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The synthesis and single-crystal X-ray structure of $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$; a novel osmium cluster containing three linked osmium triangles

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Abstract

The cluster $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$ has been prepared from the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 2,4,6-trimercapto-1,3,5-triazine ($H_3S_3C_3N_3$) and the structure has been established by a single-crystal X-ray analysis. This latter, in conjunction with spectroscopic data, shows that $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$ contains three linked osmium triangles each with thiolate and hydride bridges across a common edge.

The osmium cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ is known to react with a variety of ligands including thiols [1–4]. In a few examples where the ligand contains two functional groups X-ray analysis has shown the ligand forming a bridge between two osmium triangles [2–4]. As part of our study into osmium clusters with multifunctional ligands we report the first structural characterisation of a thiol ligand linking three osmium triangles. Such linking of multiple triangular clusters may provide a potential synthetic route to higher nuclearity clusters.

The reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 2,4,6-trimercapto-1,3,5-triazine ($H_3S_3C_3N_3$) leads to the formation of $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$ which has been characterised spectroscopically** and the structure established by a single crystal X-ray analysis†. The cluster is readily prepared under mild reaction conditions by stirring for 10 min in dry dichloromethane with the reaction, but not work up, carried out under an atmosphere of dinitrogen. An excess of ligand (1:1 ligand to starting material) results in the same product leaving unreacted ligand. It is necessary to exclude light in order to avoid decarbonylation by photochemical means [4]. One main product results and, after purification by TLC (with hexane/dichloromethane as elutant), the cluster is obtained in good yield (*c.* 90%).

The X-ray structural analysis of $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$ reveals that the cluster contains three osmium triangles each containing a thiolate bridge across an edge of the triangle (Fig. 1). The Os–Os bond lengths and angles are typical of reported values for clusters containing thiolate-bridged, triangular triosmium moieties [3–5] with the average Os–Os distances shorter than those observed in the parent decacarbonyl cluster [6], $[Os_3(CO)_{12}]$. The triangles are arranged around the ligand in a regular manner and there are no unusual intermolecular distances. The Os–C and C–O bond lengths for the carbonyls, as well as the bond lengths and angles within the ligand, are as expected by comparison with similar structures.

The hydrides were not detected crystallographically, however the ^1H NMR spectrum shows a single hydride resonance at −17.15 ppm indicating that all the hydrides are equivalent and consistent with hydrides bridging across the same edges as the thiolates. The IR spectrum of the complex in the carbonyl stretching region shows typical absorptions due to equivalent decacarbonyl moieties with bridging thiolate groups. The most abundant isotopomer in the positive ion mass spectrum (LSIMS

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**Spectral data: Positive ion LSIMS mass spectrum (NBA matrix): most abundant isotopomer *m/z* 2731. ^1H NMR ($CDCl_3$): δ (ppm) −17 15 (s, H–Os). IR spectrum (cyclohexane) ν(CO) (cm^{-1}) 2111w, 2076s, 2064m, 2027vs, 2021s, 2011m, 1990m, 1981w.

†Crystallographic data: $Os_9S_3O_{30}N_3C_{33}H_3$, $M = 2729.37$, monoclinic, space group $P2_1/n$; $a = 9.5006(7)$, $b = 26.342(3)$, $c = 23\,634(3)$ Å, $\beta = 96.043(8)$°, $U = 5882(1)$ Å^3, $Z = 4$, $D_c = 3.08$ g cm^{-3}, $F(000) = 4775$. The intensity data were collected at room temperature on a Enraf Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), with the $\omega/2\theta$ scan mode. A total of 7027 unique data was measured (merging $R = 0.04$). The structure was solved via the heavy atom method after location of the nine osmium atoms from the Patterson map. $R = 0.044$ and $R_w = 0\,050$ for the 4868 data ($F_o > 3\sigma(F_o)$, $\theta = 2–25°$) and 702 parameters refined. The bridging H atoms were not located All atoms were modelled assuming anisotropic thermal vibration and refinement was carried out by a full-matrix least-squares method An empirical absorption correction based on azimuthal scans was applied (min and max transmission 0 6351, 0.9990 respectively, μ(Mo Kα) = 195.7 cm^{-1}) Data refinement was performed with the SHELXS-86 and SHELX-76 programs.

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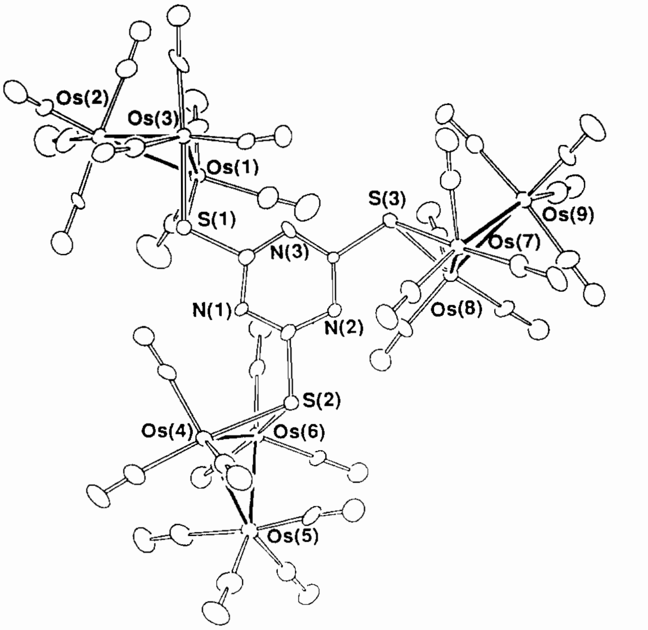

Fig 1 ORTEP drawing of $[\{Os_3H(CO)_{10}\}_3(S_3C_3N_3)]$ (ellipsoids have been drawn at the 20% probability level). Selected bond distances (Å) are as follows: Os(1)–Os(2) = 2.838(2), Os(2)–Os(3) = 2.864(2), Os(1)–Os(3) = 2.857(2), Os(4)–Os(5) = 2.852(2), Os(4)–Os(6) = 2.857(2), Os(5)–Os(6) = 2.840(2), Os(7)–Os(8) = 2.889(2), Os(7)–Os(9) = 2.847(2), Os(8)–Os(9) = 2.837(2), Os(1)–S(1) = 2.428(7), Os(3)–S(1) = 2.405(7), Os(4)–S(2) = 2.414(6), Os(6)–S(2) = 2.439(8), Os(7)–S(3) = 2.422(8), Os(8)–S(3) = 2.425(7).

technique) was observed at $m/z = 2731$ (most abundant isotopomers simulated for MH^+ 2730 and 2731).

The relative ease of formation of this cluster suggests that the preparation of linked clusters containing more than three triangles is a possibility, but more importantly, further reactivity studies on these multi-triangular species may be possible with cross interactions between the triangles leading to new cluster species.

Supplementary material

Atomic coordinates, anisotropic thermal parameters and a full list of bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

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