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Synthesis and Crystal Structure of $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$

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Abstract

The thiohalide complex of tungsten $(Et_4N)_2W_2S_4Br_4$ interacts with PPh_3 to produce the $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$ complex (I). The crystals of I are triclinic, space group $P\bar{1}$ ($a = 10.573(2)$, $b = 14.054(3)$, $c = 16.751(4)$ Å, $\alpha = 111.10(2)$, $\beta = 90.24(1)$, $\gamma = 110.01(1)°$, $Z = 2$). A total of 1623 independent observed reflections have been obtained on an automated diffractometer and the structure was refined to $R = 0.0734$. Complex I has a *syn*-$[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment. The bromine atoms are in a *trans* position. The W–W distance is 2.813(3) Å and the $W{=}S_t$ distance is 2.10(1) and 2.115(9) Å.

Introduction

It is typical for the early transition metals to form high-valence clusters, in particular, cluster chalcohalide complexes [1]. Nevertheless, cluster chalcohalide complexes of tungsten have received very little attention. So far only the following complexes have been obtained and structurally characterized: $WS_2Br_3(SeBr_2)$ [2], $W_2S_3Br_8^{2-}$ [3], $W_2S_4Br_8^{2-}$ [4], $W_2S_4Cl_2(py)_4$ [5], $W_2Se_3Cl_8^{2-}$ [6]. In a previous study [7] we reported obtaining the binuclear thiohalide complexes $(Et_4N)_2W_2S_4X_4$ by treating $(Et_4N_2)WS_4$ with HX (X = Cl, Br) in methylene chloride. In our opinion, such complexes may turn out to be convenient starting materials for the synthesis of various derivatives involving the binuclear $[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment. In the present work we have studied the interaction of $(Et_4N)_2W_2S_4Br_4$ with PPh_3 and obtained the binuclear thiobrominephosphine complex $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$ (I).

Experimental

The synthesis was carried out in the standard Schlenk apparatus under argon. Acetonitrile was distilled over P_4O_{10}, benzene over sodium metal. $(Et_4N)_2W_2S_4Br_4$ was obtained as described in ref. 7. The IR spectrum was obtained on an IFS-113 Fourier spectrometer (Bruker).

Preparation of $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$ (I)

To a suspension of $(Et_4N)_2W_2S_4Br_4$ (0.30 g, 3.27 mmol) in CH_3CN (20 ml) a solution of PPh_3 (0.17 g, 6.50 mmol) in CH_3CN (10 ml) was added dropwise with stirring. The resulting solution deposited a solid whose recrystallization from benzene/pentane mixture afforded complex I in 40% yield (0.16 g).

Anal. Calc. for $C_{42}H_{36}Br_2P_2S_4W_2$: C, 40.09; H, 2.88; Br, 12.70; S, 10.19; W, 29.22. Found: C, 39.67; H, 2.94; Br, 13.10; S, 10.03; W, 29.41%.

X-ray Diffraction Analysis

Crystals suitable for X-ray diffraction analysis were obtained by diffusing pentane vapors into a benzene solution of the complex. The crystallographic data for I are given in Table 1. The structure

TABLE 1. Crystallographic data for $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$ (I)

Formula	$C_{42}H_{36}Br_2P_2S_4W_2$
Formula weight	1258.48
Space group	$P\bar{1}$
a (Å)	10.573(2)
b (Å)	14.054(3)
c (Å)	16.751(4)
α (°)	111.10(2)
β (°)	90.24(1)
γ (°)	110.01(1)
Z	2
D_{calc} (Mg m^{-3})	1.934
Crystal dimensions (mm)	0.02 × 0.02 × 0.25
Data collection instrument	Syntex P2$_1$
μ(Cu Kα) (cm^{-1})	233.8
Radiation	Cu Kα (λ = 1.54718 Å)
Monochromator	graphite
Reflections measured	2034
Observed independent reflections	1623
Date collection method	$\theta/2\theta$
2θ range (°)	$3 < 2\theta < 70$
R_F	0.0734

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TABLE 2. Position parameters ($\times 10^4$) and equivalent temperature parameters[a] ($Å^2 \times 10^3$) for $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$

Atom	x	y	z	U ($Å^2$)
W(1)	4472(2)	1541(2)	7482(1)	37(1)
W(2)	4885(2)	2409(2)	6189(1)	38(1)
Br(1)	5985(5)	2360(4)	8916(3)	62(2)
Br(2)	4456(5)	4113(4)	6286(4)	76(3)
S(1)	3066(11)	2186(9)	6983(7)	55(5)
S(2)	6511(11)	2346(9)	7026(7)	51(5)
S(3)	3922(12)	−162(9)	6854(7)	62(5)
S(4)	4190(11)	1049(8)	4994(7)	42(5)
P(1)	2671(11)	1276(9)	8486(7)	42(5)
P(2)	6899(11)	3338(9)	5528(8)	49(5)
C(111)	2941(37)	2467(50)	9467(41)	68(31)
C(112)	3296(43)	2480(51)	10323(45)	33(24)
C(113)	3435(42)	3396(61)	11021(35)	29(23)
C(114)	3593(65)	4404(52)	10935(45)	100(37)
C(115)	3300(52)	4379(66)	10096(58)	145(44)
C(116)	3015(50)	3384(47)	9356(40)	69(28)
C(121)	1024(47)	957(46)	7990(43)	24(24)
C(122)	380(68)	47(49)	7172(41)	45(27)
C(123)	−920(92)	−248(51)	6855(37)	77(30)
C(124)	−1823(56)	165(65)	7181(60)	80(36)
C(125)	−1156(75)	1116(49)	8025(42)	46(26)
C(126)	42(81)	1377(49)	8381(32)	91(29)
C(131)	2635(62)	137(31)	8881(23)	8(19)
C(132)	3586(73)	−149(66)	8994(43)	221(50)
C(133)	3382(77)	−907(53)	9359(31)	122(35)
C(134)	1972(99)	−1321(43)	9611(37)	101(38)
C(135)	1029(62)	−906(73)	9458(52)	125(43)
C(136)	1326(93)	−222(61)	9073(34)	131(43)
C(211)	7690(44)	4861(49)	6107(40)	60(29)
C(212)	8282(45)	5110(49)	6953(42)	35(24)
C(213)	8854(46)	6187(56)	7488(40)	78(28)
C(214)	8952(41)	7096(43)	7159(34)	24(22)
C(215)	8548(73)	6643(62)	6340(61)	98(43)
C(216)	7907(44)	5647(55)	5769(34)	36(26)
C(221)	6635(80)	3211(29)	4398(27)	24(24)
C(222)	5358(56)	3030(34)	4033(38)	30(22)
C(223)	5018(52)	2935(38)	3192(38)	64(26)
C(224)	6213(99)	3015(70)	2928(99)	376(99)
C(225)	7351(99)	3113(55)	2935(38)	175(50)
C(226)	7637(50)	3272(36)	3861(51)	107(38)
C(231)	8498(94)	3030(50)	5620(33)	98(43)
C(232)	7868(54)	1991(71)	5230(28)	122(38)
C(233)	8496(70)	1382(62)	5160(33)	98(34)
C(234)	73(94)	1721(40)	5388(31)	139(38)
C(235)	10801(54)	2920(86)	5612(42)	247(53)
C(236)	9842(65)	3525(51)	5860(36)	46(27)
C(1s)	10934(52)	5749(43)	9175(32)	90
C(2s)	9747(53)	4740(41)	8864(32)	90
C(3s)	9975(52)	3928(43)	8211(32)	90
C(4s)	11156(54)	4088(42)	7802(34)	90
C(5s)	12274(56)	4860(42)	8182(32)	90
C(6s)	11922(54)	5663(43)	8781(33)	90

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

was solved by direct method using the SHELX 86 program [8] and refined by blocked full-matrix least-squares method with unit weight scheme. Absorption corrections have been made using the DIFABS program [9]. The H atoms were calculated analytically and included into the refinement with a fixed U_{iso} of 0.1 Å. The isotropic thermal parameters of the solvate benzene molecule hydrogens were fixed at

TABLE 3. Bond distances (Å) and angles (°) in $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$

Bond distances (Å)			
W(1)–W(2)	2.813(3)	W(1)–Br(1)	2.524(5)
W(1)–S(1)	2.28(1)	W(1)–S(2)	2.34(1)
W(1)–S(3)	2.10(1)	W(1)–P(1)	2.57(1)
W(2)–Br(2)	2.537(7)	W(2)–S(1)	2.34(1)
W(2)–S(2)	2.26(1)	W(2)–S(4)	2.115(9)
W(2)–P(2)	2.57(1)		
Bond angles (°)			
W(2)–W(1)–Br(1)	125.1(2)	W(2)–W(1)–S(1)	53.5(3)
W(2)–W(1)–S(2)	51.0(3)	W(2)–W(1)–S(3)	106.8(4)
W(2)–W(1)–P(1)	135.3(3)	Br(1)–W(1)–S(1)	129.7(3)
Br(1)–W(1)–S(2)	82.5(3)	Br(1)–W(1)–S(3)	114.0(4)
Br(1)–W(1)–P(1)	79.8(3)	S(1)–W(1)–S(2)	101.3(5)
S(1)–W(1)–S(3)	112.7(4)	S(1)–W(1)–P(1)	81.8(4)
S(2)–W(1)–S(3)	106.4(4)	S(2)–W(1)–P(1)	159.0(3)
S(3)–W(1)–P(1)	91.1(4)	W(1)–W(2)–Br(2)	124.1(2)
W(1)–W(2)–S(1)	51.5(4)	W(1)–W(2)–S(2)	53.6(3)
W(1)–W(2)–S(4)	106.2(4)	W(1)–W(2)–P(2)	137.8(3)
Br(2)–W(2)–S(1)	82.8(4)	Br(2)–W(2)–S(2)	126.3(3)
Br(2)–W(2)–S(4)	116.9(4)	Br(2)–W(2)–P(2)	78.4(3)
S(1)–W(2)–S(2)	101.9(4)	S(1)–W(2)–S(4)	105.4(4)
S(1)–W(2)–P(2)	160.1(4)	S(2)–W(2)–S(4)	113.2(5)
S(2)–W(2)–P(2)	84.2(4)	S(4)–W(2)–P(2)	89.2(4)
W(1)–S(1)–W(2)	75.1(4)	W(1)–S(2)–W(2)	75.4(3)

the level 0.09 Å^2. All computations were performed on an EC 1061 computer using a set of YANX programs [10]. In the final analysis, refinement of positional and thermal parameters of all atoms gave an R_{aniso} of 0.0734.

The atomic coordinates are given in Table 2 and the interatomic distances and valence angles in Table 3.

Results and Discussion

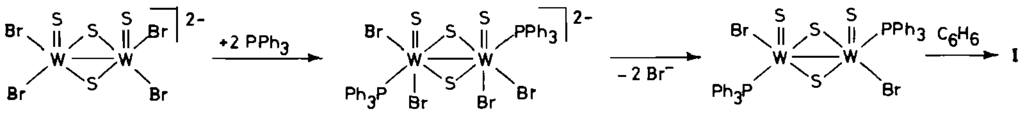
Synthesis

The $(Et_4N)_2W_2S_4Br_4$ complex is slightly soluble in acetonitrile. Addition of two equivalents of PPh_3 to a suspension of this complex in CH_3CN causes formation of a brown solution which on standing, deposits a brown solid of the $W_2S_4Br_2(PPh_3)_2$ complex (**Ia**) (We were not able to isolate this complex in an analytically pure form.) Recrystallization of **Ia** from benzene affords red crystals of $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$ solvate (**I**) (Scheme 1). It can be suggested that, as a first stage of the reaction, complex **II** forms in solution as a result of addition of two equivalents of PPh_3 and then there takes place elimination of Br^- anions to produce a precipitate of molecular complex **Ia**.

Complex **I** is a red air-stable crystalline substance. It is readily soluble in benzene, less so in toluene and not soluble in most of the other organic solvents.

In the IR spectrum there is a band of medium intensity at 224 cm^{-1} which should be assigned to essentially valence vibrations of W–Br. The ν(W=S) and $\delta(W_2S_2)$ vibration bands are superimposed by strong PPh_3 vibration bands.

In our opinion, additions of nucleophiles or nucleophilic substitutions in the $W_2S_4X_4{}^{2-}$ com-



II

Ia

green crystals of the Et_4N^+ salt, poorly soluble in CH_3CN

a proposed structure of the product of nucleophilic addition

brown precipitate in CH_3CN, well soluble in C_6H_6

red crystals

Scheme 1. The interaction of $(Et_4N)_2W_2S_4Br_4$ with PPh_3.

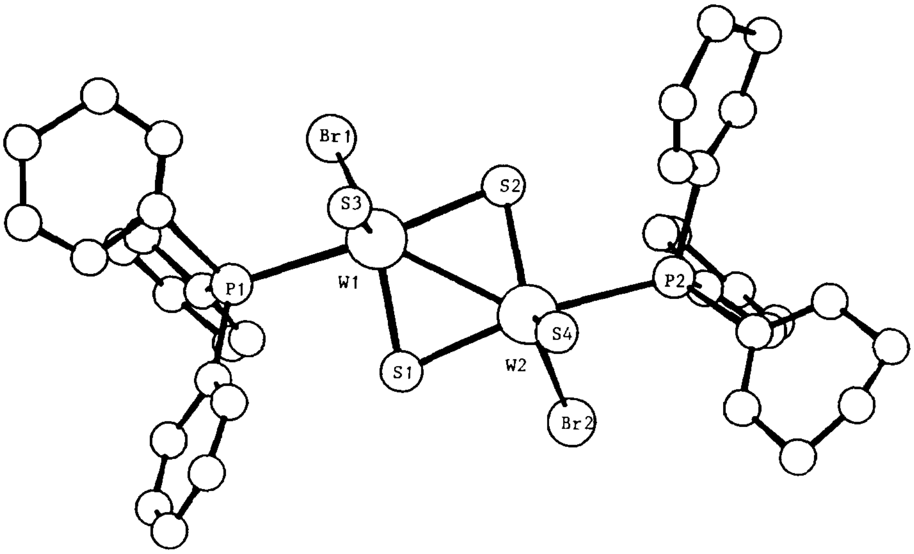


Fig. 1. The structure of $W_2S_4Br_2(PPh_3)_2$.

plexes (X = Cl, Br) may be one of the routes to various complexes having a $[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment.

At the present time, the following complexes containing an analogous fragment, $W_2S_4^{2+}$, have been obtained and structurally characterized: $W_2S_{12}^{2-}$ [11], $W_4S_{12}^{2-}$ [12], $W_2S_4[S_2P(OEt)_2]_2$ [13], $W_2S_4(S_2CNEt_2)_2$ [13], $W_2S_4(SCH_2CH_2S)_2^{2-}$ [14] and $W_2S_4Cl_2(py)_4$ [5]. To synthesize these compounds the following reactions are used: (a) interaction of O–H or S–H acids and WS_4^{2-} [12, 14]; (b) thermolysis of WS_4^{2-} in DMF in the presence of S_8 [11]; (c) interaction of WS_2Cl_2 with different nucleophiles [13]; (d) interaction of WS_4^{2-} or $W(CO)_6$ with $(Et_2NCS_2)_2$ [13, 15]; (e) interaction of $(Et_2NH_2)_2WS_4$ and CS_2 [15]. All these reactions involve a change in the oxidation state of the tungsten atoms. On the contrary, in the reaction of $W_2S_4Br_4^{2-}$ with PPh_3 studied by us the nucleophilic substitution is not accompanied by oxidation–reduction.

Structure

The structure of I is a molecular one. There are $W_2S_4Br_2(PPh_3)_2$ molecules and benzene molecules in the crystal. The structure of the $W_2S_4Br_2(PPh_3)_2$ molecule is shown in Fig. 1. Figure 2 shows the unit cell of I. The $W_2S_4^{2+}$ tungsten fragment in the $W_2S_4Br_2(PPh_3)_2$ molecule are coordinated by two terminal bromine atoms in a *trans* position and two phosphors of the PPh_3 ligands, also in a *trans*-position. Idealized coordination polyhedra of the two tungsten atoms (without the W–W bond) represent square pyramids with the vertices occupied by sulphur atoms in mutually *syn*-positions. In the literature there have been reports of a series of binuclear complexes of tungsten having a *syn*-$[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment [5, 11–14]. Among them there is only one example of a $W_2S_4Cl_2(py)_4$ complex [5], which has an octahedral environment of its tungsten atoms. In the other known complexes, as in complex I, the tungsten atoms have a square-pyramidal environment [11–14]. No complexes containing an *anti*-$[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment are known although there have been reports of $[(S)Mo(\mu_2\text{-}S)_2\text{-}Mo(S)]^{2+}$ complexes [16]. Table 4 shows comparative geometrical characteristics of *syn*-$[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ complexes having a square-pyramidal environment of the tungsten atoms. As can be easily seen from the Table, the structure of I is rather typical of this type of compound. The main characteristics of the *syn*-$W_2S_4^{2+}$ fragment are little changed from compound to compound, being practically independent of the type of ligand and the overall charge of the complex.

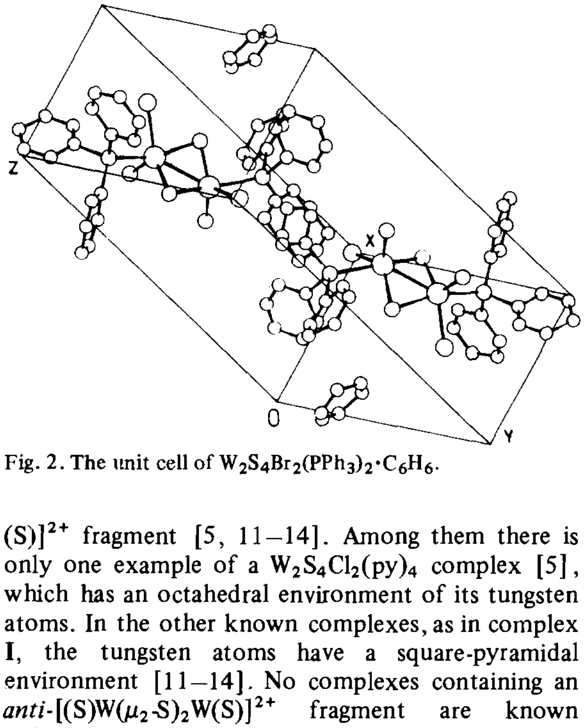


Fig. 2. The unit cell of $W_2S_4Br_2(PPh_3)_2 \cdot C_6H_6$.

TABLE 4. The main geometrical parameters of the *syn*-$[(S)W(\mu_2\text{-}S)_2W(S)]^{2+}$ fragment of binuclear complexes with a square-pyramidal environment of tungsten atoms

Complex	W–W (Å)	W–S_t (Å)	W–S_{br} (Å)	WS_{br}–W–S_{br}	WW–S_{br}–W (°)	α (°)[a]	*h* (Å)[b]	Reference
$(PPh_4)_2W_2S_4(S_2C_2H_4)_2$	2.862	2.14	2.33	100.7	75.9	148.9	0.72	14
$(PPh_4)_2W_4S_{12}$	2.918	2.09	2.33	98.7	77.2	147.5	0.65	12
$W_2S_4[S_2P(OEt)_2]_2$	2.816	2.09	2.39	101.9	75.2	151.8	0.72	13
$W_2S_4(S_2NCEt_2)_2$	2.795	2.09	2.38	101.9	74.5	149.3	0.73	13
$(Et_4N)_2W_2S_{12}$	2.836	2.12	2.32	100.1	75.3	144.3	0.71	11
$W_2S_4Br_2(PPh_3)_2$	2.813	2.11	2.29	101.6	75.3	149.7	0.68	this work

[a] Angle between the $W(S_{br})_2$ planes. [b] The distance between the tungsten atoms and the bases of the square pyramids.

We think, however, that it would be more correct to represent the environment of the tungstens as trigonal bipyramids with the W(1), Br(1), S(1), S(3) and W(2), Br(2), S(2), S(4) atoms in the equatorial planes (deviations from the least-squares planes do not exceed 0.06 Å, the BrWS and SWS valence angles are in the range 120 ± 6.5°). The P(1), S(2) and P(2), S(1) atoms occupy the axial sites (deviations from the equatorial planes are by 2.354, 2.459 and 2.36, 2.468 Å, respectively, the P(1)W(1)S(2) and P(2)W(2)S(1) valence angles are 159.0(3) and 160.1(4)°. The equatorial planes of the two bipyramids are practically parallel (the angle between them is 4.1°).

No appreciable non-valence contacts have been found in the structure of **I**.

Supplementary Material

Thermal parameters are available from the authors on request.

References

1 V. E. Fedorov, A. V. Mischenko and V. P. Fedin, *Uspekhi Khimii, 54* (1985) 694 (in Russian).
2 S. V. Volkov, V. A. Kolesnichenko and N. I. Timoschenko, *J. Coord. Chem., Sect. A, 17* (1988) 367.
3 P. Klingelhöfer and U. Müller, *Z. Anorg. Allg. Chem., 542* (1986) 7.
4 A. V. Virovets, *Mater. Vses. Nauchn. Stud. Conf. Khim.*, (1988) 33 (in Russian).
5 M. G. B. Drew, R. J. Hobson, D. A. Rice and N. Turp, *J. Chem. Soc., Dalton Trans.*, (1986) 2165.
6 M. G. B. Drew, G. W. A. Fowles, E. M. Page and D. A. Rice, *J. Am. Chem. Soc., 101* (1979) 5827.
7 V. P. Fedin, Yu. V. Mironov, M. N. Sokolov, Yu. I. Mironov and V. E. Fedorov, *Inorg. Chim. Acta, 163* (1989) 55.
8 G. M. Sheldrick in G. M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, London, 1985.
9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
10 R. G. Gerr, A. I. Yanovskii and Yu. T. Strutchkov, *Kristallogr., 28* (1983) 1029 (in Russian).
11 S. A. Cohen and E. I. Stiefel, *Inorg. Chem., 24* (1985) 4657.
12 F. Secheresse, J. Lefevre, J. C. Daran and Y. Jeannin, *Inorg. Chem., 21* (1982) 1311.
13 M. G. B. Drew, R. H. Hobson, P. P. E. M. Mumba, D. A. Rice and N. Turp, *J. Chem. Soc., Dalton Trans.*, (1987) 1163.
14 W.-H. Pan, T. Chandler, J. H. Enemark and E. I. Stiefel, *Inorg. Chem., 23* (1984) 4265.
15 M. A. Ansari, J. Chandrasekaran and S. Sarkar, *Bull. Chem. Soc. Jpn., 61* (1988) 2265.
16 G. Bunzey and J. H. Enemark, *Inorg. Chem., 17* (1978) 682.