Evidence of the $W(O)(S_2)_2$ core as an intermediate in the acidification of WS_4^{2-}. Structural characterization of $W(O)(S_2)_2(bpy)$ and $W(O)(S_2)_2(phen)$

Corine Simonnet-Jegat, Nathalie Jourdan, Francis Robert and Claudette Bois
Laboratoire de Chimie des Métaux de transition, URA 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05 (France)

Francis Sécheresse*
Laboratoire d'Electrochimie et Chimie de Solides Inorganiques (LECSI), Université de Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex (France)

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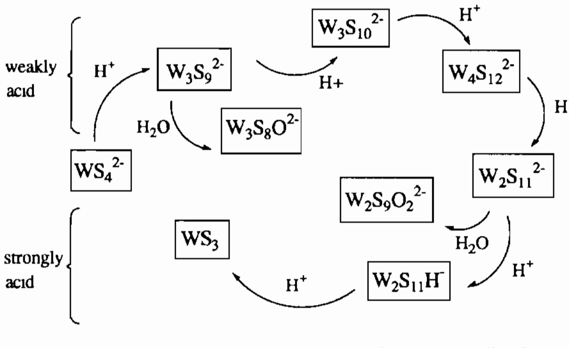
Abstract

Acidification of WS_4^{2-} by HCl in MeCN in the presence of 2,2′-bipyridine (bpy) led to the discrete mononuclear compound $W(O)(S_2)_2(bpy)$ (**1**) isolated at room temperature as crystals: monoclinic, space group *C*2/*c*, $a = 25.670(8)$, $b = 8.472(3)$, $c = 12.466(4)$ Å, $\beta = 106.26(3)°$, $V = 2603$ Å^3, $Z = 8$, $R = 0.061$. $W(O)(S_2)_2(bpy)$ (**2**) was obtained by reaction of $[Ni(bpy)_2]Cl_2$ with WS_4^{2-}, followed by crystallization at −30 °C, monoclinic, space group $P2_1/n$, $a = 8.875(7)$, $b = 12.205(6)$, $c = 12.363(3)$ Å, $\beta = 90.12(5)°$, $V = 1339(1)$ Å^3, $Z = 4$, $R = 0.062$. Compounds **1** and **2** differ in their stackings. The alignment of the bpy ligands in **1** is parallel; in **2** the alignment is nearly perpendicular. Addition of 1,10-phenanthroline (phen) under the same conditions of acidity yielded $W(O)(S_2)_2(phen)$ (**3**) isolated at room temperature as crystals· monoclinic, $P2_1$, $a = 6.798(4)$, $b = 14.807(5)$, $c = 7.048(2)$ Å, $\beta = 92.25(3)°$, $V = 709$ Å^3, $Z = 2$. The three complexes can all be described as a W-pentagonal bipyramid, with four sulfur atoms and a nitrogen atom forming the equatorial plane, the two axial positions being occupied by the remaining nitrogen atom of the bpy ligand and an oxo group. Formation of the $W(O)(S_2)_2$ core in solution is postulated through a redox process involving elemental sulfur produced *in situ*.

Key words: Crystal structures; Tungsten complexes; Chalcogenide complexes

Introduction

The trichalchogenides MS_3 (M = Mo, W) are amorphous materials which have been widely studied for their potential uses as precursors in catalysis [1] or as the cathode in lithium cells [2]. Two modes of preparation are known [3], based on thermal or solution techniques. Acidification of WS_4^{2-} in aqueous solution represents a facile source of amorphous trisulfide WS_3, but the reaction rate of protonation is too fast to allow the characterization of intermediate species essential to understand the mechanism of the formation of WS_3. In non-aqueous media, such as acetonitrile, dichloromethane and dimethylformamide, a limited set of soluble complexes was isolated, which can be considered as intermediates between the starting material WS_4^{2-} and the final insoluble WS_3. Scheme 1 gives a summary of the compounds unambiguously structurally characterized and their possible connections to each other.



Scheme 1. Scheme giving the compounds structurally characterized in the acidification of WS_4^{2-}, and their possible connections.

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*Author to whom correspondence should be addressed Present address. Laboratoire de Chimie des Métaux de Transition, URA 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

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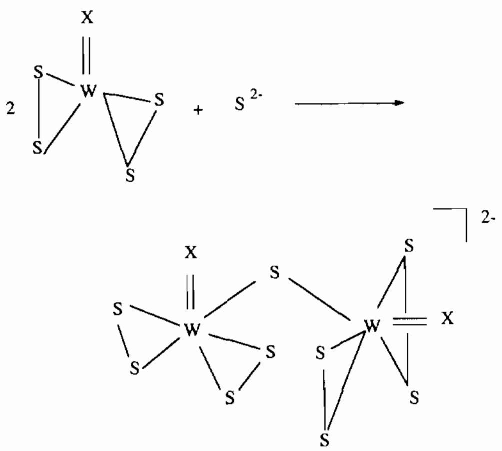


Scheme 2 Scheme illustrating the possible dimerization of $W(X)(S_2)_2$ fragment into $W_2S_9X_2^{2-}$.

Compounds isolated in a weakly acid medium contain a reduced tungsten atom, W(IV) in $W_3S_9^{2-}$ [4], $W_3S_8O_2^{2-}$ [5] and $W_3S_{10}^{2-}$ [6], W(II) in $W_3S_8^{2-}$ [7], or two reduced W(V) as in $W_4S_{12}^{2-}$ [8].

In more acidic medium, sulfur ligands were shown to be oxidized as disulfido groups as reported for $W_2S_{11}^{2-}$ [9], $W_2S_{11}H^-$ [10] and $W_2S_9O_2^{2-}$ [11]. The latter compounds can be formally described as the products of dimerization of the $[W(X)(S_2)_2$, X=O, S] fragment, through a bridging sulfide as represented in Scheme 2.

The present work shows that addition of 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) to a solution of WS_4^{2-} previously acidified by HCl results in the formation of the discrete mononuclear complexes $W(O)(S_2)_2$(bpy) and $W(O)(S_2)_2$(phen) containing the $W(X)(S_2)_2$ fragment already observed in $W_2S_9O_2^{2-}$ [11]. We have confirmed that the bidentate bpy ligand prevents the dimerization of the postulated intermediate core $W(X)(S_2)_2$ to $W_2S_9X_2^{2-}$, X=O, S.

A recent paper [12] reported that $W(O)(S_2)_2$(bpy) (**4**) could also be isolated from a mixture of WO_4^{2-}, polysulfides and 2,2′-bipyridine.

In addition to the comparison of our compounds with the previously reported analogue **4**, we have found that $W(O)(S_2)_2$(bpy) could be isolated in the solid state with two different stacking arrangements, namely **1** and **2**.

Experimental

All reactions were carried out under a nitrogen atmosphere. Chemicals were used as received from Aldrich; acetonitrile was dried on 4 Å molecular sieves. Elemental analyses were performed by the Laboratoire Central d'Analyses du CNRS, Solaize, France. IR spectra of the samples as KBr pellets were obtained on a FTIR Nicolet 550 spectrophotometer. Electronic spectra were recorded on a Shimadzu 2101 spectrophotometer.

Preparations

$W(O)(S_2)_2$(bpy) (1)

To a solution of $[NEt_4]_2[WS_4]$ (0.0572 g, 0.1 mmol) in 10 ml of CH_3CN was added HCl (0.1 mmol) previously dissolved in CH_3CN. The yellow solution turned rapidly from orange to brown. After stirring for 30 min, bipyridine (0.031 g, 0.2 mmol) was added, and the mixture was filtered. Storage of the solution several days at room temperature yielded red–black crystals of $W(O)(S_2)_2$(bpy) which were washed with Et_2O (yield 10%). *Anal.* Found: C, 25.07; H, 1.68; N, 5.77; S, 26.10; W, 38.86. Calc.: C, 24.8; H, 1.65; N, 5.78; S, 26.44; W, 38.01%.

IR (KBr pellets): 3105(w), 3063(vw), 3028(vw), 1600(s), 1492(m), 1471(m), 1436(s), 1420(sh), 1315(m), 1220(vw), 1240(vw), 1154(m), 1103(w), 1074(vw), 1061(vw), 1031(w), 936(vs), 766(s), 728(m), 660(vw), 649(w), 639(w), 529(m), 478(vw), 419(w), 366(vw), 339(w), 319(w).

$W(O)(S_2)_2$(bpy) (2)

A suspension of $[NEt_4]_2[WS_4]$ (0.097 g, 0.17 mmol) and $[Ni(bpy)_2]Cl_2$ (0.075 g, 0.17 mmol) in a mixture of 20 ml of toluene and 10 ml of CH_3CN was refluxed with stirring for 4 h. After cooling to room temperature, the brown suspension was filtered and the solution was concentrated to *c.* 15 ml. Storage for 3 weeks at −30 °C afforded red–black crystals of $W(O)(S_2)_2$(bpy) which were washed with Et_2O.

$W(O)(S_2)_2$(phen) (3)

To a suspension of $[NEt_4]_2[WS_4]$ (0.057 g, 0.1 mmol) in 10 ml of CH_3CN was added 1 ml of HCl 0.1 M in acetonitrile. After stirring for 30 min, 1,10-phenanthroline (0.036 g, 0.2 mmol) was added, and the solution was stored at room temperature for several days. Red–black crystals of $W(O)(S_2)$phen (**3**) were deposited together with an unidentified orange precipitate.

IR (KBr pellets): 3078(vw), 3056(vw), 1630(m), 1604(m), 1579(m), 1515(s), 1490(w), 1423(vs), 1342(vw), 1317(vw), 1307(vw), 1252(vw), 1221(w), 1204(vw), 1148(m), 1106(w), 1094(vw), 1053(vw), 941(vs), 911(w), 873(w), 843(s), 767(w), 741(w), 714(s), 652(m); 605(vw), 535(m), 505(w), 454(vw), 447(w), 432(w), 344(m), 320(m).

The three compounds were identified by complete structure determinations and spectroscopy.

Crystal structure determinations

Crystals were mounted on an Enraf-Nonius CAD-4 automatic four-circle diffractometer, and data were collected via the $\theta/2\theta$ scan method, at 20 °C. Unit-cell parameters for both compounds were obtained from least-squares refinement of 25 reflections. Corrections for polarization and Lorentz effects were applied. Data for both crystals were corrected for absorption [13]. The three structures were solved by direct methods using the SHELX86 program [14] and subsequent Fourier syntheses. Hydrogen atoms were located on difference electron density maps and their positions were refined. They were given fixed isotropic thermal parameters.

In structures **1** and **2** the non-hydrogen atoms were refined anisotropically, and for structure **3** they were refined isotropically. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\Sigma\omega(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in $\omega=\omega'[1-(\Delta F/6\sigma(F)^2]^2$ with $\omega'=1/\Sigma_1{}^n ArTr(X)$ where n ($n=3$) is the number of coefficients, Ar, for a Chebyshev series, for which X is $F_c/F_c(\max)$ [15]. The model reached convergence with $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ and $R_w=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega(F_o)^2]^{1/2}$ having values of 0.062 ($R_w=0.063$) for **1**, and 0.061 ($R_w=0.063$) for **2**. Criteria for a satisfactory complete analysis were the ratios of r.m.s. shift to standard deviation being less than 0.1 and no significant features in the final difference map. Crystal parameters and details of the data collection are given in Table 1. Atomic coordinates are given in Tables 2 and 3. Comparative dimensions in the tungsten coordination sphere are given in Table 4.

Results and discussion

Molecular structure of $W(O)(S_2)_2(bpy)$

Complexes are, within error, similar in their molecular arrangements as confirmed by the selected bond distances and angles given in Table 4. ORTEP drawings of $W(O)(S_2)_2(bpy)$ and $W(O)(S_2)_2(phen)$ are given in Figs. 1 and 2. The overall molecular arrangement is described as a pentagonal bipyramid centred on a heptacoordinated tungsten atom. The five equatorial positions are occupied by the two persulfide ligands S(1)–S(4), S(2)–S(3), and the N(1) atom of the bipyridine (or phen). An oxo group and the remaining N(2) atom of the bipyridine (or phen) are located in the axial positions of the bipyramid. In both compounds **1** and **2** the W–N(2) bonds *trans* to the oxo group are longer than the equatorial W–N(1) lengths, and the tungsten atom is located above the S(1)S(2)S(3)S(4)N(1) plane, by 0.35, 0.33 and 0.31 Å for **1**, **2** and **3**, respectively. The W–S lengths involving the persulfide ligands show significant asymmetry as was reported earlier for similar $W(O)(S_2)_2$ fragments [9, 10, 11, 16, 17], the longest W–S distances corresponding to the *trans* S(3) and S(4) atoms. The W atom is located in the plane of the bipyridines or phenanthroline with a deviation of 0.028 Å for **1**, 0.063 Å for **2** and 0.074 Å for **3**; the angle

TABLE 1. Crystallographic data for $W(O)(S_2)_2(bpy)$ (**1** and **2**) and $W(O)(S_2)_2(phen)$ (**3**)

Formula	$W(O)(S_2)_2(bpy)$ (**1**)	$W(O)(S_2)_2(bpy)$ (**2**)	$W(O)(S_2)_2(phen)$ (**3**)
Formula weight	484	484	508 2
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1$
a (Å)	25.670(8)	8.875(7)	6.798(4)
b (Å)	8.472(3)	12 205(6)	14 807(5)
c (Å)	12 466(4)	12 363(3)	7.048(2)
β (°)	106 26(3)	90.12(5)	92 25(3)
V (Å^3)	2603(6)	1339(1)	709(1)
Z	8	4	2
D_{calc} (g cm^{-3})	2.47	2.40	2.38
Systematic absences	hkl $h+k=2n+1$, $h0l$ $h+1=2n+1$	$h0l$ $h+1=2n+1$, $0k0$ $k=2n$	$0k0$ $k=2n+1$
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Radiation (Å)	Mo Kα (0 71069)	Mo Kα (0 71069)	Mo Kα (0.71069)
Linear absorption coefficient (cm^{-1})	96 72	93.97	88.8
Scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Scan range (°)	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ
θ Limits (°)	1–25	1–25	1–25
Octants collected	−30,29; 0,10, 0,14	−10,10, 0,14; 0,14	−8,8; −17,17; 0,8
No. data collected	2577	2601	2695
No. unique data collected	2288	2355	1299
No. unique data used	1503 ($(F_o)^2>3\sigma(F_o)^2$)	1427 ($(F_o)^2>3\sigma(F_o)^2$)	641 ($(F_o)^2>3\sigma(F_o)^2$)
Decay (%)	<1	<1	<1
$R=(\|F_o-\|F_c\|\|)/\|F_o\|$	0.061	0 062	0.052
$R_w=(w(\|F_o\|-\|F_c\|)^2/wF_o{}^2)^{1/2}$	0.074	0 063	0 064

TABLE 2. Fractional atomic coordinates for W(O)$(S_2)_2$(bpy) (**1** and **2**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	U_{iso}
Compound **1**					
W(1)	−0.14092(4)	−0.2140(1)	−0.37674(9)	0.0302	
S(1)	−0.0714(3)	−0.3415(9)	−0.2422(6)	0.0480	
S(2)	−0.1039(3)	−0.3333(9)	−0.5107(6)	0.0474	
S(3)	−0.1601(3)	−0.1628(9)	−0.5758(6)	0.0462	
S(4)	−0.1104(3)	−0.1683(8)	−0.1772(5)	0.0397	
O(1)	−0.1982(9)	−0.330(2)	−0.382(2)	0.0451	
N(1)	−0.1864(9)	−0.001(3)	−0.377(2)	0.0339	
N(2)	−0.0865(9)	0.005(3)	−0.375(2)	0.0341	
C(1)	−0.239(1)	−0.012(3)	−0.376(2)	0.0377	
C(2)	−0.270(1)	0.122(4)	−0.364(2)	0.0472	
C(3)	−0.246(1)	0.265(4)	−0.356(2)	0.0465	
C(4)	−0.191(1)	0.284(4)	−0.363(2)	0.0374	
C(5)	−0.1642(9)	0.143(3)	−0.370(2)	0.0270	
C(6)	−0.1084(9)	0.148(3)	−0.371(2)	0.0234	
C(7)	−0.081(1)	0.285(4)	−0.384(2)	0.0439	
C(8)	−0.027(1)	0.273(4)	−0.394(2)	0.0457	
C(9)	−0.003(1)	0.124(3)	−0.389(2)	0.0380	
C(10)	−0.033(1)	−0.007(3)	−0.382(2)	0.0330	
H(1)	−0.2545	−0.1150	−0.4550		0.0598
H(2)	−0.2987	0.1002	−0.3813		0.0598
H(3)	−0.2617	0.4044	−0.3479		0.0598
H(4)	−0.1855	0.4118	−0.4287		0.0598
H(7)	−0.0978	0.3959	−0.3589		0.0598
H(8)	−0.0076	0.4135	−0.3848		0.0598
H(9)	0.0332	0.1012	−0.3734		0.0598
H(10)	−0.0097	−0.1115	−0.3797		0.0598
Compound **2**					
W(1)	0.43379(9)	0.08242(6)	0.24449(6)	0.0291	
S(1)	0.3655(6)	0.0797(5)	0.0600(4)	0.0453	
S(2)	0.4731(8)	−0.1062(5)	0.2231(5)	0.0523	
S(3)	0.4675(7)	−0.0541(5)	0.3827(5)	0.0452	
S(4)	0.3121(6)	0.2240(4)	0.1393(4)	0.0368	
O(1)	0.611(1)	0.132(1)	0.244(1)	0.0404	
N(1)	0.384(2)	0.189(1)	0.381(1)	0.0500	
N(2)	0.181(2)	0.053(1)	0.295(1)	0.0290	
C(1)	0.491(2)	0.256(2)	0.424(1)	0.0365	
C(2)	0.462(3)	0.325(2)	0.507(2)	0.0460	
C(3)	0.325(2)	0.326(2)	0.550(2)	0.0340	
C(4)	0.212(2)	0.261(2)	0.511(2)	0.0403	
C(5)	0.245(2)	0.192(1)	0.426(1)	0.0229	
C(6)	0.131(2)	0.117(2)	0.376(1)	0.0314	
C(7)	−0.017(2)	0.110(2)	0.409(2)	0.0537	
C(8)	−0.112(2)	0.035(2)	0.361(2)	0.0528	
C(9)	−0.057(2)	−0.023(2)	0.282(2)	0.0432	
C(10)	0.092(2)	−0.015(2)	0.245(2)	0.0257	
H(1)	0.5947	0.2474	0.3984		0.0237
H(2)	0.5273	0.3737	0.5308		0.0237
H(3)	0.3142	0.3673	0.5926		0.0237
H(4)	0.0905	0.2541	0.5316		0.0237
H(7)	−0.0491	0.1666	0.4796		0.0237
H(8)	−0.2099	0.0173	0.3590		0.0237
H(9)	−0.1304	−0.0673	0.2463		0.0237
H(10)	0.1296	−0.0550	0.1778		0.0237

between the equatorial and bpy or phen planes is 92.9, 91.7 and 90.1° for **1**, **2** and **3**, respectively. In compound **1**, oxygen was partly replaced by sulfur giving a longer W=O distance, as usually observed for such fragments. Related bond distances and angles for compound **4** are given in Table 4 [12].

Packing of W(O)$(S_2)_2$(bpy)

Figure 3 is a projection of the cell of compound **1** in the *ac* plane, showing the parallel alignment of the bpy ligands along the *a* axis.

Figure 4 is a similar projection of compound **2** in the *bc* plane illustrating that in this latter packing, the

TABLE 3. Fractional atomic coordinates for $W(O)(S_2)_2(phen)$

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
W(1)	0.3897(3)	0.0038	0.0723(2)	0.0321(5)
S(1)	0.320(2)	0.0473(9)	−0.241(2)	0.050(3)
S(2)	0.107(2)	−0.093(1)	0.026(2)	0.058(4)
S(3)	0.203(2)	−0.082(1)	0.301(2)	0.041(3)
S(4)	0.525(2)	0.126(1)	−0.096(2)	0.048(3)
O(1)	0.569(4)	−0.070(2)	0.056(4)	0.033(7)
N(1)	0.540(5)	0.059(3)	0.336(5)	0.033(9)
N(2)	0.196(6)	0.114(3)	0.183(6)	0.04(1)
C(1)	0.715(6)	0.020(5)	0.393(6)	0.05(1)
C(2)	0.802(7)	0.061(3)	0.562(7)	0.04(1)
C(3)	0.709(7)	0.135(3)	0.655(6)	0.04(1)
C(4)	0.532(6)	0.166(3)	0.597(6)	0.03(1)
C(5)	0.443(6)	0.131(3)	0.413(6)	0.03(1)
C(6)	0.270(6)	0.156(3)	0.346(6)	0.03(1)
C(7)	0.169(7)	0.233(4)	0.435(7)	0.04(1)
C(8)	−0.015(7)	0.252(3)	0.344(7)	0.04(1)
C(9)	−0.090(8)	0.212(4)	0.202(7)	0.05(1)
C(10)	0.011(6)	0.137(3)	0.112(6)	0.03(1)
C(11)	0.435(8)	0.239(4)	0.675(7)	0.05(1)
C(12)	0.270(9)	0.265(4)	0.608(9)	0.07(2)

TABLE 4 Selected bond distances and angles for compounds **1–4**

	1	**2**	**3**	**4**[a]
Bond distances (Å)				
W(1)–S(1)	2.343(8)	2.359(5)	2.33(1)	2.379(8)
W(1)–S(2)	2.367(7)	2.343(6)	2.41(2)	2.359(6)
W(1)–S(3)	2.430(7)	2.405(5)	2.45(1)	2.426(6)
W(1)–S(4)	2.421(7)	2.416(5)	2.37(1)	2.429(6)
W(1)–O(1)	1.75(2)	1.69(1)	1.65(3)	1.691(17)
W(1)–N(1)	2.15(2)	2.17(2)	2.24(3)	2.163(19)
W(1)–N(2)	2.32(2)	2.35(2)	2.26(4)	2.310(18)
S(1)–S(4)	2.07(1)	2.072(8)	2.05(2)	2.060(9)
S(2)–S(3)	2.04(1)	2.074(8)	2.03(2)	2.059(10)
Bond angles (°)				
S(1)–W(1)–S(4)	51.3(2)	51.4(2)	51.9(5)	50.7(2)
S(2)–W(1)–S(3)	50.4(3)	51.8(2)	49.3(5)	50.9(2)
N(1)–W(1)–N(2)	69.9(8)	71.9(6)	72.6(13)	71.6(7)
S(1)–W(1)–O(1)	103.4(7)	103.8(4)	104.0(10)	101.7(6)
S(2)–W(1)–O(1)	103.4(7)	102.3(6)	100.5(10)	104.9(6)
S(3)–W(1)–O(1)	97.6(7)	97.9(5)	95.9(11)	101.2(6)
S(4)–W(1)–O(1)	99.0(7)	99.0(5)	99.9(10)	95.1(6)
N(1)–W(1)–O(1)	91.1(9)	89.0(6)	89.3(13)	90.5(7)
N(2)–W(1)–O(1)	160.9(9)	160.9(6)	161.8(13)	161.9(7)

[a] From ref. 12, courtesy of R. Bhattacharyya.

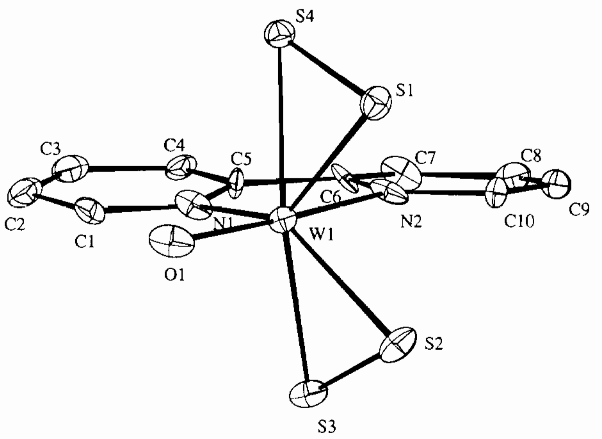


Fig 1. View of the $W(O)(S_2)_2(bpy)$ (**1**) molecule showing the atom numbering scheme

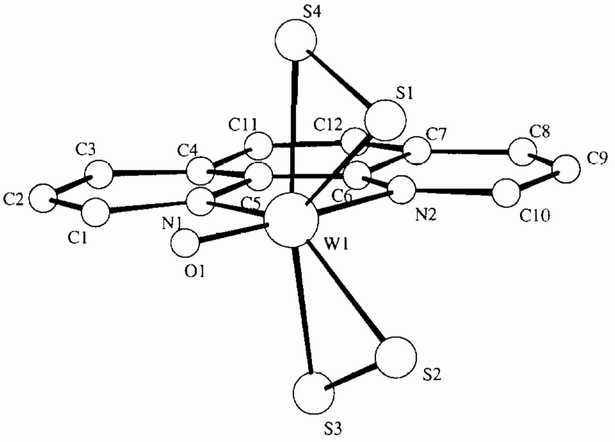


Fig. 2. View of the $W(O)(S_2)_2(phen)$ (**3**) molecule

bpy ligands of two neighbouring units are perpendicular.

Powder diffraction patterns obtained between −60 and +60 °C showed that no phase transition occurred between **1** and **2** in this temperature range.

Two different packing arrangements of the same molecular species $W(O)(S_2)_2(bpy)$ were obtained by two different chemical routes. The selectivity of the preparations clearly depends on the chemical route used, since **1** was only obtained by acidification of WS_4^{2-} in the presence of bpy, and **2** only by ligand transfer from $[Ni(bpy)_2]Cl_2$. Moreover, crystals of **1** were obtained exclusively from acidified solutions stored at room temperature; attempts to isolate crystals of **1** from acidified solutions of thiotungstate and bpy at −30 °C failed, even after 2 months of storage at low temperature The cooled solutions (10^{-2} and 5×10^{-3} mol l^{-1}) after warming up to room temperature yielded black crystals of **1** within a few days.

Addition at room temperature of $[Ni(bpy)_2]Cl_2$ to a solution of WS_4^{2-} in acetonitrile led to $[WS_4(Ni(bpy)_2)_2]Cl_2$ (IR: 1596(vs), 1492(m), 1471(m), 1441(vs), 1313(s), 1021(vs), 908(w), 772(vs), 738(vs), 654(m), 633(w), 463(vs), 439(m), 418(w), 285(m) cm^{-1}). The former suspension of tetrathiotungstate and $[Ni(bpy)_2]Cl_2$ refluxed for 4 h gave only the insoluble starting material $[Ni(bpy)_2]Cl_2$.

A suspension of $[Ni(bpy)_2]Cl_2$ and WS_4^{2-} in acetonitrile acidified by HCl led to $[W_3S_9][Ni(bpy)_2]_2$ for $x=HCl/W=1$, and to $[W_4S_{12}][Ni(bpy)_2]_2$ for $x=3$, but did not yield compound **2**.

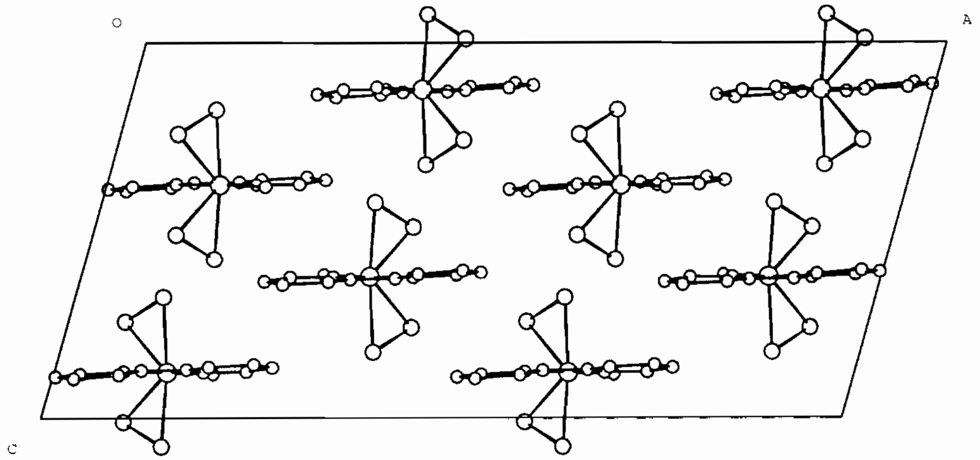


Fig. 3 Projection in the *ac* plane showing the parallel alignment of the bpy ligands in **1**

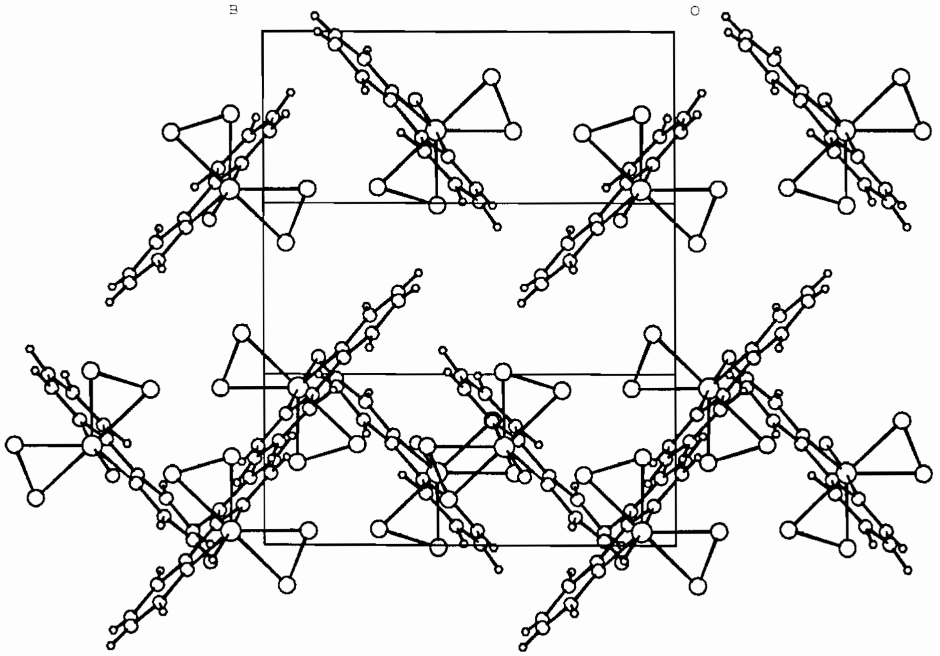


Fig. 4 Projection in the *bc* plane showing the perpendicular arrangement of the bpy ligands in **2**

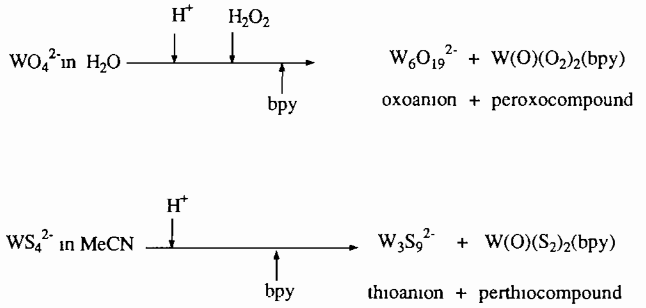
The type of packing obtained appeared to be imposed by the chemical route used without any physical or chemical possible interconversion.

Acidification of WS_4^{2-}

In a previous paper [10], we reported that the acidification of WS_4^{2-} by HCl led to the three soluble metal sulfides $W_3S_9^{2-}$, $W_4S_{12}^{2-}$ and $W_2S_{11}H^-$, depending on the degree of acidification $x = [HCl]/[WS_4^{2-}]$. In the acidic conditions of formation of **1** ($0 < x < 1$), the first electronic spectrum recorded 1 min after addition of HCl showed absorption at 395 nm characteristic of unreacted WS_4^{2-} [10]. In the presence of bpy, spectra of the acidified solution also exhibit absorption near 400 nm, and addition of Et_2O precipitated unreacted WS_4^{2-}. In the resultant red filtrate, $W_3S_9^{2-}$ was identified by spectrophotometry and by IR spectra of the red solid obtained by concentration and precipitation of the filtrate. Thus, in this acidic range, three soluble compounds WS_4^{2-}, $W_3S_9^{2-}$ and $W(O)(S_2)_2(bpy)$ coexist.

Addition of 1,10-phenanthroline instead of 2,2′-bipyridine allowed the trapping of the $W(O)(S_2)_2$ core as $W(O)(S_2)_2(phen)$, structurally similar to **1**, which confirms the role of bidentate ligands in the stabilization of the $W(O)(S_2)_2$ fragment, probably present in solution as a solvated species such as $W(O)(S_2)_2(solvent)_2$. The two molecules of solvent are easily replaced by a chelating agent.

The isolation of **1** or **2** can be compared with the preparation of peroxo homologues obtained by acidification of WO_4^{2-} in the presence of H_2O_2 and bpy



Scheme 3 Scheme illustrating the analogy in the formation of oxo- and thiotungstates by oxidizing acidification

[18]. Scheme 3 illustrates the similar pathways of the two modes of preparation. In both cases, acidification of an oxo- or thiotungstate led to the formation of an oxo- or thiopolyanion together with a peroxo- or perthio neutral compound with an analogous composition.

In contrast to the oxidation of O^{2-} anions of WO_4^{2-} by H_2O_2, oxidation of sulfides in WS_4^{2-} does not occur by addition of an external oxidizing agent, but is probably due to oxidation by the elemental sulfur produced by the reductive condensation of WS_4^{2-} to $W_3S_9^{2-}$, according to the following equations:

$$6WS_4^{2-} + 8H^+ \longrightarrow 2W_3S_9^{2-} + 4H_2S + 2S^0 \quad (1)$$

$$WS_4^{2-} + 2H^+ + 2S^0 + bpy + H_2O \longrightarrow W(O)(S_2)_2(bpy) + 2H_2S \quad (2)$$

resulting in the global equation:

$$7WS_4^{2-} + 10H^+ + H_2O + bpy \longrightarrow 2W_3S_9^{2-} + 6H_2S + W(O)(S_2)_2(bpy) \quad (3)$$

Elemental sulfur was postulated as the oxidizing agent instead of the possible disulfido group S_2^{2-}, because crystallized sulfur was identified among the reaction products. An oxidation of S_2^{2-} into S^0 was prevented by using a nitrogen atmosphere.

The low yield obtained for compound **1** is expected since eqns. (1)–(3) show that $W_3S_9^{2-}$ represents the main compound in the reaction scheme. In more acidic media (x = 1.5 and 1.8) $W_3S_9^{2-}$ is, as expected [10], replaced by $W_4S_{12}^{2-}$, and a new compound was isolated in place of **1**, which will be described elsewhere.

The low yield of **1** is also related to the reactivity of the transient $W(O)(S_2)_2(solvent)_2$ which must be considered as the soluble precursor species of $W_2S_{11}^{2-}$ and $W_2S_9O_2^{2-}$, both displaying the same skeleton as **1** and **3**.

Supplementary material

Table S11, listing of complete bond distances and angles for **1**, Table S12, anisotropic thermal parameters for **1**, Table S13, mean-plane equations with W-deviations for **1**, Table S14, listing of observed and calculated structure factors for **1** (2 pages in reduced form); Table S21, listing of complete bond distances and angles for **2**, Table S22, anisotropic thermal parameters for **2**, Table S23 mean-plane equations with W-deviations for **2**, Table S24, listing of observed and calculated structure factors for **2** (3 pages in reduced form); Table S31, listing of complete bond distances and angles for **3**, Table S32, isotropic thermal parameters for **3**, Table S33, mean-plane equations with W-deviations for **3**, Table S34, listing of observed and calculated structure factors for **3** (2 pages in reduced form) are available from the authors on request.

Acknowledgements

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