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Triangular trinuclear clusters of tungsten containing bromine atoms as terminal ligands: syntheses and structural characterizations of $[W_3S_4Br_3(dmpe)_3][Y]$, where dmpe = 1,2-bis(dimethylphosphino)ethane and $Y^- = Br^-$ or PF_6^-

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Abstract

The triangular trinuclear cluster $[W_3S_4Br_3(dmpe)_3]^+$ has been prepared in high yield by reactions between WBr_5 and $NaBH_4$ or $NaB(C_2H_5)_3H$ as reducing agent in THF, and subsequent addition of methanolic solutions of NaHS and dmpe ligand. It has been isolated as the bromide, $[W_3S_4Br_3(dmpe)_3]Br$ (**1**) and as the fluorophosphate, $[W_3S_4Br_3(dmpe)_3]PF_6$ (**2**). Compound **1** crystallizes in the orthorhombic space group *Fdd*2 with $a = 26.112(7)$, $b = 64.970(21)$, $c = 20.555(4)$ Å, $V = 34881(27)$ Å^3 and $Z = 32$. The final refinement converged to the residual values $R = 0.053$ and $R_w = 0.068$. There are two independent formula units in the unit cell, but the virtually identical cations are both chiral and possess C_3 symmetry. Compound **2** crystallizes in the cubic space group *I*23 with $a = 20.999(2)$ Å, $V = 9260(3)$ Å^3 and $Z = 8$; $R = 0.039$, $R_w = 0.057$. The cation has crystallographic three-fold symmetry. The cation in **2** is identical to those in **1**. The W–W distances are in the range 2.760–2.770 Å (for **1a**) and 2.732–2.766 Å (for **1b**) and the average W–Br distances in **1a** and **1b** are 2.640(4) and 2.626(4) Å, respectively. The W–W distances and the W–Br distances in **2** are 2.759(2) and 2.641(4) Å, respectively. Each metal atom in the $[W_3S_4Br_3(dmpe)_3]^+$ ions is attached to one capping sulfur atom, two bridging sulfur atoms, one bromine atom and one chelating dmpe ligand. One P atom in dmpe ligand is *trans* to μ_3-S and the other P atom is *trans* to a μ_2-S atom. UV–Vis and NMR spectra for **1** are also reported.

Introduction

The earliest report describing the compounds that we now know to contain Mo–Mo bonded $Mo_3O_4^{4+}$ cores was made in 1929 by Spittle and Wardlaw [1]. The existence of these units as part of extended solid state structures was first recognized in 1957 [2] and the metal–metal bonding was described in terms of delocalized molecular orbitals in 1964 by Cotton [3]. The discovery of numerous new discrete M_3X_{13} clusters began in the late seventies. The first example in the case of tungsten was the $[W_3O_4F_9]^{5-}$ ion [4] while that for molybdenum was $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ reported from our laboratory [5]. The past decade has seen a phenomenal rate of growth in the chemistry of these and related $M_3X_4L_9$ compounds [6].

One of the most interesting and important subsets of these complexes are those containing the $M_3S_4^{4+}$ core with a set of metal–metal single bonds. This paper makes a further contribution to our knowledge of those compounds that contain the $W_3S_4^{4+}$ core. Although other types exist and have been reported by other groups [7–9] we are particularly interested in those $M_3S_4^{4+}$ (M = Mo, W) compounds that have a combination of phosphines and X^- ions (X = Cl, Br, H) as outer ligands [10, 11]. Two methods of preparation have so far been employed, one of which [10] begins with WCl_4 and leads to products with X = Cl or H and the other [11] begins with $W_3S_7Br_4$ [12] and is the only route so far reported that leads to products with X = Br.

Since WBr_4, unlike WCl_4, is not available as a starting material, and the use of $W_3S_7Br_4$ may not always be feasible, we looked for a way to employ WBr_5. Recently, we have found that it is possible to proceed in this way and we reported [13] two compounds containing the $[W_3S_4Br_3(depe)_3]^+$ cluster ion by employing this new, convenient and non-aqueous method similar to the one reported here. In this paper we offer further evidence of the generality of this method by presenting here the detailed preparative procedure as well as the structural and spectroscopic characterization of two compounds containing the $[W_3S_4Br_3(dmpe)_3]^+$ ion.

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Experimental

Materials and methods

Although the compounds reported here are stable in air, both as solids and in solution, all experimental manipulations were carried out under an atmosphere of argon using standard vacuum line and Schlenk techniques [14]. The solvents were freshly distilled under nitrogen from the appropriate drying agents. Chemicals were used as received from the following sources: 1,2-bis(dimethylphosphino)ethane (dmpe), Strem Chemical Company; WBr_5, $NaBH_4$ and 1 M $NaB(C_2H_5)_3H$ in THF, Aldrich Chemical Company; dmpe and $NaB(C_2H_5)_3H$ were transferred in separate Schlenk tubes under an atmosphere of argon and were stored in the refrigerator when not in use. NaHS was prepared according to the literature method [15].

Physical measurements

The UV–Vis spectrum was obtained with a CH_2Cl_2 solution of the compound on a Cary 17D spectrophotometer. The $^{31}P\{^1H\}$ NMR spectrum of the compound in CH_2Cl_2 was recorded on a Varian XL-200 spectrometer in a tube containing a small amount of C_6D_6. The ^{31}P shifts are reported relative to external 85% H_3PO_4 by using the chemical shift difference, δ −128.23.

Preparations of $[W_3S_4Br_3(dmpe)_3]Br$ (1) and $[W_3S_4Br_3(dmpe)_3][PF_6]$ (2)

In a three-neck flask WBr_5 (583 mg, 1 mmol) and $NaBH_4$ (38 mg, 1 mmol) were placed under an atmosphere of argon using a dry box and 20 ml THF was added to this mixture. Addition of 5 ml methanol (to dissolve the $NaBH_4$) gave a deep green solution in 20 min and to this solution a methanolic solution of NaHS (a slight excess) and 0.3 ml of dmpe ligand were introduced. The reaction mixture was refluxed for 2 h and then a blue–black solution was separated from a solid by filtering through Celite under an atmosphere of argon. The blue–black solution was taken to dryness under vacuum and the solid was redissolved in CH_2Cl_2. This solution was layered with hexane in a Schlenk tube and set aside for crystallization. A large crop of crystals suitable for X-ray diffraction studies were formed within two days. Yield 55–65%. A band appeared at 560 nm in the UV–Vis spectrum.

Compound **2** was prepared by adding NH_4PF_6 to the 1,2-dichloroethane solution of **1**. After filtering the mixture through Celite, the filtrate was layered with hexane and X-ray quality crystals were formed within three days.

Spectroscopic measurements (UV–Vis and NMR) have shown that the $[W_3S_4Br_3(dmpe)_3]^+$ ion can also

TABLE 1. Crystal data for $[W_3S_4Br_3(dmpe)_3]Br$ (1) and $[W_3S_4Br_3(dmpe)_3][PF_6]$ (2)

Compound	1	2
Formula	$C_{18}H_{48}Br_4P_6S_4W_3$	$C_{18}H_{48}Br_3F_6P_7S_4W_3$
Formula weight	1449.87	1514.93
Space group	*Fdd*2 (No. 43)	I23 (No. 197)
Systematic absences	hkl, $h+k$, $k+l$, $l+h \neq 2n$; $0kl$, $k+l \neq 4n$, k, $l \neq 2n$; $h0l$, $h+l \neq 4n$, h, $l \neq 2n$	$h+k+l \neq 2n$
a (Å)	26.112(7)	20.999(2)
b (Å)	64.970(21)	
c (Å)	20.555(4)	
V (Å^3)	34881(27)	9260(3)
Z	32	8
D_{calc} (g/cm^3)	2.209	2.173
Crystal size (mm)	0.27×0.22×0.15	0.20×0.20×0.13
μ(Mo Kα) (cm^{-1})	121.15	106.14
Instrument used	Enraf-Nonius CAD-4	Nicolet P3
Radiation used, λ (Å)	Mo Kα, 0.71073	
Temperature (°C)	−60	20±1
Scan method	ω	ω–2θ
Data collection 2θ limits (°)	4–46	4–46
No. unique data, no. with $F_o^2 > 3\sigma(F_o^2)$	6261, 4876	670, 664
No. parameters refined	590	127
Transmission factors: max., min. (%)	99.81, 69.54	99.99, 66.98
R[a]	0.05269	0.03877
R_w[b]	0.06836	0.05724
Quality-of-fit[c]	1.541	1.462
Largest shift/e.s.d., final cycle	0.02	0.06
Largest peak (e/Å^3)	3.10	0.47

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

be made by using $NaB(C_2H_5)_3H$ as reducing agent instead of $NaBH_4$ in the above procedure.

X-ray crystallography

In each case a crystal of suitable size and quality was mounted on the tip of a thin glass fiber with the use of epoxy cement. X-ray data were collected on an automated four-circle diffractometer, equipped with monochromated MoKα radiation, following the general procedures and practices of this laboratory [16]*. Axial lengths and Laue class were confirmed with oscillation photographs. Lorentz, polarization and empirical absorption corrections based on azimuthal scans of several reflections with setting angles (χ) near 90° were applied to the data [17]. Crystallographic data pertaining to cell parameters, data collection and structure refinement for **1** and **2** are summarized in Table 1.

Crystal structure of [$W_3S_4Br_3$(dmpe)$_3$]Br (1)

A blue–black crystal of dimensions 0.27×0.22×0.15 mm was selected from the product and was mounted on the goniometer head of an Enraf-Nonius CAD-4 diffractometer. Twenty five reflections in the range $20 \leq 2\theta \leq 31°$ were centered to refine the reduced cell parameters corresponding to the orthorhombic crystal system. *F*-Centering and symmetry elements were checked with additional oscillation photographs. During the data collection three intensity standards were collected every 2 h; no significant decay was observed during the 84.4 h of exposure to X-rays. The ω scan mode was used to scan the data points for the *F*-centered orthorhombic crystal system at −60 °C.

The crystal system belongs to the Laue class *mmm*. Systematic absences uniquely determined the space group *Fdd*2 and this was confirmed by successful refinement of the structure. The unit cell volume suggested the presence of two independent trimers in it. The positions of all atoms heavier than carbon for the two independent trinuclear clusters were obtained from the direct methods program, MULTAN, and the rest of the structure was developed by alternating difference Fourier maps and least-squares cycles, employing the Enraf-Nonius structure determination package. All atoms in the clusters and the anions, except nine of the carbon atoms in the phosphine ligands, were refined anisotropically. One of the anionic Br^- ions was at a special position and hence the third Br^- was refined with half occupancy. Hydrogen atoms were not included in the model. The final difference Fourier map showed several peaks greater than 1 e/Å^3 (highest 3.10 e/Å^3, 1.05 Å away from W(3)) in the vicinity of the trinuclear cores, but otherwise it was featureless. The last cycle

TABLE 2. Positional and isotropic equivalent displacement parameters and their e.s.d.s for [$W_3S_4Br_3$(dmpe)$_3$]Br

Atom	*x*	*y*	*z*	*B* (Å^2)^a
W(1)	0.20839(5)	0.00339(2)	0.663	2.45(2)
W(2)	0.28642(5)	−0.01374(2)	0.73651(7)	2.69(3)
W(3)	0.30929(5)	0.01136(2)	0.63214(7)	3.13(3)
Br(1)	0.1687(1)	0.04058(5)	0.6487(2)	3.40(7)
Br(2)	0.2467(1)	−0.00954(6)	0.8548(2)	3.75(7)
Br(3)	0.3849(2)	0.03323(7)	0.6789(2)	5.3(1)
S(1)	0.2668(3)	0.0216(1)	0.7307(4)	3.1(2)
S(2)	0.2160(3)	−0.0308(1)	0.6942(4)	2.8(2)
S(3)	0.3432(4)	−0.0209(2)	0.6582(5)	4.2(2)
S(4)	0.2470(4)	0.0006(2)	0.5641(4)	3.6(2)
P(1)	0.1334(3)	0.0044(1)	0.7476(4)	2.8(2)
P(2)	0.1309(3)	−0.0058(1)	0.5983(4)	2.8(2)
P(3)	0.3065(4)	−0.0494(2)	0.7809(5)	3.8(2)
P(4)	0.3659(4)	−0.0074(2)	0.8118(5)	3.7(2)
P(5)	0.3691(4)	0.0076(2)	0.5394(5)	4.8(2)
P(6)	0.3013(4)	0.0464(2)	0.5738(5)	4.7(2)
C(1)	0.130(1)	0.0253(5)	0.813(2)	3.1(7)
C(2)	0.122(1)	−0.0187(5)	0.794(2)	3.8(7)
C(3)	0.072(2)	0.0078(5)	0.707(2)	4.7(9)
C(4)	0.072(1)	−0.0066(6)	0.645(2)	4.0(8)
C(5)	0.125(2)	0.0128(7)	0.534(2)	6(1)^a
C(6)	0.135(1)	−0.0291(5)	0.561(2)	4.4(9)
C(7)	0.322(2)	−0.0681(8)	0.726(3)	8(1)^a
C(8)	0.255(2)	−0.0612(7)	0.833(2)	8(1)
C(9)	0.364(2)	−0.0493(5)	0.830(2)	5.0(9)
C(10)	0.366(1)	−0.0294(6)	0.869(2)	4.3(8)
C(11)	0.366(1)	0.0158(5)	0.862(2)	3.9(8)
C(12)	0.430(1)	−0.0088(6)	0.773(2)	4.3(9)
C(13)	0.440(1)	0.0039(5)	0.561(2)	4.4(8)^a
C(14)	0.354(2)	−0.0158(7)	0.487(2)	6(1)^a
C(15)	0.369(1)	0.0294(5)	0.486(2)	4.9(8)
C(16)	0.359(2)	0.0494(7)	0.522(2)	6(1)
C(17)	0.249(2)	0.0489(7)	0.512(2)	6(1)
C(18)	0.303(2)	0.0709(5)	0.628(3)	12(1)
W(4)	0.53019(6)	0.10954(2)	0.10464(7)	3.38(3)
W(5)	0.48845(5)	0.14032(2)	0.17832(7)	2.83(3)
W(6)	0.47172(5)	0.10028(2)	0.21292(7)	2.84(3)
Br(4)	0.5133(2)	0.12421(7)	−0.0128(2)	5.6(1)
Br(5)	0.3989(1)	0.15695(6)	0.2004(2)	4.82(9)
Br(6)	0.4198(2)	0.06799(5)	0.1729(2)	4.27(8)
S(5)	0.4419(3)	0.1160(1)	0.1183(4)	3.5(2)
S(6)	0.5717(4)	0.1379(2)	0.1493(5)	4.7(2)
S(7)	0.4988(4)	0.1259(2)	0.2825(6)	5.4(3)
S(8)	0.5532(3)	0.0873(1)	0.1883(4)	3.3(2)
P(7)	0.6196(4)	0.1044(2)	0.0608(5)	4.5(2)
P(8)	0.5196(4)	0.0768(2)	0.0363(5)	4.4(2)
P(9)	0.4852(5)	0.1697(1)	0.0974(5)	4.4(2)
P(10)	0.5179(4)	0.1710(1)	0.2443(5)	4.0(2)
P(11)	0.4842(4)	0.0779(2)	0.3145(5)	4.6(2)
P(12)	0.3850(4)	0.1034(2)	0.2768(5)	4.0(2)
C(19)	0.650(2)	0.1230(9)	0.004(3)	9(2)
C(20)	0.676(2)	0.1009(7)	0.131(3)	8(1)
C(21)	0.622(2)	0.0803(7)	0.014(2)	6(1)
C(22)	0.570(2)	0.0743(7)	−0.023(2)	6(1)
C(23)	0.463(1)	0.0752(7)	−0.015(2)	6(1)
C(24)	0.525(2)	0.0504(6)	0.075(2)	5.3(9)
C(25)	0.434(2)	0.1722(8)	0.036(3)	8(1)^a
C(26)	0.546(2)	0.1739(8)	0.049(3)	7(1)^a
C(27)	0.482(2)	0.1943(6)	0.144(2)	5.6(9)

(continued)

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*Calculations were done on a Local Area VAX Cluster (VMS V4.6) with the commercial package SDP/V V 3.0.

TABLE 2. (*continued*)

Atom	x	y	z	B (Å^2)^a
C(28)	0.524(1)	0.1938(6)	0.194(2)	4.2(8)
C(29)	0.581(2)	0.1664(8)	0.287(3)	8(1)^a
C(30)	0.478(2)	0.1794(9)	0.313(3)	9(2)^a
C(31)	0.508(2)	0.0527(6)	0.296(3)	6(1)
C(32)	0.529(2)	0.0886(8)	0.375(3)	8(1)^a
C(33)	0.426(1)	0.0741(6)	0.360(2)	4.2(8)
C(34)	0.376(1)	0.0796(5)	0.329(2)	4.4(8)
C(35)	0.326(1)	0.1057(7)	0.235(3)	7(1)
C(36)	0.380(2)	0.1259(7)	0.335(2)	7(1)
Br(7)	0.4736(3)	0.3535(1)	0.2042(4)	12.7(2)
Br(8)	0.2466(4)	0.7393(3)	0.1926(5)	14.0(5)
Br(9)	0.500	0.000	0.3845(3)	4.1(1)

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

TABLE 3. Positional and isotropic equivalent displacement parameters and their e.s.d.s for $[W_3S_4Br_3(dmpe)_3][PF_6]$

Atom	x	y	z	B (Å^2)^a
W(1)	0.70692(7)	0.26444(8)	0.18923(8)	2.50(4)
Br(1)	0.7545(2)	0.2854(3)	0.0747(2)	4.3(1)
S(1)	0.7991(5)	0.2009(5)	0.2009(5)	3.3(2)
S(2)	0.7331(5)	0.3631(5)	0.2324(5)	3.5(2)
P(1)	0.6466(6)	0.1831(6)	0.1171(5)	3.7(3)
P(2)	0.6171(6)	0.3300(6)	0.1456(6)	3.6(3)
C(1)	0.692(3)	0.124(2)	0.069(2)	6(1)
C(2)	0.589(2)	0.132(2)	0.152(2)	5(1)
C(3)	0.599(2)	0.229(2)	0.060(2)	4(1)
C(4)	0.559(2)	0.285(2)	0.090(2)	5(1)
C(5)	0.562(2)	0.365(2)	0.207(3)	6(1)
C(6)	0.640(2)	0.401(2)	0.094(2)	5(1)
P(3)	0.000	0.000	0.500	3.9(7)
F(1)	−0.078(2)	0.000	0.500	7(1)
F(2)	0.000	0.000	0.427(2)	7(1)
F(3)	0.000	−0.076(2)	0.500	12(2)
P(4)	0.405(3)	0.405(3)	0.595(3)	16(7)^a
F(4)	0.413(3)	0.463(3)	0.643(3)	8(4)^a
F(4)′	0.452(3)	0.364(3)	0.636(3)	8(4)^a
F(4)″	0.347(3)	0.380(3)	0.634(3)	8(4)^a
F(5)	0.398(3)	0.348(3)	0.546(3)	8(4)^a
F(5)′	0.359(3)	0.447(3)	0.553(3)	8(4)^a
F(5)″	0.464(3)	0.431(3)	0.555(3)	8(4)^a

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

of refinement included the fit of 590 parameters to 4876 unique data with $F_o^2 > 3\sigma(F_o^2)$ and gave residuals of $R=0.053$ and $R_w=0.068$. The final atomic positional and isotropic equivalent displacement parameters are listed in Table 2.

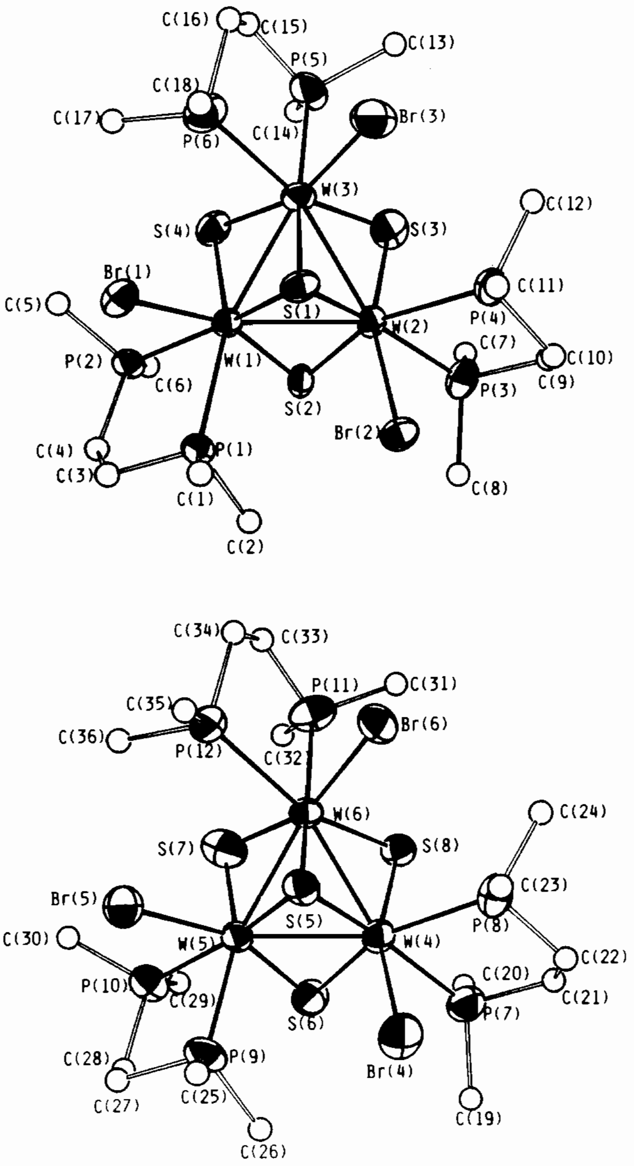


Fig. 1. The two cations in **1**.

Crystal structure of $[W_3S_4Br_3(dmpe)_3][PF_6]$ *(2)*

A crystal of good quality was selected from the product and was mounted on the goniometer head of a Nicolet P3 diffractometer. Cell parameters determined by the routine procedures were indicative of the cubic crystal system. Body centering and symmetry elements were checked with additional oscillation photographs, which also pointed to the Laue class $m\bar{3}$. The ω–2θ scan mode was used to scan the data points over an octant of reciprocal space with the body centering condition, $h+k+l=2n$. Periodically monitored check reflections showed no significant decay of the crystal during the period of data collection (52.5 h).

The full data set indicated three possible space groups $I23$, $I2_13$ or $Im\bar{3}$, but the last one was not suitable for this kind of molecule since it would require an inversion

TABLE 4. Selected bond distances (Å) and bond angles (°) for $[W_3S_4Br_3(dmpe)_3]Br$

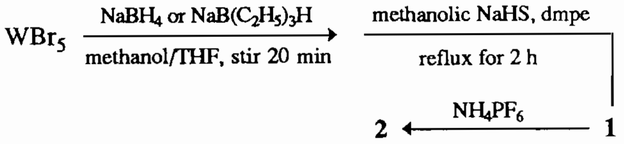
Bond distances					
W(1)–W(2)	2.770(2)	W(2)–P(4)	2.62(1)	W(4)–P(8)	2.56(1)
W(1)–W(3)	2.760(2)	W(3)–Br(3)	2.616(4)	W(5)–W(6)	2.732(2)
W(1)–Br(1)	2.645(4)	W(3)–S(1)	2.404(8)	W(5)–Br(5)	2.615(4)
W(1)–S(1)	2.380(8)	W(3)–S(3)	2.34(1)	W(5)–S(5)	2.345(9)
W(1)–S(2)	2.319(8)	W(3)–S(4)	2.257(9)	W(5)–S(6)	2.26(1)
W(1)–S(4)	2.277(9)	W(3)–P(5)	2.48(1)	W(5)–S(7)	2.35(1)
W(1)–P(1)	2.620(8)	W(3)–P(6)	2.58(1)	W(5)–P(9)	2.53(1)
W(1)–P(2)	2.496(8)	W(4)–W(5)	2.735(2)	W(2)–P(10)	2.53(1)
W(2)–W(3)	2.760(2)	W(4)–W(6)	2.766(2)	W(6)–Br(6)	2.630(4)
W(2)–Br(2)	2.659(4)	W(4)–Br(4)	2.633(4)	W(6)–S(5)	2.332(9)
W(2)–S(1)	2.354(8)	W(4)–S(5)	2.361(9)	W(6)–S(7)	2.30(1)
W(2)–S(2)	2.317(8)	W(4)–S(6)	2.33(1)	W(6)–S(8)	2.345(8)
W(2)–S(3)	2.238(9)	W(4)–S(8)	2.326(9)	W(6)–P(11)	2.56(1)
W(2)–P(3)	2.55(1)	W(4)–P(7)	2.53(1)	W(6)–P(12)	2.63(1)
Bond angles					
W(2)–W(1)–W(3)	59.88(5)	Br(1)–W(1)–S(4)	98.5(3)	W(1)–W(2)–S(1)	54.6(2)
W(2)–W(1)–Br(1)	135.73(9)	Br(1)–W(1)–P(1)	75.9(2)	W(1)–W(2)–S(2)	53.3(2)
W(2)–W(1)–S(1)	53.7(2)	Br(1)–W(1)–P(2)	80.9(2)	W(1)–W(2)–S(3)	100.3(2)
W(2)–W(1)–S(2)	53.3(2)	S(1)–W(1)–S(2)	105.0(3)	W(1)–W(2)–P(3)	135.4(2)
W(2)–W(1)–S(4)	97.4(2)	S(1)–W(1)–S(4)	106.1(3)	W(1)–W(2)–P(4)	147.3(2)
W(2)–W(1)–P(1)	101.5(2)	S(1)–W(1)–P(1)	94.5(3)	W(3)–W(2)–Br(2)	137.3(1)
W(2)–W(1)–P(2)	142.3(2)	S(1)–W(1)–P(2)	162.1(3)	W(3)–W(2)–S(1)	55.4(2)
W(3)–W(1)–Br(1)	100.22(9)	S(2)–W(1)–S(4)	97.6(3)	W(3)–W(2)–S(2)	99.3(2)
W(3)–W(1)–S(1)	55.2(2)	S(2)–W(1)–P(1)	84.6(3)	W(3)–W(2)–S(3)	54.5(3)
W(3)–W(1)–S(2)	99.3(2)	S(2)–W(1)–P(2)	89.3(3)	W(3)–W(2)–P(3)	140.5(2)
W(3)–W(1)–S(4)	52.2(2)	S(4)–W(1)–P(1)	157.8(3)	W(3)–W(2)–P(4)	101.2(2)
W(3)–W(1)–P(1)	149.5(2)	S(4)–W(1)–P(2)	82.2(3)	Br(2)–W(2)–S(1)	82.0(2)
W(3)–W(1)–P(2)	134.2(2)	P(1)–W(1)–P(2)	75.7(3)	Br(2)–W(2)–S(2)	94.7(2)
Br(1)–W(1)–S(1)	82.1(2)	W(1)–W(2)–W(3)	59.86(4)	Br(2)–W(2)–S(3)	159.8(3)
Br(1)–W(1)–S(2)	159.8(2)	W(1)–W(2)–Br(2)	99.83(9)	Br(2)–W(2)–P(3)	81.1(2)
Br(2)–W(2)–P(4)	75.7(2)	W(1)–W(3)–S(4)	52.8(2)	S(1)–W(3)–S(4)	106.0(3)
S(1)–W(2)–S(2)	105.9(3)	W(1)–W(3)–P(5)	139.5(2)	S(1)–W(3)–P(5)	165.3(3)
S(1)–W(2)–S(3)	108.0(3)	W(1)–W(3)–P(6)	101.2(3)	S(1)–W(3)–P(6)	96.4(3)
S(1)–W(2)–P(3)	161.9(3)	W(2)–W(3)–Br(3)	101.5(1)	S(3)–W(3)–S(4)	97.9(3)
S(1)–W(2)–P(4)	92.9(3)	W(2)–W(3)–S(1)	53.7(2)	S(3)–W(3)–P(5)	81.3(4)
S(2)–W(2)–S(3)	99.1(3)	W(2)–W(3)–S(3)	51.3(2)	S(3)–W(3)–P(6)	158.1(3)
S(2)–W(2)–P(3)	82.1(3)	W(2)–W(3)–S(4)	98.2(2)	S(4)–W(3)–P(5)	87.0(3)
S(2)–W(2)–P(4)	157.7(3)	W(2)–W(3)–P(5)	132.6(3)	S(4)–W(3)–P(6)	85.8(4)
S(3)–W(2)–P(3)	86.2(3)	W(2)–W(3)–P(6)	149.8(3)	P(5)–W(3)–P(6)	77.3(4)
S(3)–W(2)–P(4)	86.1(3)	Br(3)–W(3)–S(1)	83.6(2)	W(1)–S(1)–W(2)	71.6(2)
P(3)–W(2)–P(4)	76.6(3)	Br(3)–W(3)–S(3)	96.7(3)	W(1)–S(1)–W[(3)	70.5(2)
W(1)–W(3)–W(2)	60.25(4)	Br(3)–W(3)–S(4)	160.1(3)	W(2)–S(1)–W(3)	70.9(2)
W(1)–W(3)–Br(3)	137.6(1)	Br(3)–W(3)–P(5)	82.0(3)	W(1)–S(2)–W(2)	73.4(2)
W(1)–W(3)–S(1)	54.4(2)	Br(3)–W(3)–P(6)	75.7(3)	W(2)–S(3)–W(3)	74.2(3)
W(1)–W(3)–S(3)	98.1(2)	S(1)–W(3)–S(3)	103.3(3)	W(1)–S(4)–W(3)	75.0(3)
W(5)–W(4)–W(6)	59.55(5)	Br(4)–W(4)–S(8)	161.1(2)	W(4)–W(5)–S(5)	54.7(2)
W(5)–W(4)–Br(4)	100.2(1)	Br(4)–W(4)–P(7)	82.9(3)	W(4)–W(5)–S(6)	54.5(3)
W(5)–W(4)–S(5)	54.2(2)	Br(4)–W(4)–P(8)	77.3(3)	W(4)–W(5)–S(7)	99.6(3)
W(5)–W(4)–S(6)	52.2(3)	S(5)–W(4)–S(6)	105.5(3)	W(4)–W(5)–P(9)	101.5(2)
W(5)–W(4)–S(8)	98.5(2)	S(5)–W(4)–S(8)	106.0(3)	W(4)–W(5)–P(10)	138.7(2)
W(5)–W(4)–P(7)	131.5(3)	S(5)–W(4)–P(7)	165.7(3)	W(6)–W(5)–Br(5)	101.8(1)
W(5)–W(4)–P(8)	150.1(3)	S(5)–W(4)–P(8)	96.1(3)	W(6)–W(5)–S(5)	54.0(2)
W(6)–W(4)–Br(4)	136.4(1)	S(6)–W(4)–S(8)	94.6(3)	W(6)–W(5)–S(6)	99.0(3)
W(6)–W(4)–S(5)	53.4(2)	S(6)–W(4)–P(7)	79.4(4)	W(6)–W(5)–S(7)	53.3(3)
W(6)–W(4)–S(6)	96.4(3)	S(6)–W(4)–P(8)	157.5(4)	W(6)–W(5)–P(9)	152.0(2)
W(6)–W(4)–S(8)	54.0(2)	S(8)–W(4)–P(7)	86.7(3)	W(6)–W(5)–P(10)	131.2(2)
W(6)–W(4)–P(7)	140.3(3)	S(8)–W(4)–P(8)	85.2(3)	Br(5)–W(5)–S(5)	84.6(2)
W(6)–W(4)–P(8)	101.6(2)	P(7)–W(4)–P(8)	78.1(3)	Br(5)–W(5)–S(6)	159.1(3)
Br(4)–W(4)–S(5)	83.1(2)	W(4)–W(5)–W(6)	60.78(5)	Br(5)–W(5)–S(7)	96.3(3)
Br(4)–W(4)–S(6)	98.8(3)	W(4)–W(5)–Br(5)	139.0(1)	Br(5)–W(5)–P(9)	76.9(3)

(*continued*)

TABLE 4. (*continued*)

Br(5)–W(5)–P(10)	81.6(3)	W(4)–W(6)–S(8)	53.4(2)	S(5)–W(6)–S(8)	106.3(3)
S(5)–W(5)–S(6)	108.3(3)	W(4)–W(6)–P(11)	135.1(2)	S(5)–W(6)–P(11)	166.0(3)
S(5)–W(5)–S(7)	105.7(3)	W(4)–W(6)–P(12)	149.5(2)	S(5)–W(6)–P(12)	95.5(3)
S(5)–W(5)–P(9)	98.3(3)	W(5)–W(6)–Br(6)	139.5(1)	S(7)–W(6)–S(8)	96.7(3)
S(5)–W(5)–P(10)	166.1(3)	W(5)–W(6)–S(5)	54.5(2)	S(7)–W(6)–P(11)	82.2(4)
S(6)–W(5)–S(7)	95.9(4)	W(5)–W(6)–S(7)	54.9(3)	S(7)–W(6)–P(12)	84.1(4)
S(6)–W(5)–P(9)	84.9(4)	W(5)–W(6)–S(8)	98.1(2)	S(8)–W(6)–P(11)	81.7(3)
S(6)–W(5)–P(10)	84.4(4)	W(5)–W(6)–P(11)	137.0(3)	S(8)–W(6)–P(12)	156.7(3)
S(7)–W(5)–P(9)	154.4(4)	W(5)–W(6)–P(12)	101.2(2)	P(11)–W(6)–P(12)	75.3(3)
S(7)–W(5)–P(10)	77.9(3)	Br(6)–W(6)–S(5)	85.2(2)	W(4)–S(5)–W(5)	71.1(3)
P(9)–W(5)–P(10)	76.7(3)	Br(6)–W(6)–S(7)	158.1(3)	W(4)–S(5)–W(6)	72.2(3)
W(4)–W(6)–W(5)	59.68(5)	Br(6)–W(6)–S(8)	96.5(2)	W(5)–S(5)–W(6)	71.5(3)
W(4)–W(6)–Br(6)	101.9(1)	Br(6)–W(6)–P(11)	82.4(3)	W(4)–S(6)–W(5)	73.2(3)
W(4)–W(6)–S(5)	54.4(2)	Br(6)–W(6)–P(12)	76.9(2)	W(5)–S(7)–W(6)	71.8(4)
W(4)–W(6)–S(7)	100.0(3)	S(5)–W(6)–S(7)	107.7(4)	W(4)–S(8)–W(6)	72.6(2)

Numbers in parentheses are e.s.d.s in the least significant digits.



Scheme 1.

center in the cation. The space group *I*23 allowed the determination of positions for the tungsten, bromine, sulfur and phosphorus atoms in the cation by direct methods (MULTAN), and refinement of these proceeded smoothly. Carbon atoms in the dmpe ligand and the phosphorus and fluorine atoms for a set of six PF_6^- anions on a special position (intersection of three two-fold axes) were found by alternating difference Fourier maps and least-squares cycles. All atoms in the cation and in the anion were refined anisotropically and the residual values were $R = 0.0406$ and $R_w = 0.0606$. At this stage the other set of PF_6^- ions was revealed in the Fourier map at a special position (three-fold axis) with a quarter occupancy and highly disordered. It was treated as a rigid group having perfect octahedral geometry in the final refinement of the structure. The last cycle of refinement gave residuals of $R = 0.0388$ and $R_w = 0.0572$. Hydrogen atoms were not included in the model. The final difference Fourier map had a maximum peak of 0.47 e/Å^3. the final atomic positional and isotropic equivalent displacement parameters are listed in Table 3.

Results

A new type of synthetic entry to the $W_3S_4^{4+}$ core (where W is in oxidation state IV) from mononuclear tungsten halides in a higher oxidation state, namely, V, has been developed by using two different reducing agents (Scheme 1). It should be noted here that these compounds are prepared in high yield without any chromatographic separation as required for all other compounds reported so far. Compounds **1** and **2** were then fully characterized by X-ray diffraction studies. We shall present these results first and then the NMR and UV–Vis spectroscopic results.

Crystal structures

Compound 1

There are two independent trinuclear cations in the asymmetric unit. The structures of the two independent trinuclear cations in **1** are nearly identical and are shown in Fig. 1. Table 4 gives a list of the principal bond lengths and angles in both cations. The highest possible symmetry for the cation as a whole is C_3, and deviations from C_{3v} symmetry in the W_3S_4 core may

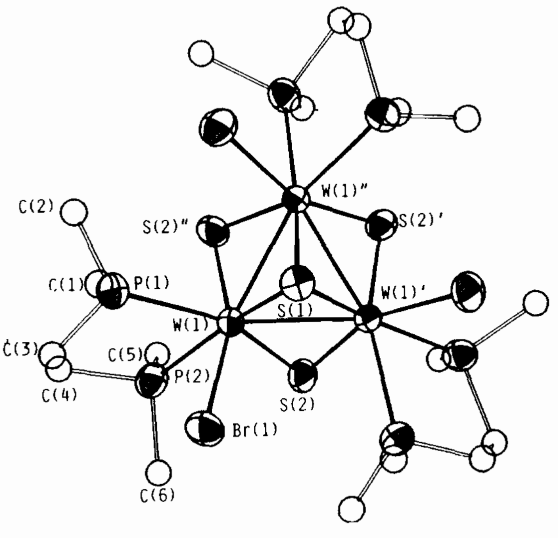


Fig. 2. The cation in **2**.

TABLE 5. Selected bond distances (Å) and bond angles (°) for $[W_3S_4Br_3(dmpe)_3][PF_6]$

Bond distances					
W(1)–W(1)′	2.759(2)	W(1)–S(2)″	2.30(1)	P(3)–F(2)	1.54(4)
W(1)–Br(1)	2.641(4)	W(1)–P(1)	2.61(1)	P(3)–F(3)	1.60(5)
W(1)–S(1)	2.37(1)	W(1)–P(2)	2.51(1)		
W(1)–S(2)	2.33(1)	P(3)–F(1)	1.65(4)		
Bond angles					
W(1)″–W(1)′–W(1)	60.00(6)	Br(1)–W(1)–S(1)	83.0(3)	S(2)″–W(1)–P(1)	84.8(4)
W(1)″–W(1)–Br(1)	137.1(1)	Br(1)–W(1)–S(2)	96.7(3)	S(2)″–W(1)–P(2)	86.5(4)
W(1)″–W(1)–S(1)	54.3(2)	Br(1)–W(1)–S(2)″	159.7(3)	P(1)–W(1)–P(2)	77.4(4)
W(1)″–W(1)–S(2)	98.6(3)	Br(1)–W(1)–P(1)	76.4(3)	W(1)–S(1)–W(1)′	71.4(3)
W(1)″–W(1)–S(2)″	53.9(3)	Br(1)–W(1)–P(2)	82.0(3)	W(1)–S(2)–W(1)′	73.3(3)
W(1)″–W(1)–P(1)	100.9(3)	S(1)–W(1)–S(2)	105.6(3)	F(1)–P(3)–F(1)′	180(0)
W(1)″–W(1)–P(2)	140.0(3)	S(1)–W(1)–S(2)″	106.6(4)	F(1)–P(3)–F(2)	90(0)
W(1)′–W(1)–Br(1)	100.7(1)	S(1)–W(1)–P(1)	95.0(4)	F(1)–P(3)–F(3)	90(0)
W(1)′–W(1)–S(2)	52.9(3)	S(1)–W(1)–P(2)	164.4(4)	F(2)–P(3)–F(2)′	180(0)
W(1)′–W(1)–S(2)″	99.4(3)	S(2)–W(1)–S(2)″	97.8(4)	F(2)–P(3)–F(3)	90(0)
W(1)′–W(1)–P(1)	149.1(3)	S(2)–W(1)–P(1)	157.4(4)	F(3)–P(3)–F(3)′	180(0)
W(1)′–W(1)–P(2)	133.2(3)	S(2)–W(1)–P(2)	80.3(4)		

Numbers in parentheses are e.s.d.s in the least significant digits.

be attributed to the arrangement of the two P atoms and one Br atom in the external sites on each metal atom. The W_3 core of each cation is a nearly equilateral triangle with an average W–W distance of 2.763(2) (for **1a**) and 2.758(2) (for **1b**). Each metal atom in each cation is coordinated to one capping and two bridging sulfur atoms, one chelating dmpe ligand, and one bromine atom, which is *cis* to the capping sulfur atom. The W–(μ_2-S) distances that are *trans* to W–P bonds are significantly longer, by an average value of 0.040(9) Å (for **1a**) and 0.047(9) Å (for **1b**), than the W–(μ_2-S) distances that are *trans* to W–Br bonds. One of the W–Br distances in each cation is shorter than the average of the other two W–Br distances by 0.036(4) Å (for **1a**) and 0.017(4) Å (for **1b**). The two types of W–P distances differ by an average of 0.03(1) Å (for **1a**) and 0.08(1) Å (for **1b**) with the one *trans* to the capping sulfur being shorter.

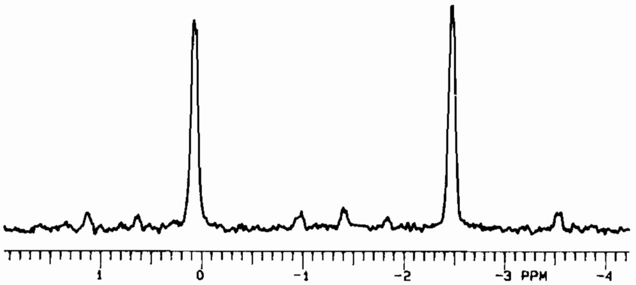


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of **1**.

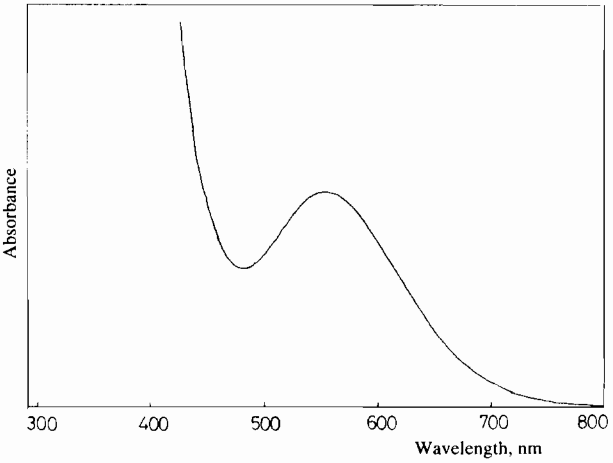


Fig. 4. UV–Vis spectrum of **1**.

Compound 2

The structure of the cation in **2** is shown in Fig. 2. Selected bond distances and angles for this compound are listed in Table 5. The cation of this compound has crystallographic C_3 symmetry and is identical within experimental error with those of **1**; the W–W distance is 2.759(2) Å. Although the W–W and W–(μ_3-S) distances are all equal due to crystallographically imposed three-fold symmetry, there are two kinds of W–(μ_2-S) distances which differ in such a way that the W–(μ_2-S) distance that is roughly *trans* to a W–P bond is longer, by 0.03 Å, than the one that is roughly *trans* to a W–Br bond. The two types of W–P distances also differ, by 0.10 Å, with the one *trans* to the capping sulfur atom being shorter.

NMR spectra

The $^{31}P\{^1H\}$ NMR spectrum of **1** is shown in Fig. 3. It is fundamentally an AA′ spectrum indicative of two non-equivalent phosphorus nuclei ($\delta = 0.060$ and -2.484 ppm). Tungsten satellites caused by ^{183}W nuclei

TABLE 6. Comparison of bond distances and $^{31}P\{^1H\}$ NMR data for $[M_3S_4X_3(dmpe)_3]^+$ complexes[a]

Compound	Type of bond (Å)				*J* Value (Hz)		Reference
	M–M	M–μ_3S	M–μ_2S	M–P	^1J(P–M)	^2J(P–P)	
$[W_3S_4Br_3(dmpe)_3]Br$ (**1**)	2.763(2) 2.758(2)	2.379(8) 2.346(9)	2.291(9) 2.318(10)	2.558(9) 2.556(10)	171.4 172.6		this work
$[W_3S_4Br_3(dmpe)_3][PF_6]$ (**2**)	2.759(2)	2.37(1)	2.31(1)	2.56(1)			this work
$[W_3S_4Cl_3(dmpe)_3]PF_6 \cdot H_2O$ (**3**)	2.755(1)	2.382(5)	2.308(4)	2.569(8)	171.66 174.48	2.7	10b
$[Mo_3S_4Cl_3(dmpe)_3]Cl \cdot 2CH_3OH$ (**4**)	2.774(2) 2.771(2)	2.353(6) 2.350(6)	2.304(6) 2.314(6)	2.565(6) 2.562(6)		5.6	12
$[Mo_3S_4Cl_3(dmpe)_3]PF_6 \cdot CH_3OH$ (**5**)	2.766(4)	2.360(9)	2.313(7)	2.557(3)			10b
$[W_3S_4H_3(dmpe)_3]]BPh_4]$ (**6**)	2.751(0)	2.353(5)	2.335(5)	2.499(5)	113.90 184.20		10b

[a]Two different values in each column indicate that there are two independent trinuclear clusters in the asymmetric unit.

(nuclear spin = 1/2; *c.* 14% natural abundance) are also observed. The ^1J(P–W) values are 171.4 and 172.6 Hz. No P–P coupling is observed in the spectrum, due to the fact that the linewidths in the spectrum are greater than the expected coupling constant. It might be detectable under high magnetic field (400 MHz), but we have not pursued this.

The UV–Vis spectrum of **1**, Fig. 4, shows a band at 560 nm, and is very typical for compounds of this type.

Discussion

The work reported here shows that WBr_5 is a satisfactory and convenient starting material for the preparation of $W_3S_4^{4+}$ compounds. Reducing agents such as $NaBH_4$ (or $NaB(C_2H_5)_3H$) were used and the workup procedures were similar to those previously reported from this laboratory.

The compounds reported are not unusual, nor are their structures, which belong to the M_3X_{13} family [18]. Compound **1** is very similar to its molybdenum analog, $[Mo_3S_4Cl_3(dmpe)_3]Cl \cdot 2CH_3OH$ (**4**). However, **1** and **4** are not crystallographically isomorphous. Crystals of **4** contain interstitial methanol molecules, whereas those of **1** contain no solvent of crystallization. Compounds **2** and **3** are very similar to each other but they are not crystallographically isomorphous. Crystals of compound **3** contain interstitial water molecules, whereas those of **2** contain no solvent of crystallization. It is not known whether this inclusion of solvent is the cause of, or is caused by, the difference in the overall crystal structures.

In Table 6, we compare the important bond distances and $^{31}P\{^1H\}$ NMR data in the present compound with those previously reported for other compounds containing dmpe ligand. It is clear that the four principal types of distances in all complexes listed in this Table are substantially the same except that the M–P distance in **6** is approximately 0.05 Å shorter than that in all other complexes. From Table 6, it is seen that the change from Cl to Br has only a small effect on the ^1J(P–W) values while the substitution of three Cl or three Br ligands by three H ligands markedly affects this value; the ^2J(P–P) coupling constant is observed only in chloro complexes.

Supplementary material

Full listing of bond distances and angles, anisotropic displacement parameters for **1** and **2** (12 pages), and observed and calculated structure factors for **1** and **2** (30 pages) are available from author F.A.C.

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