bonded carbonyl groups and a thioxane ligand bridging Os(2) and Os(6). Its molecular structure is presented in Figure 3 and some selected bond parameters are given in Table 5. Interestingly, the structure can be regarded as a monocapped Os(7) atom on the hexanuclear species  $[\text{Os}_6(\text{CO})_{16}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  previously reported by us.<sup>[20]</sup> The three metal–metal bonds between Os(7) and Os(4), Os(5), and Os(6) differ widely, to range from 2.678(4) to 2.866(4)  $\text{\AA}$ , with a slightly tilted capping as a result. However, this is not observed for both clusters **1** and **2**. Cyclic voltammograms of cluster **3** have the same features found for **1** and **2**, with a pair of cathodic and anodic waves at ca.  $E_p = -0.17$  V and  $+0.38$  V vs Ag/AgCl, respectively. The reduction wave of compound **3**, however, is less cathodic than that of its disubstituted counterparts, reflecting the reduction in electron donation by a single thioxane, and hence a lower LUMO energy.

Table 5. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for cluster **3**

Os(1)–Os(2)	2.757(4)	Os(4)–Os(7)	2.678(4)
Os(1)–Os(3)	2.941(4)	Os(5)–Os(6)	2.792(4)
Os(1)–Os(4)	2.694(4)	Os(5)–Os(7)	2.830(4)
Os(2)–Os(3)	2.845(4)	Os(6)–Os(7)	2.866(4)
Os(2)–Os(4)	2.674(4)	Os(2)–S(1)	2.26(2)
Os(2)–Os(6)	2.760(4)	Os(6)–S(1)	2.32(2)
Os(3)–Os(4)	2.738(4)		
Os(3)–Os(5)	2.867(4)		
Os(3)–Os(6)	2.911(4)	Os(2)–S(1)–Os(6)	74.1(5)
Os(4)–Os(5)	2.723(4)	S(1)–Os(6)–Os(2)	52.0(5)
Os(4)–Os(6)	2.727(4)	Os(6)–Os(2)–S(1)	53.9(5)

Although compounds **1**, **2**, and **3** have identical metal architectures and similar ligand dispositions, there is no evidence for their interconversion. Neither **3** nor **4** could be obtained from prolonged carboxylation of **1** in  $\text{CHCl}_3$ .

Similarly, treating **3** with an excess of thioxane did not lead to the isolation of **4**, and vice versa. The change of the metal core in **1**, **2** and **3** from the starting osmium cluster  $\text{Os}_7(\text{CO})_2$ , can take place in the preparation of  $\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2$ . However, we have not been able to obtain the structure of  $\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2$ .

## Experimental Section

**General:** All reactions and manipulations were carried out under dry argon with standard Schlenk techniques. All solvents were purified and dried by standard methods prior to use.<sup>[21]</sup> Chemicals were purchased from Aldrich Chemicals and were used as received. Vacuum pyrolysis of  $[\text{Os}_3(\text{CO})_{12}]$  gave the heptaosmium cluster  $[\text{Os}_7(\text{CO})_{21}]$ .<sup>[22]</sup>  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$  was prepared as described below. – Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer, in 0.5 mm thick calcium fluoride solution cells. –  $^1\text{H}$  NMR and  $^1\text{H}\{^1\text{H}\}$  COSY spectra were recorded on a Bruker DPX-300 NMR spectrometer, in  $\text{CD}_2\text{Cl}_2$  with reference to  $\text{SiMe}_4$  ( $\delta = 0$ ). – Mass spectra were measured on a Finnigan MAT 95 instrument by the fast atom bombardment technique, with *m*-nitrobenzyl alcohol or  $\alpha$ -thioglycerol as the matrix solvents. – Elemental analyses were conducted by Butterworth Laboratories, UK. – Routine separation of products in air was performed by thin-layer chromatography (TLC), on plates coated with Merck kieselgel 60 GF<sub>254</sub>. – All electrochemical measurements were performed under an argon purge, to exclude oxygen, in a conventional two-compartment cell, separated by a sintered glass disc. Acetonitrile was freshly distilled and de-aerated prior to use. The supporting electrode was 0.1 M tetra-*n*-butylammonium tetrafluoroborate in MeCN. Voltammetric experiments were carried out with a Princeton Applied Research (PAR) model 273A potentiostat, connected to an interfaced computer. A standard three-electrode cell consisting of an Ag/AgCl reference electrode (Bioanalytical), a platinum wire counter electrode (Aldrich), and a glassy carbon working electrode (Bioanalytical) were employed. The ferrocenium/ferrocene couple ( $\text{FcP}_2^{+/0}$ ) was used as internal reference.

**Preparation of  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$ :** The compound  $[\text{Os}_7(\text{CO})_{21}]$  (200 mg, 0.104 mmol) was dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  (90  $\text{cm}^3$ ) and MeCN (7.2  $\text{cm}^3$ ) to give a bright orange solution. The reaction mixture was stirred at  $-78^\circ\text{C}$  for 30 min before dropwise addition of a  $\text{Me}_3\text{NO}$  solution (16 mg, 2 mol-equiv) in  $\text{CH}_2\text{Cl}_2$  from a pressure-equalizing dropping funnel. After all the  $\text{Me}_3\text{NO}$  solution had been added, the reaction mixture was further stirred for 15 min before leaving it to warm up at ambient temperature. Excess  $\text{Me}_3\text{NO}$  was then filtered off and the solvent was removed in vacuo to give a bright brown solid residue. (Yield: 102 mg, 50%)

**Preparation of  $[\text{Os}_7(\text{CO})_{16}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**1**),  $[\text{Os}_7(\text{CO})_{17}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}\{\text{S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**2**), and  $[\text{Os}_7(\text{CO})_{18}\{\mu\text{-S}(\text{CH}_2)_2\text{OCH}_2\text{C}^a\text{H}_2(\text{S}-\text{C}^a)\}]$  (**3**):** The cluster  $[\text{Os}_7(\text{CO})_{19}(\text{MeCN})_2]$  (120 mg, 0.062 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ) and stirred while a dilute solution of 1,4-thioxane (0.57  $\text{cm}^3$  diluted in 10  $\text{cm}^3$   $\text{CH}_2\text{Cl}_2$ ) was added dropwise over 30 min at ambient conditions. After the reaction continued for a further 6 h, the solution was filtered and the volume was reduced to ca. 5  $\text{cm}^3$  in vacuo. The residue was subsequently purified by TLC using hexane/ $\text{CH}_2\text{Cl}_2$  (10:20 v/v) as eluent. Three brown bands: **1** ( $R_f = 0.77$ , 20 mg, 0.010 mmol, 16%), **2** ( $R_f = 0.59$ , 45 mg, 0.022 mmol, 36%), and **3** ( $R_f = 0.32$ , 18 mg, 0.016 mmol, 27%), together with several uncharacterized, low-yield products were then eluted consecutively. Brown crystals suitable for diffraction analyses of **1** and **3** were obtained, separately, from  $\text{CHCl}_3$ .

Table 6. Summary of crystal data and data collection parameters for clusters **1**, **2**, and **3**

Compound	<b>1</b>	<b>2</b> · C <sub>7</sub> H <sub>8</sub>	<b>3</b>
Empirical formula	C <sub>24</sub> H <sub>16</sub> O <sub>18</sub> Os <sub>7</sub> S <sub>2</sub>	C <sub>32</sub> H <sub>24</sub> O <sub>19</sub> Os <sub>7</sub> S <sub>2</sub>	C <sub>22</sub> H <sub>8</sub> O <sub>19</sub> Os <sub>7</sub> S
<i>M</i>	1987.90	2108.05	1939.75
Crystal colour, habit	brown, cubic	brown, rod	brown, cubic
Crystal size [mm]	0.21 × 0.25 × 0.19	0.16 × 0.18 × 0.25	0.18 × 0.18 × 0.19
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>C2/c</i> (#15)	<i>P1bar</i> (#2)	<i>P2<sub>1</sub>/n</i> (#14)
<i>a</i> [Å]	21.818(1)	11.302(1)	18.904(1)
<i>b</i> [Å]	10.325(1)	14.639(2)	9.410(1)
<i>c</i> [Å]	18.687(1)	17.050(1)	19.729(1)
<i>α</i> [°]	—	72.05(1)	—
<i>β</i> [°]	118.43(1)	89.59(1)	111.92(1)
<i>γ</i> [°]	—	69.67(1)	—
<i>V</i> [Å <sup>3</sup> ]	3702.1(5)	2500.7(5)	3255.8(6)
<i>Z</i>	4	2	4
<i>D</i> [g cm <sup>−3</sup> ]	3.566	2.799	3.957
<i>F</i> (000)	3472	1864	3360
<i>μ</i> (Mo- <i>K</i> <sub>α</sub> ) [cm <sup>−1</sup> ]	240.95	178.46	273.33
No. reflections collected	16211	21001	28739
No. unique reflections	3708	6491	4877
No. observed reflections [ <i>I</i> > 1.50σ( <i>I</i> )]	2776	3620	2205
<i>R</i>	0.049	0.089	0.084
<i>R</i> '	0.057	0.097	0.083
Goodness of fit	1.38	1.49	1.31
Maximum Δ/σ	0.00	0.00	0.00
No. parameters	231	258	237
Maximum, minimum density in ( <i>F</i> map/e3.60, −2.99 Å <sup>−3</sup> , close to Os)		3.72, −2.99	3.15, −2.95

toluene solutions (1:8 v/v), at room temperature, after 3 and 6 d, respectively. Compound **2** was obtained, by slow evaporation of a toluene/CHCl<sub>3</sub> solution at −10 °C for 4 d, as brown, rod-shaped crystals, as a solvate of stoichiometry **2**·C<sub>7</sub>H<sub>8</sub>. — **1**: C<sub>24</sub>H<sub>16</sub>S<sub>2</sub>O<sub>18</sub>Os<sub>7</sub>: calcd. C 14.5, H 0.8, S, 3.2; found C 14.2, H 0.8, S 3.2. — **2**: C<sub>25</sub>H<sub>16</sub>S<sub>2</sub>O<sub>19</sub>Os<sub>7</sub>: calcd. C 14.9, H 0.8, S 3.2; found C 15.0, H 0.9, S 3.2. — **3**: C<sub>22</sub>H<sub>8</sub>SO<sub>19</sub>Os<sub>7</sub>: calcd. C 13.6, H 0.4, S 1.7; found C 13.4, H 0.4, S 1.7.

**Carboxylation and Hydrogenation of 2:** Compound **2** (40 mg, 0.020 mmol) was continuously purged with a stream of carbon monoxide, in refluxing CHCl<sub>3</sub> (10 cm<sup>3</sup>). Reaction progress was monitored by solution infrared and spot TLC over a period of 4 h. The solvent was then removed in vacuo, the residue was redissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and purified by TLC, with hexane:CH<sub>2</sub>Cl<sub>2</sub> (10:20 v/v) as eluent, to give compounds **4** (*R*<sub>f</sub> = 0.66, 11 mg, 0.006 mmol, 29%) and unchanged **2** (*R*<sub>f</sub> = 0.38, 20 mg, 0.010 mmol, 50%). The procedure described was repeated with hydrogen, but no observable changes were detected by either spot TLC or IR monitoring.

**Crystallography:** Single crystals, suitable for X-ray crystallography, were chosen for clusters **1** and **3**. Compound **3** was mounted on a glass fibre while **2** was mounted in a Lindermann glass capillary with epoxy resin. Diffraction data were collected at ambient temperature on a MAR research imaging plate diffractometer for exposure periods of 300, 600, and 360 s per frame for compounds **1**, **2**, and **3** respectively. All intensity data were corrected for Lorentz and polarization effects. An approximation of absorption correction by inter-image scaling was applied for all compounds. Space groups were determined for all the crystals from a Laue symmetry check, and their systematic absences, and were then confirmed by successful refinement. The structures were solved by direct method SIR92<sup>[22]</sup> and expanded by difference Fourier technique. For **1**, the solution was refined on *F* by full-matrix least-squares analysis with all atoms refined anisotropically while all the hydrogen atoms in the ligand were generated in their idealized positions (C–H 0.95

Å) and fixed throughout. However, for **2**, attempts to refine all non-hydrogen atoms anisotropically gave unreasonably high thermal parameters for the C and O atoms. Therefore, only the heavy atoms (Os and S) were included in subsequent anisotropic refinement cycles. Initial attempts to refine the toluene solvent in **2** by rigid-group constraint gave high *B*<sub>eq</sub> values, indicating considerable disorder. It was then fixed throughout in the subsequent refinement processes to give a significant improvement. As a result of the poor quality of the diffraction data for complex **3**, only heavy atoms such as osmium and sulfur were subjected to anisotropic refinement. A summary of the crystallographic data is given in Table 6. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.<sup>[23]</sup> Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-119664 to 119666. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int) +44-1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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