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Note

Preparation and crystal structure of the cluster complex $Os_7H_2(CO)_{21}P(OMe)_3$ ☆

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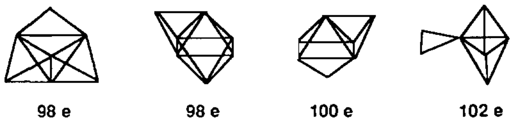
Abstract

The new osmium cluster complex $Os_7H_2(CO)_{21}P(OMe)_3$, in which $P(OMe)_3$ is trimethylphosphite, has been synthesized and characterized by X-ray crystallographic analysis. This complex was prepared by the addition of $P(OMe)_3$ to $Os_7H_2(CO)_{21}$. Crystals are monoclinic, space group $P2_1/c$, with $a=14.220(3)$, $b=12.071(3)$, $c=24.019(7)$ Å, $\beta=109.63(2)°$ and $Z=4$. The metal atom arrangement consists of a trigonal bipyramid sharing an equatorial vertex with a triangle. The phosphite ligand is bound to one of the outer vertices of the triangular unit. The physical and chemical behavior of this complex is compared with that of two previously reported clusters alleged to be isomers of $Os_7H_2(CO)_{22}$.

Keywords: Osmium complexes; Heptanuclear cluster; Carbonyl complexes; Cluster complexes; Phosphite ligand complexes; Crystal structures

1. Introduction

The structural characterization of heptanuclear osmium clusters has been the subject of several recent investigations [1–8]. With the exception of a few that contain carbido- or alkyne-derived ligands, these Os_7 clusters exhibit four different metal atom framework geometries. The 98-electron cluster, $Os_7H_2(CO)_{20}$, has an edge-bridged, bicapped tetrahedral metal atom arrangement [1]. Two other 98*e* clusters, $Os_7(CO)_{21}$ [2] and $Os_7(CO)_{20}P(OMe)_3$ [3], have capped octahedral geometries. The 100*e* cluster $Os_7H_2(CO)_{21}$ has an edge-shared, capped square pyramidal structure [4], while the metal skeleton of the 102*e* cluster $Os_7H_2(CO)_{22}$ is best described as a trigonal bipyramid sharing an equatorial vertex with a triangle [4] (Scheme 1).



Scheme 1.

There is good evidence for the existence of a second isomer of $Os_7H_2(CO)_{22}$. The above-mentioned cluster with this formula is a yellow compound, **1**, that was prepared by the addition of $OsH_2(CO)_4$ to $Os_6(CO)_{18}$ [4]. This compound readily loses one CO ligand to become $Os_7H_2(CO)_{21}$. However, attempts to regenerate **1** by addition of CO to $Os_7H_2(CO)_{21}$ result in the formation of an orange compound, **2** [4]. This second compound exhibits different physical and chemical properties to the first, although electron impact mass spectra of both **1** and **2** are identical with a parent ion peak corresponding to $[Os_7H_2(CO)_{20}]^+$. Due to this loss of CO during mass spectrometry, unequivocal assignment of the molecular formula for **2** is impossible without crystallographic analysis. Herein, we supply additional evidence in support of the assignment of **2** as an isomer of **1** by describing the synthesis and structural characterization of $Os_7H_2(CO)_{21}P(OMe)_3$, the phosphite-substituted analogue of cluster **2**.

2. Experimental

Although the new compound reported herein is not air-sensitive, all reactions were carried out under an atmosphere of dry nitrogen using dried, air-free solvents.

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Products were separated in air by thin-layer chromatography (TLC) on plates coated with 0.25 mm of silica gel of 0.002–0.025 mm mean particle size (Aldrich Chemical Co.) and using dichloromethane–hexane (1:1) as eluant.

All solvents as well as $P(OMe)_3$ were purchased from Aldrich. The complex $Os_7H_2(CO)_{21}$ was prepared by the literature method [4]. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer between 2150 and 1850 cm^{-1} using CaF_2 solution cells and dichloromethane as solvent. Mass spectral and NMR data were obtained at Cambridge University on an AEI MS12 mass spectrometer and a Bruker AM 400 Fourier transform NMR spectrometer, respectively.

2.1. Preparation of $Os_7H_2(CO)_{21}P(OMe)_3$ (3)

To a solution of $Os_7H_2(CO)_{21}$ (27 mg, 0.014 mmol) in 30 ml of CH_2Cl_2 was added $P(OMe)_3$ (0.053 ml, 0.045 mmol). Spot TLC was used to track the reaction's progress. After 4 h of stirring at 25 °C, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and treated with TLC to yield three distinct bands. The top two bands were due to $Os_7H_2(CO)_{20}$ and unreacted $Os_7H_2(Co)_{21}$. The third and lowest band was the desired yellow product $Os_7H_2(CO)_{21}P(OMe)_3$ (**3**). Yield 10 mg (40%). An IR spectrum revealed absorption maxima at 2087(m), 2075(m), 2064(vs) and 2028(s) cm^{-1}. A mass spectrum of the product contained a parent ion peak corresponding to $[Os_7H_2(CO)_{19}P(OMe)_3]^+$.

2.2. X-ray crystallography

Crystals (rectangular parallelepipeds) of **3** suitable for X-ray analysis were grown from a solution of hexane and dichloromethane that was slowly evaporated at −10 °C. The crystalline solid appears black except under intense light when it is dark red. Data collection and processing was performed by the Crystalytics Company of Lincoln, NB. A crystal with dimensions 0.30 × 0.38 × 0.40 mm was mounted inside a thin-walled glass capillary with its longest dimension nearly parallel to the ϕ axis of a modified Syntex P1 diffractometer emitting Mo Kα radiation. Unit cell parameters were determined from least-squares refinement of 15 reflections with $2\theta > 15°$. The ω scan technique was employed at a scan rate of 2.0°/min over the range $3.0 \leq 2\theta \leq 35.9°$ and at a rate of 1.0°/min over the range $35.9 \leq 2\theta \leq 45.8°$. The background counts were measured at ω settings 0.90° above and below the calculated value for each reflection. Six check reflections, monitored after each 300 reflections, showed negligible change during the course of measuring 5347 reflections. The intensity data were corrected empirically for absorption effects using ψ scans for 8 reflections having 2θ between 4.6 and 35.4° and were then reduced to relative squared amplitudes by means of standard Lorentz and polarization corrections.

Structure solution and refinement was accomplished with use of SDP-VAX software on a VAX-11/785 computer at Abilene Christian University. Equivalent reflections were averaged with agreement factors of

Table 1
Summary of crystallographic data for $Os_7H_2(CO)_{21}P(OMe)_3$

Formula	$C_{24}H_{11}O_{24}Os_7P$
a (Å)	14.220(3)
b (Å)	12.071(3)
c (Å)	24.019(7)
β (°)	109.63(2)
V (Å^3)	3883
Z	4
Space group	$P2_1/c$ (No. 14)
Crystal size (mm)	0.30 × 0.38 × 0.40
μ(Mo Kα) (cm^{-1})	229.7
Radiation (monochromated in incident beam), λ (Å)	Mo Kα, 0.71073
Temperature (°C)	20 ± 1 (room temp.)
Scan method	ω
Data collection range, 2θ (°)	4–45.8
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3064
No. parameters refined	485
R [a]	0.0404
R_w [b]	0.0498
Quality-of-fit indicator [c]	1.021
Largest shift/e.s.d., final cycle	0.45
Largest peak (e Å^{-3})	1.58

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2
Spectroscopic data for compounds **1**–**3**

Compound	IR ν(C–O) (cm^{-1}) in CH_2Cl_2	^{1}H NMR (δ) in CD_2Cl_2
$Os_7H_2(CO)_{22}$ (**1**)	2121(w), 2085(m), 2075(m), 2061(s), 2024(s)	-19.7(d), -21.9(d) J(H–H) = 2.1 Hz
$Os_7H_2(CO)_{22}$ (**2**)	2139(w), 2097(m), 2088(m), 2069(s), 2029(m)	-20.5(s), -22.7(s)
$Os_7H_2(CO)_{21}P(OMe)_3$ (**3**)	2087(m), 2075(m), 2064(s), 2028(s)	-20.18(s), -23.94(d) J(P–H) = 36.1 Hz

0.037 and 0.025 based on intensity and F_o, respectively. This left 3064 data with $F_o > 3\sigma(F_o)$. The positions of the osmium atoms were located from a Patterson function. The remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. An additional absorption correction (spherical, θ dependent) was applied. No attempt was made to locate or include the hydrogen atoms. The three methyl carbon atoms, C(1), C(2) and C(3), as well as one of the carbonyl carbon atoms, C(72), were refined isotropically, while all other non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement of the 485 parameters resulted in residuals of $R = 0.0404$ and $R_w = 0.0498$, where $w = 1/[\sigma^2(F_o) + 0.0007F_o^2]$. A summary of crystallographic data appears in Table 1.

3. Results and discussion

The chemistry of the cluster complex **3** mirrors that reported previously for cluster **2** (believed to be an isomer of $Os_7H_2(CO)_{22}$ (**1**)). The cluster $Os_7H_2(CO)_{22}$ (**1**) readily loses CO in solution at room temperature to give $Os_7H_2(CO)_{21}$, but addition of CO to $Os_7H_2(CO)_{21}$ results in the formation of cluster **2** instead of **1**. The new complex $Os_7H_2(CO)_{21}P(OMe)_3$ (**3**) has been formed in an analogous manner by the addition of $P(OMe)_3$ to $Os_7H_2(CO)_{21}$. Unlike the behavior of cluster **1**, heating cluster **2** in solution results in no reaction, indicating that it is thermally stable with regard to CO loss. Heating the new complex **3** in toluene at 85 °C for 2 h also results in no change.

The spectroscopic data given in Table 2 also indicate that cluster **3** is more closely related in structure to cluster **2** than cluster **1**. Proton NMR spectra reveal that the two hydride ligands in cluster **1** are relatively close to one another, while those in clusters **2** and **3** are not close enough to display any H–H coupling. For cluster **3**, the large $^{31}P\{^1H\}$ coupling constant allows the assignment of the upfield resonance ($\delta = -23.94$) to a hydride ligand bridging the long Os(6)–Os(1) bond. Since the downfield resonance ($\delta = -20.18$) is a singlet, the other hydride ligand is most likely located around the Os(2)–Os(3)–Os(4)–Os(5) butterfly metal framework. It has not been possible through crystallographic analysis to locate the hydrogen atoms in either **1** or **2**, but our conclusion from the NMR data is that in solution the hydride ligands of clusters **2** and **3** are in analogous locations, while the hydride ligands of cluster **1** are positioned differently.

Despite the resemblances between cluster **3** and cluster **2**, the overall molecular geometry of **3** is remarkably similar to that of $Os_7H_2(CO)_{22}$ (**1**) with a metal atom skeleton best described as a trigonal bipyramid sharing an equatorial vertex with a triangle. An ORTEP view of **3** is shown in Fig. 1. Important bond distances for compounds **1** and **3** are listed in Table 3. The $P(OMe)_3$ ligand is bonded to Os(6), along with three CO ligands. There are two CO ligands attached to Os(1) and four CO ligands attached to Os(7). All of the other Os atoms are bonded to three carbonyl groups. The $P(OMe)_3$ ligand is a weaker π-acceptor than CO, resulting in a shift to lower energy in the carbonyl stretching frequencies and an average lengthening of the metal–metal bonds involving Os(6) by 0.028 Å in relation to the analogous bonds of **1** (see Table 3). A similar result was observed in the case of $Os_7(CO)_{20}P(OMe)_3$, where the Os–Os distances associated with the phosphite-bound osmium atom are 0.047 Å longer than the corresponding distances in $Os_7(CO)_{21}$ [3].

With the exception of a phosphite ligand in place of a carbonyl ligand on one of the outer osmium atoms

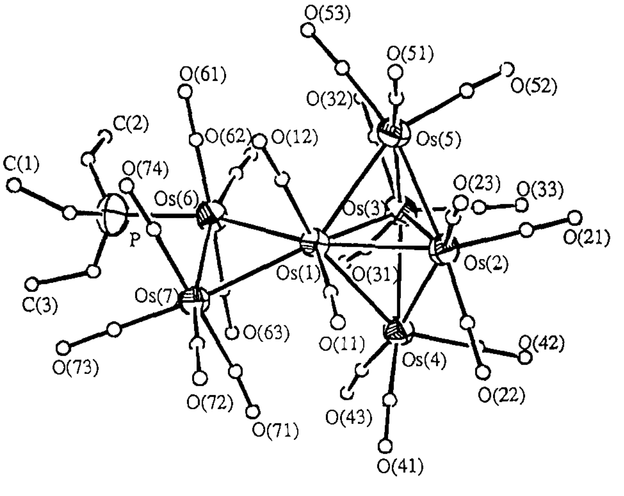

Fig. 1. An ORTEP drawing of the molecular structure of $Os_7H_2(CO)_{21}P(OMe)_3$ (**3**) showing the atomic numbering scheme. Thermal ellipsoids for the Os and P atoms are at the 50% probability level. For the sake of clarity, all carbon and oxygen atoms are represented by spheres with arbitrarily small radii.

Table 3
Comparison of $Os_7H_2(CO)_{21}P(OMe)_3$ (**3**) bond distances (Å) with corresponding $Os_7H_2(CO)_{22}$ (**1**) bond distances

	Complex **3**	Complex **1**
Os(1)–Os(2)	2.841(2)	2.854(2)
Os(1)–Os(3)	2.882(1)	2.878(2)
Os(1)–Os(4)	3.047(2)	2.952(2)
Os(1)–Os(5)	2.958(2)	3.039(2)
Os(1)–Os(6)	3.070(2)	3.048(2)
Os(1)–Os(7)	2.907(1)	2.914(2)
Os(2)–Os(3)	2.771(2)	2.773(2)
Os(2)–Os(4)	2.801(2)	2.747(2)
Os(2)–Os(5)	2.757(2)	2.790(2)
Os(3)–Os(4)	2.747(2)	2.727(2)
Os(3)–Os(5)	2.714(2)	2.762(2)
Os(6)–Os(7)	2.882(1)	2.849(2)
Os(6)–P	2.29(1)	

Numbers in parentheses are e.s.d.s in the last digit.

of the triangle, the solid state structure of **3** appears to be the same as that of **1**. However, the spectroscopic data reveal different locations for the hydride ligands in these two clusters. Unfortunately, the hydride ligand positions could not be located in the X-ray analysis. It is, of course, entirely possible that the metal atom arrangements of some or all of these clusters are different in solution than in the solid state. In any case, the results reported herein lend strong support to the assignment of cluster **2** as an isomer of cluster **1**. The similarity of clusters **3** and **2** in terms of spectra and reactivity indicates that they are chemical analogues of each other. Thus it appears as if complex **2** is in fact $Os_7H_2(CO)_{22}$ with a structure that differs from cluster **1** in regard to the location of the hydride ligands.

4. Supplementary material

Tables of atomic coordinates, structure factors, bond distances and angles, and anisotropic thermal parameters are available from author G.L.P.

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