

## Preliminary communication

Metal cluster-induced desulphurization  
of *N*-(*p*-methoxybenzoyl)-*S*-benzoylsulphenamide.  
Crystal and molecular structures of  $[\text{Os}_6(\text{CO})_{20}(\mu_4\text{-S})(\text{MeCN})]$ 

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**Abstract**

Reaction of *N*-(*p*-methoxybenzoyl)-*S*-benzoylsulphenamide **1** with  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  at room temperature gives  $[\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})]$  **2** and  $[\text{Os}_6(\text{CO})_{20}(\mu_4\text{-S})(\text{MeCN})]$  **3** in moderate yield. The crystal structure of **3** has been determined. Complex **2** is an intermediate in the formation of **3**. Complex **3** undergoes dissociation of CO to give  $[\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})]$  and  $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$ .

**Keywords:** Osmium; Carbonyl; Cluster; Desulfurization; Crystal structure

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Studies of the reactions of oxygen- and sulphur-containing molecules with metal clusters are currently of interest [1–3]. Previously we reported the preparation of some triosmium clusters containing sulphur and oxygen donor ligands in interesting bonding modes [4]. We have now studied the cluster complexes containing ligands with more than two types of donor atoms, and report below synthesis and characterization of clusters derived from *N*-(*p*-methoxybenzoyl)-*S*-benzoylsulphenamide [5], which possesses three different donor atoms, sulphur, oxygen and nitrogen.

In contrast to *S*-alkoylsulphenamides and some *S*-benzoylsulphenamides, which are known to decompose to elemental sulphur and amide by a bimolecular process [6], *N*-(*p*-methoxybenzoyl)-*S*-benzoylsulphenamide **1** is known to be stable in both solid and liquid states [5]. However, reaction of  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  with **1** in dichloromethane at room temperature gives  $[\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})]$  **2** (33%) and  $[\text{Os}_6(\text{CO})_{20}(\mu_4\text{-S})(\text{MeCN})]$  **3** (35%) (see Scheme 1), which contain only the *S*-atom from the organic reactant; i.e. the cluster has brought about desulphurization.

The IR spectrum of **3** reveals that only terminal carbonyl ligands are present, and in the <sup>1</sup>H NMR spectrum the singlet at δ2.90 indicates the presence of

MeCN [7]. Single crystals of **3** were obtained from slow evaporation of a chloroform/*n*-hexane solution at 0°C and its molecular structure was determined by X-ray crystallographic studies [8]. The molecular structure is shown in Fig. 1 together with some important bonding parameters.

The metal core of **3** is a combination of an open triosmium unit and a closed triosmium cluster by direct bonding between Os(3) and Os(6). The interplanar angle between the plane formed by Os(1), Os(2) and Os(3) and that formed by Os(4), Os(5) and Os(6) is 80.95°. There is a quadruply-bridging sulphido ligand. The Os–S bond distances fall in a range 2.393(5)Å to 2.431(5)Å consistent with those in other quadruply bridged sulphido-osmium cluster [9–11]. The Os(4)–Os(5) distance is relatively short [2.695(1)Å], perhaps owing to the contracting effect of the bridging sulphido ligand. All the other Os–Os distances are of rather similar lengths [range: 2.940–2.978(1)Å], and are significantly longer than those in  $[\text{Os}_3(\text{CO})_{12}]$  [12]. The non-bonding distance between Os(1)···Os(3) is 3.980(1)Å. An interesting feature of **3** is that it contains a coordinated acetonitrile ligand in the axial position of Os(1). The Os–N bond distance (2.11(2)Å) is comparable to those in  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  (average 2.127(13)Å) and  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$  (2.074(23)Å) [13]. The cluster valence electron of **3** is 96 (S(1) being taken as a six-electron donor), in accordance with the EAN

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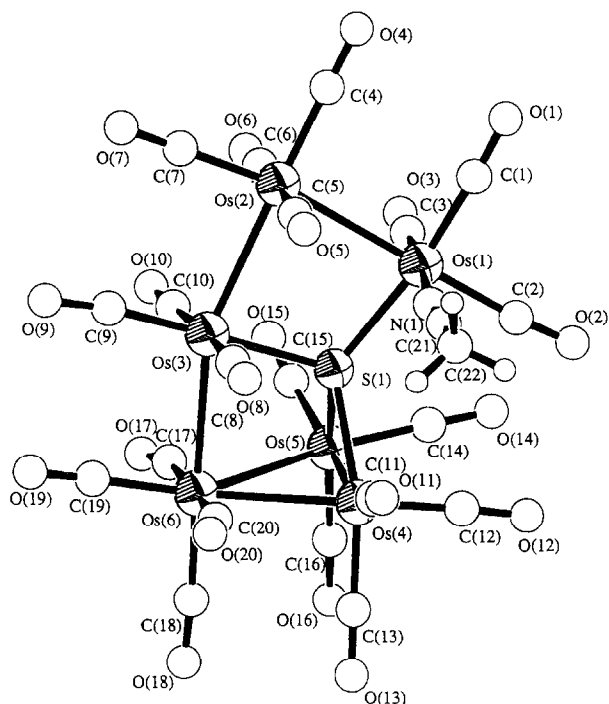


Fig. 1. A perspective view of  $[\text{Os}_6(\text{CO})_{20}(\mu_4\text{-S})(\text{MeCN})]$  (**3**) showing the atomic labelling scheme. Principal bond lengths (Å) and angles ( $^\circ$ ): Os(1)–Os(2) 2.949(1), Os(2)–Os(3) 2.947(1), Os(3)–Os(6) 2.940(1), Os(4)–Os(5) 2.695(1), Os(4)–Os(6) 2.956(1), Os(5)–Os(6) 2.978(1), Os(1)–S(1) 2.431(5), Os(3)–S(1) 2.409(5), Os(4)–S(1) 2.411(5), Os(5)–S(1) 2.393(5), Os(1)–N(1) 2.11(2), N(1)–C(21) 1.16(3); Os(1)–Os(2)–Os(3) 84.78(3), Os(2)–Os(3)–Os(6) 155.90(4), Os(5)–Os(4)–Os(6) 63.42(3), Os(4)–Os(5)–Os(6) 62.56(3), Os(3)–Os(6)–Os(4) 83.97(3), Os(3)–Os(6)–Os(5) 83.38(3), S(1)–Os(3)–Os(6) 74.4(1), Os(1)–S(1)–Os(3) 110.4(2), Os(1)–S(1)–Os(4) 125.4(2), Os(1)–S(1)–Os(5) 126.6(2), Os(3)–S(1)–Os(4) 109.8(2), Os(3)–S(1)–Os(5) 110.1(2), Os(4)–S(1)–Os(5) 68.3(1), Os(1)–N(1)–C(21) 172(1).

rule. Unlike  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  and  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ , which also contain a coordinated-labilized MeCN, complex **3** is stable towards  $\text{H}_2$ , CO and  $\text{PPh}_3$ .

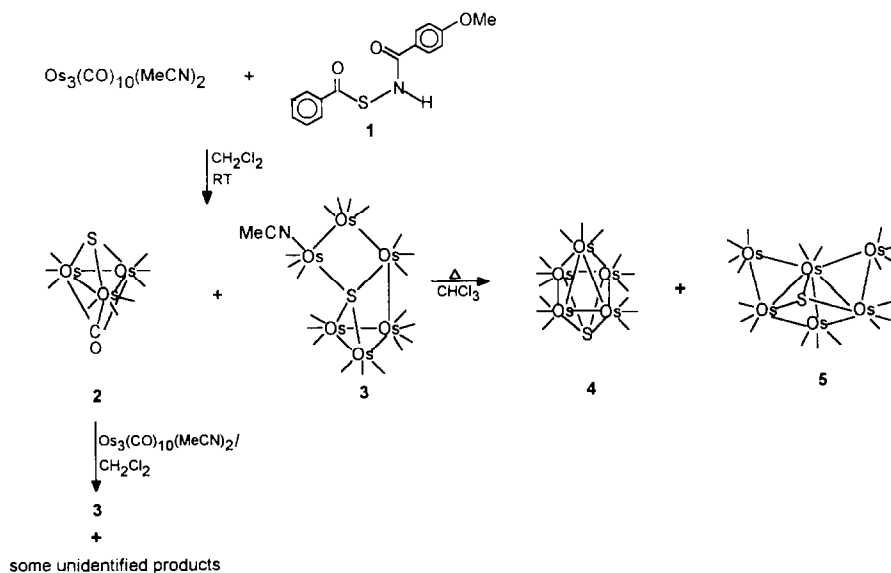
Thermolysis of **3** in refluxing chloroform for 45 minutes gave two known compounds,  $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$  **4** and  $[\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})]$  **5**, which were previously obtained by Adams and coworkers by other methods [14]. We have shown that **4** and **5** can also be obtained in good yield if the mixture of **1** and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  is heated in chloroform. This leads us to believe that **3** is probably an intermediate in the formation of  $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$  and  $[\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})]$  from **1**.

We also found that when  $[\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})]$  **2** was added to the solution of  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  in dichloromethane at room temperature, complex **3** was obtained (after chromatographic work-up) as the major product together with some unidentified products in low yields (see Scheme 1). We thus believe that **2** is probably a precursor of **3**.

Though the detailed mechanism is still under investigation, it is reasonable to suggest that reaction of **1** with  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  gives **2** and then **2** further with another  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  to give **3** with the loss of one MeCN molecule. Upon heating, **3** is converted into  $[\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})]$  and  $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$ .

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Scheme 1.

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- [8] Crystal data for **3**:  $\text{C}_{22}\text{H}_3\text{NO}_{20}\text{Os}_6\text{S}$ ,  $M = 1774.52$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.860(3)\text{\AA}$ ,  $b = 24.503(2)\text{\AA}$ ,  $c = 12.697(3)\text{\AA}$ ,  $\beta = 97.75(2)^\circ$ ,  $V = 3347(1)\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 3.520\text{ g cm}^{-3}$ ,  $F(000) = 3096$ , Mo  $K\alpha$  radiation,  $\lambda = 0.71073\text{\AA}$ ,  $\mu(\text{Mo } K\alpha) = 228.13\text{ cm}^{-1}$ . Red plate, crystal dimensions: 0.12  $\times$  0.26  $\times$  0.29  $\text{mm}^3$ , 4788 data collected on a Rigaku-AFC7R diffractometer ( $4 < 2\theta < 45^\circ$ ), corrected for absorption by  $\Psi$ -scan method, 2900 unique observed reflections [ $I > 3\sigma(I)$ ]. Structure solved by direct methods (SIR88) [15] and Fourier difference techniques, refined by full-matrix least-squares analysis (Os and S anisotropic) with 231 parameters to  $R = 0.037$ ,  $R_w = 0.036$ ,  $w = 4F_o^2 / [\sigma^2(F_o^2) + 0.003(F_o^2)^2]$ , program used teXsan [16]. Atomic coordinates, thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.
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