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The First Seven-Electron Triangular Tungsten Sulfide Cluster

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Abstract—A new cluster complex $[W_3S_4(Dppe)_3Br_3] \cdot 3THF$ (Dppe = $Ph_2PCH_2CH_2PPh_2$), the first example of a triangular tungsten cluster with a seven-electron core, was synthesized. The molecular and crystal structures of the compound were determined by X-ray diffraction.

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INTRODUCTION

The interest in the chalcogenide cluster complexes is due to their important role in some biological and industrial catalytic processes, in particular, fixation of atmospheric nitrogen. Recently new approaches to the preparation of materials based on Mo and W clusters were proposed; these are based on the use of redox active dithiolate ligands [1]. These complexes are considered as one-component molecular conductors with the prospect of combining the conducting properties with some other, for example, magnetic or optical properties [2, 3].

Also, it is known that a cluster core is capable of spontaneous restoration. However, there are only three examples of paramagnetic clusters with the Mo_3S_4 core: $[Mo_3S_4Cp_3]$ [4], $[Mo_3S_4Cp_3^*]$ [5], and $[Mo_3S_4(PEt_3)(Dppe)_2Cl_3]$ (Dppe = 1,2-bis(diphenylphosphino)ethane) [6], whereas for tungsten these clusters are unknown.

Recently we studied the reactions of bromide and mixed-halide cationic clusters $[Mo_3S_4(Dppe)_3X_3]X$ (X = Br (**Ia**); $Br_{0.8}Cl_{0.2}$ (**Ib**)) with elemental gallium or carbonylmolybdate $K[Mo(CO)_3Cp^*]$ [7]. Both reactions gave products of single-electron reduction of the initial cationic clusters, neutral complexes $[Mo_3S_4(Dppe)_3X_3]$ (X = Br (**IIa**), $Br_{0.85}Cl_{0.15}$ (**IIb**)) with seven cluster skeletal electrons. This communication deals with the reactions of the cationic tungsten cluster $[W_3S_4(Dppe)_3Br_3]Br$ (**III**) with liquid gallium metal.

EXPERIMENTAL

All procedures were carried out under argon using the standard Schlenk glassware. $[W_3S_4(Dppe)_3Br_3]Br$ were synthesized by a reported procedure [8]. The solvents for the syntheses were dehydrated and degassed by refluxing and by distillation under inert gas from appropriate dehydrating agents [9]. IR spectra were recorded on a SCIMITAR FTS 2000 instrument, the elemental analysis of samples for C, H, N were performed on a Euro EA 3000 instrument of the Laboratory for Microanalysis of the Institute of Inorganic Chemistry, Siberian Branch of the RAS.

Synthesis of $[W_3S_4(Dppe)_3Br_3] \cdot 3THF$ (IV · 3THF). Compound **III** (130 mg, 0.059 mmol) and Ga (250 mg, 3.59 mmol) were placed into a Schlenk vessel, THF (15 mL) was condensed into the vessel under reduced pressure with liquid nitrogen cooling, and then the vessel was evacuated down to a residual pressure of ~1 mm Hg. The resulting mixture was warmed up to room temperature and refluxed for 14 days with intense stirring (bath temperature 55°C). Then the reaction mixture was cooled down to room temperature and allowed to settle. The dark brown solution was filtered from the gray precipitate through a paper filter (blue ribbon grade) into one knee of an H-shaped Schlenk vessel, and freshly distilled diethyl ether (25 mL) was placed into the other knee, and the vessel was allowed to stand at room temperature up to complete mixing. Coarse dark brown crystals suitable for X-ray diffraction were formed. Yield 35 mg (25%).

IR (KBr; ν, cm^{-1}): 3050 m, 2917 w, 1959 w, 1620 w, 1572 w, 1483 m, 1433 s, 1413 m, 1191 m, 1097 s, 1027 w, 999 w, 872 m, 820 m, 742 m, 694 vs, 519 s, 493 m.

For $C_{78}H_{72}Br_3P_6S_4W_3$ (**IV**)			
anal. calcd., %:	C, 44.30;	H, 3.43;	S, 6.07. *
Found, %:	C, 43.9;	H, 3.5;	S, 6.3.

X-Ray diffraction study of IV · 3THF. All measurements were carried out by a standard procedure on a Bruker-Nonius X8 APEX four-circle automated diffractometer (two-coordinate CCD detector, λ =

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* Due to the easy partial loss of the solvation molecules of **IV** · 3THF, the elemental analysis was performed for a vacuum-dried sample.

0.71073 Å, graphite monochromator). The reflection intensities were measured by φ scanning of narrow (0.5°) frames to $2\theta_{max} = 52.74°$. The absorption corrections were applied empirically (SADABS) [10]. The structure was solved by the direct method and refined by full-matrix least-squares calculations in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [10]. The hydrogen atoms were located geometrically and refined in the rigid-body approximation. The crystallographic characteristics of the complex and X-ray experiment details are presented in Table 1 and selected interatomic distances are given in Table 2. The crystal data are deposited with the Cambridge Crystallographic Data Centre (no. 902425; http://www.ccdc.cam.ac.uk/conts/retrieving.html) and are available from the authors.

RESULTS AND DISCUSSION

Heating of a suspension of cluster **III** with excess Ga in THF in a sealed vessel for 2 weeks at 50–55°C results in disappearance of the blue precipitate of the initial cluster complex to give a dark brown solution. Slow diffusion of Et_2O into this solution gave virtually black crystals whose composition, according to X-ray diffraction data, was described as $[W_3S_4(Dppe)_3Br_3] \cdot 3THF$ (**IV** · 3THF). The tungsten cluster reacts according to the same pattern as the molybdenum cluster but completion of the reaction requires longer time, which is in line with the lower reactivity of W clusters compared with Mo clusters.

X-Ray diffraction data indicate that the structure of cluster **IV** is similar to its molybdenum analogs **IIa** and **IIb** and the cluster cation $[W_3S_4(Dppe)_3Br_3]^+$, which was characterized as the salt $[W_3S_4(Dppe)_3Br_3]_2(ZnBr_4)$ [11]. The tungsten atoms form a nearly regular triangle; the W–W distances are 2.7914(6)–2.8137(7) Å. The average W–(μ_3-S) and W–(μ-S) distances are 2.373(2) and 2.321(15) Å, respectively (figure). The crystal has intermolecular C–H···π and π···π interactions, which contribute to structure stabilization together with the van der Waals contacts.

Table 1. Crystallographic data and X-ray experiment details for structure **IV** · 3THF

Parameter	Value
Molecular fortmula	$C_{90}H_{96}O_3P_6S_4Br_3W_3$
M	2331.01
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature, K	153
a, Å	18.962(4)
b, Å	23.432(5)
c, Å	25.104(9)
β, deg	128.29(2)
V, Å^3	8755(4)
Z	4
ρ_{calcd}, g cm^{-3}	1.768
$F(000)$	4564
μ_{MoK_α}, mm^{-1}	5.555
Crystal size, mm	0.22 × 0.17 × 0.15
Data collection range on θ, deg	1.62–26.37
Ranges of h, k, l	$-22 \le h \le 23$, $-29 \le k \le 29$, $-31 \le l \le 31$
The number of measured reflections	64937
The number of independent reflections (R_{int})	17871 (0.0888)
The number of observed reflections ($I > 2\sigma(I)$)	13196
The number of refined parameters	910
Weighting scheme	$1/[2\sigma^2(F_o^2) + (0.0436P)^2]$, $P = (F_o^2 + 2F_c^2)/3$
R_1 ($F^2 > 2\sigma(F^2)$), $wR_2(F^2)$	0.0415; 0.0928
GOOF	0.954
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.79, −1.37

Using the structural data for cluster **IV**, it was possible to compare the pair of clusters $[\mathbf{III}]^+$ and **IV**, which differ only by the oxidation state, while the cluster core, phosphine, and halogen are the same (Table 2). The average W–W distance in $[\mathbf{III}]^+$ is 2.776(3), the W–(μ_3-S) distance is 2.363(3) Å, and W–(μ-S) is 2.307(16) Å. Analysis of the bond lengths indicates that the W–W distances are elongated upon reduction, as in the case of Mo, by ~0.03 Å. In the reduced **IV** cluster, the W_3 triangle becomes somewhat less symmetrical: the difference between the W–W bond lengths increases to 0.027 Å, although it is smaller than in the case of **IIb**. The W–Br distances are elongated upon reduction by 0.03 Å, and the other bond lengths change to lesser extent. The W–P distances in the *trans*-positions to the μ_3-S ligand are

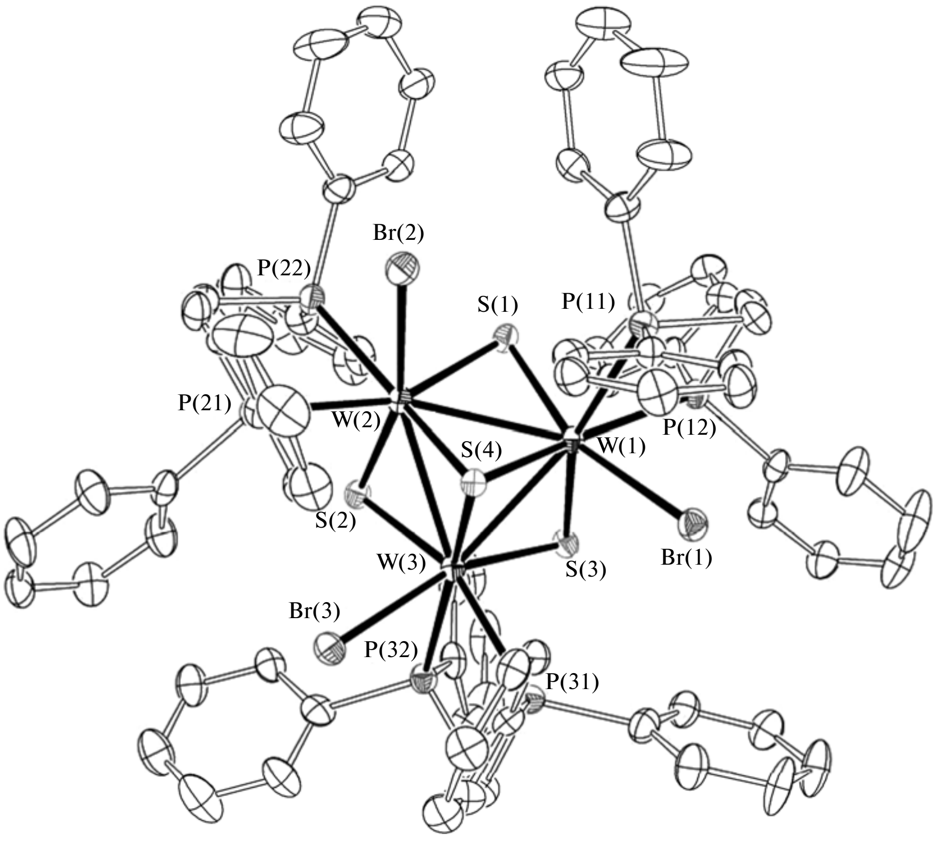
Table 2. Selected bond lengths (Å) in cluster **IV** and its analogs

Bond	$[W_3S_4(Dppe)_3Br_3]$	$[W_3S_4(Dppe)_3Br_3]^+$	$[Mo_3S_4(Dppe)_3Br_3]$
M–M	2.7911(12)–2.8134(9) (2.802(11))	2.770–2.794 (2.779(3))	2.7809(5)–2.8381(5) (2.82(3))
M–(μ_3-S)	2.3722(17)–2.3750(16) (2.374(2))	2.359–2.367 (2.363(2))	2.3545(10)–2.3804(10) (2.368(13))
M–(μ-S)	2.3039(18)–2.3397(17) (2.323(15))	2.283–2.331 (2.306(1))	2.2691(10)–2.3402(10) (2.31(3))
M–P	2.529(2)–2.642(2)(2.58(6))	2.547–2.669 (2.61(5))	2.5397(10)–2.6764(10) (2.60(6))
M–Br	2.6306(9)–2.6399(9) (2.636(4))	2.585–2.608 (2.592(2))	2.6311(5)–2.6573(5) (2.647(14))

somewhat shorter than the same distances in the *trans*-position to the μ-S-ligands both in neutral **IV** and in cationic [**III**]$^+$.

The EPR spectrum of the polycrystalline sample of **IV** · 3THF could not be recorded at 300 or 77 K. Note that the EPR spectrum of crystalline **IIa** and **IIb** could be recorded only below 80 K. The IR spectrum of **IV** · 3THF in KBr mainly contains the bands of coordinated Dppe ligands and is almost identical to the spectrum of **III**.

Thus, the first example of a triangular tungsten cluster containing seven skeletal electrons was synthesized and characterized by X-ray diffraction. It was found that reduction leads to elongation of the W–W bonds by ~0.03 Å, as in the case of reduction of similar molybdenum cluster.



Structure of the cluster complex **IV**. The hydrogen atoms of the Dppe ligands are not shown. The thermal ellipsoids are shown at the 50% probability level.

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