Acidification of $[WS_4]^{2-}$. Synthesis and Structures of Di-μ-sulfido-bis[(2,2′-bipyridine)chlorooxotungsten(V)] and Di-μ-sulfido-bis[(2,2′-bipyridine)bromooxotungsten(V)]†

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Acidification of $[WS_4]^{2-}$ by HCl or HBr in MeCN in the presence of 2,2′-bipyridine (bipy) led to the neutral dinuclear complexes $[W_2S_2O_2X_2(bipy)_2]$ (X = Cl **1** or Br **2**) which have been isolated as crystals. The structures of **1** and **2** were solved by X-ray diffraction methods, and were found to be isomorphous. Each tungsten(V) is bonded to a bipy ligand through the two nitrogen atoms, one in an axial, and the other in an equatorial position. The remaining axial position of the octahedron is occupied by a terminal oxygen. The co-ordination is completed by a terminal halide and a bridging sulfur. A metal–metal bond is postulated between the two W^V atoms, in accord with the diamagnetism of the crystals. The formation of compounds **1** and **2** has been analysed in comparison to the formation of $[W_4S_{12}]^{2-}$ under the same conditions of acidity but in the absence of 2,2′-bipyridine.

The chemistry of molybdenum and tungsten combined with sulfur is extremely rich in its chemical and structural diversity and practical importance. The crystallized dichalcogenides MS_2 are structurally well characterized and are used frequently because of their catalytic and electrochemical properties.[1] In contrast, the amorphous nature of the trichalcogenides MS_3 (M = Mo or W), whether prepared[2] by thermal decomposition or acidification of aqueous solutions of $[MS_4]^{2-}$, has hindered their structural characterization.[3]

Thus, the acidification of $[WS_4]^{2-}$ has attracted the attention of numerous groups during the past decade. Many compounds have been isolated and structurally characterized which can be considered as intermediates between $[WS_4]^{2-}$ and WS_3, including $[N(PPh_3)_2]_2[W_3S_8]$,[4] $[PPh_4]_2[W_3S_9]$,[5] $[PPh_4]_2[W_3S_{10}]$,[6] $[PPh_4]_2[W_4S_{12}]$,[7] $[PPh_4]_2[W_2S_{11}]$,[8] $[PPh_4]_2[W_2S_9O_2]$[9] and $[PPh_4]_2[W_2S_{11}H]$[10] (see Fig. 1). Such intermediates have helped to elucidate some structural features of the amorphous WS_3, and proposals have been put forward regarding its composition;[11] WS_3 was presumed to contain tungsten in various oxidation states, and probably both terminal and bridging sulfur atoms.

Many steps remain unknown in the acidification process of $[WS_4]^{2-}$, notably those allowing the explanation of the structural and chemical differences of the compounds isolated in weakly or more strongly acidic solutions.

The tri-[5,6] or tetra-nuclear[7] compounds isolated under weakly acidic conditions ($H^+ : W < 2:1$), contain a tungsten reduced to the formal state W^{IV} in $[W_3S_9]^{2-}$, and two W^V in $[W_4S_{12}]^{2-}$. In contrast, under more acidic conditions ($H^+ : W > 3:1$), condensation was limited to dinuclear compounds with the oxidation located exclusively on the ligands (S_2^{2-}), as in $[W_2S_{11}]^{2-}$,[8] $[W_2S_{11}H]^-$ [10] or $[W_2S_9O_2]^{2-}$.[9] In order to understand the connection between these two clearly separated acidic regions, the intermediates containing part of the framework of complexes already fully characterized in these media must be isolated. In order to trap such transient species, the chelating ligand 2,2′-bipyridine (bipy) was added to an acidified solution of $[WS_4]^{2-}$. Thus, under the acidic conditions which would lead to the formation of $[W_4S_{12}]^{2-}$ (ref. 7) we succeeded in isolating and characterizing two new dimers having the central $W_2S_2E_2{}^{2+}$ (E = O or S) core present in $[W_4S_{12}]^{2-}$

Experimental

All manipulations were carried out in air. Chemicals were used as purchased. Acetonitrile was dried on 4 Å molecular sieves. $[PPh_4]_2[WS_4]$ and $[NEt_4]_2[WS_4]$ were prepared by usual methods. Infrared spectra (KBr pellets) were recorded on a FTIR Magna 550 Nicolet spectrophotometer. Electronic spectra were recorded at 20 °C on a Shimadzu PC 210 spectrophotometer between 600 and 200 nm. Elemental analyses were performed by the Service Central d'Analyses du CNRS, Solaize, France.

Preparations.—$[W_2S_2O_2Cl_2(bipy)_2]\cdot MeCN$ **1**. To a solution of $[NEt_4]_2[WS_4]$ (0.0572 g, 0.1 mmol) in MeCN (10 cm^3) was added HCl (0.2 mmol) previously dissolved in MeCN. The mixture was stirred for 30 min at room temperature, the yellow solution turning rapidly from orange to brown. Then a solution of 2,2′-bipyridine (0.0156 g, 0.1 mmol) dissolved in HCl (0.1 mmol)–MeCN was added to the brown mixture, followed by rapid addition of additional HCl in MeCN (0.1 mmol).

Black crystals of compound **1** were obtained after standing overnight at −30 °C (yield 35%) (Found: C, 28.40; H, 2.20; Cl, 8.00; N, 7.25; S, 11.50; W, 40.50. Calc. for $C_{20}H_{16}Cl_2N_4O_2S_2W_2\cdot CH_3CN$: C, 29.70; H, 2.15; Cl, 8.00; N, 7.90; S, 7.20; W, 41.40); ν_{max}/cm^{-1}: (W=O) 951s, 937s; (W=S) 503s; (W–S) 456w, 439m, 428m, 421 (sh); (W–N) 331w;[7] $\lambda_{max}/nm(Me_2SO)$: 425, 310 and 250, values of molecular extinction coefficients are not given because of the poor solubility of the compound.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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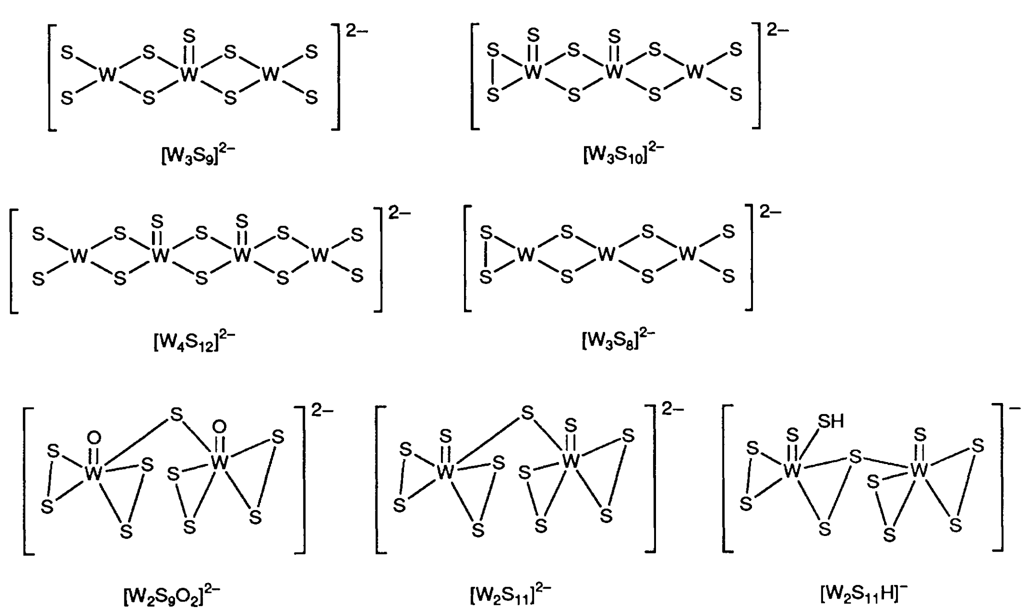


Fig. 1 Representation of characterized intermediates between WS_4^{2-} and WS_3

$[W_2S_2O_2Br_2(bipy)_2]$ **2**. To a solution of $[NEt_4]_2[WS_4]$ (0.0572 g, 0.1 mmol) and $[NEt_4][Br]$ (0.082 g, 0.4 mmol) in MeCN (5 cm^3) was added H_2SO_4 (0.1 mmol) previously dissolved in MeCN. The yellow solution turned rapidly from orange to brown. After stirring for 30 min, 2,2′-bipyridine (0.015 g, 0.1 mmol) and additional H_2SO_4 (0.1 mmol) previously dissolved in MeCN were added. The mixture was stirred for 15 min and filtered. Storage of the filtrate for several days at room temperature yielded a brown powder and black crystals of $[W_2S_2O_2Br_2(bipy)_2]$ which were washed with Et_2O (yield in crystals = 15%); ν_{max}/cm^{-1}: 3111vw, 3055vw, 2854vw, 2923vw, 1636vw, 1601s, 1570w, 1558vw, 1495w, 1472m, 1441s, 1385w, 1315 m, 1280w, 1243w, 1229w, 1167w, 1159m, 1119w, 1108w, 1076w, 1065w, 1045w, 1028m, 1017 (sh), 949vs, 777s, 730m, 654m, 635m, 457w, 442m, 429m, 421 (sh) and 329w.

Direct acidification of $[WS_4]^{2-}$ in acetonitrile by hydrobromic acid, (HCl was used for **1**), led to a mixture of **2** and of $[WO(S_2)_2(bipy)]$.[12]

Crystal Structure Analysis of Complexes **1** *and* **2**.—A selected crystal was mounted on an automatic diffractometer. Unit-cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well centred reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 1. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections[13] were applied. Computations were performed by using the CRYSTALS program[14] adapted on a MicroVax II. Atomic form factors for neutral W, S, N, O, Br, Cl, C and H were taken from ref. 15. Anomalous dispersion was taken into account. The structure was solved by direct methods using the SHELX 86 program.[16] For compound **1**, hydrogen atoms for the bipy were found on difference electron density maps, but were introduced in the refinement as fixed contributors in calculated positions. Their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. Hydrogen atoms for **2** could not be located on Fourier difference maps and thus were not introduced in the refinement. For both compounds, H atoms for the solvent molecule were not located. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. Least-squares refinements with an approximation to the normal matrix were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used was $w = w'\{1 - [\Delta F/6\sigma(F)]^2\}^2$ with $w' = 1/\Sigma_1{}^n A_r T_r(X)$ where $n(n = 3)$ is the number of coefficients, A_r, for a Chebyshev series, for which X is $F_c/F_c(\max)$.[17] The model reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$ having values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of the root mean square shift to the standard deviation being less than 0.1 and no significant features in a final difference map. Atomic coordinates for **1** and **2** are given in Tables 2 and 3, respectively.

Table 1 Crystal data and data collection parameters for the structures of $[W_2S_2O_2Cl_2(bipy)_2]\cdot MeCN$ **1** and $[W_2S_2O_2Br_2(bipy)_2]\cdot MeCN$ **2***

Formula	$C_{22}H_{19}Cl_2N_5O_2S_2W_2$	$C_{22}H_{19}Br_2N_5O_2S_2W_2$
M	887.92	976.82
a/Å	9.958(3)	10.085(4)
b/Å	11.331(7)	11.451(5)
c/Å	11.689(4)	11.734(10)
α/°	90.70(4)	92.76(6)
β/°	99.02(3)	98.78(5)
γ/°	92.33(4)	91.79(3)
U/Å^3	1301(6)	1336(11)
D_c/g cm^{-3}	2.267	2.43
F(000)	832	904
μ/cm^{-1}	94.18	119.29
Reflections collected	4859	4927
Reflections used ($F_o^2 > 3\sigma F_o^2$)	3427	1867
R	0.0358	0.056
R'	0.0433	0.066

* Details in common: triclinic, space group $P\bar{1}$, $Z = 2$, Enraf-Nonius diffractometer ($\lambda = 0.710\,69$ Å), θ–2θ scan type, scan range 0.8 + 0.345 tan θ, 1 < θ < 25°, 316 refined parameters.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure Determination of Complex **1**.—A view of the molecular dinuclear complex **1** is shown in Fig. 2 with the atomic numbering scheme. Selected bond distances and angles for **1** are given in Table 4. The two tungsten atoms are

Table 2 Fractional atomic coordinates for $[W_2S_2O_2Cl_2(bipy)_2]\cdot MeCN$ **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0.220 59(3)	0.269 80(2)	0.303 08(2)
W(2)	0.274 14(3)	0.038 98(2)	0.235 62(2)
S(1)	0.168 1(2)	0.181 6(2)	0.118 7(2)
S(2)	0.244 4(2)	0.105 8(2)	0.420 7(2)
Cl(1)	0.191 9(2)	0.388 4(2)	0.476 5(2)
Cl(2)	0.247 7(3)	−0.087 7(2)	0.059 7(2)
O(1)	0.380 1(6)	0.329 5(5)	0.303 7(6)
O(2)	0.445 2(6)	0.062 2(5)	0.238 0(6)
N(1)	0.137 4(7)	0.428 6(6)	0.211 6(6)
N(2)	−0.015 4(7)	0.268 7(6)	0.298 0(6)
N(3)	0.067 4(6)	−0.066 7(5)	0.239 8(5)
N(4)	0.315 0(7)	−0.130 0(6)	0.323 7(6)
C(1)	0.221 7(9)	0.504 3(7)	0.165 4(7)
C(2)	0.178(1)	0.604 4(8)	0.112 4(8)
C(3)	0.041(1)	0.627 7(8)	0.100 6(8)
C(4)	−0.046(1)	0.550 1(9)	0.145 0(8)
C(5)	0.005(1)	0.451 3(8)	0.199 5(7)
C(6)	−0.081 6(9)	0.361 5(8)	0.249 9(7)
C(7)	−0.219(1)	0.370(1)	0.249(1)
C(8)	−0.290 5(9)	0.281(1)	0.295(1)
C(9)	−0.224(1)	0.187(1)	0.342 9(9)
C(10)	−0.086 0(9)	0.183 9(9)	0.344 5(8)
C(11)	−0.052 7(8)	−0.034 9(8)	0.186 2(8)
C(12)	−0.172 8(9)	−0.090 0(9)	0.205 3(8)
C(13)	−0.167(1)	−0.182 9(9)	0.281 9(9)
C(14)	−0.044(1)	−0.219 3(8)	0.332 0(7)
C(15)	0.073 7(8)	−0.161 2(7)	0.308 5(6)
C(16)	0.212 6(8)	−0.202 6(6)	0.349 5(7)
C(17)	0.235(1)	−0.308 0(8)	0.401 8(7)
C(18)	0.367(1)	−0.344 6(8)	0.429 4(8)
C(19)	0.472(1)	−0.271 8(8)	0.407 5(9)
C(20)	0.442(1)	−0.166 7(8)	0.354 7(9)
N(5)	0.412 3(6)	0.403 9(6)	−0.127 8(8)
C(21)	0.486(1)	0.244(2)	0.024(1)
C(22)	0.445(1)	0.335(1)	−0.058(1)

Table 3 Fractional atomic coordinates for $[W_2S_2O_2Br_2(bipy)_2]\cdot MeCN$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0.2748(2)	0.0411(1)	0.7348(1)
W(2)	0.2184(2)	0.2714(1)	0.8037(1)
S(1)	0.245(1)	0.1120(8)	0.9186(9)
S(2)	0.167(1)	0.1791(9)	0.6199(9)
Br(1)	0.2501(5)	−0.0972(4)	0.5474(4)
Br(2)	0.1885(4)	0.4009(4)	0.9896(4)
O(1)	0.454(2)	0.069(2)	0.732(2)
O(2)	0.379(2)	0.337(1)	0.807(2)
N(1)	0.316(3)	−0.124(3)	0.818(3)
N(2)	0.076(3)	−0.066(2)	0.739(2)
C(1)	0.445(4)	−0.158(4)	0.850(4)
C(2)	0.476(4)	−0.266(3)	0.899(3)
C(3)	0.375(5)	−0.334(3)	0.931(4)
C(4)	0.238(4)	−0.299(3)	0.906(3)
C(5)	0.217(4)	−0.198(3)	0.851(3)
C(6)	0.081(3)	−0.153(3)	0.812(3)
C(7)	−0.037(4)	−0.214(4)	0.835(4)
C(8)	−0.160(4)	−0.174(3)	0.778(3)
C(9)	−0.165(3)	−0.090(3)	0.702(3)
C(10)	−0.049(3)	−0.029(3)	0.686(3)
N(3)	−0.015(3)	0.263(3)	0.802(3)
N(4)	0.134(4)	0.430(3)	0.717(3)
C(11)	−0.077(4)	0.186(3)	0.857(3)
C(12)	−0.217(4)	0.189(4)	0.846(4)
C(13)	−0.283(5)	0.285(4)	0.797(5)
C(14)	−0.222(5)	0.368(4)	0.742(4)
C(15)	−0.073(4)	0.354(4)	0.749(4)
C(16)	−0.002(4)	0.446(3)	0.701(3)
C(17)	−0.049(5)	0.549(4)	0.642(4)
C(18)	0.039(6)	0.621(4)	0.599(4)
C(19)	0.175(5)	0.594(3)	0.608(4)
C(20)	0.218(4)	0.499(3)	0.670(4)
N(5)	0.413(7)	0.413(6)	0.380(6)
C(21)	0.437(6)	0.338(7)	0.450(5)
C(22)	0.477(6)	0.256(6)	0.529(5)

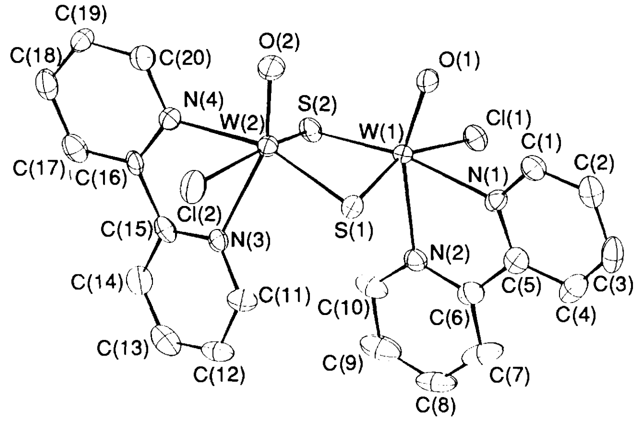


Fig. 2 An ORTEP representation[18] of compound **1**, 30% ellipsoids shown

octahedrally co-ordinated, which can be considered as unusual in Group 6 compounds containing the $W_2S_2E_2$ (E = O or S) core, as noted previously.[19] Each tungsten atom is bonded to a 2,2′-bipyridine ligand through the two nitrogen atoms, one in a pseudo-equatorial position and the other in a pseudo-axial position, the remaining axial position being occupied by a terminal oxygen atom.

The octahedral co-ordination at each tungsten is achieved by a terminal chlorine and a bridging sulfur atom. Very few compounds containing the $W_2S_2E_2$ central core have been structurally characterized. In $[W_4S_{12}]^{2-}$,[7] $[W_2S_4(S_2C_2H_4)_2]^{2-}$,[20] $[W_2S_4\{S_2P(OEt)_2\}_2]$, $[W_2S_4(S_2CNEt_2)_2]$[21] and $[W_2S_4\{S_2(S)PPh\}_2]^{2-}$,[22] the two central tungsten atoms are five-co-ordinate, and in $[W_2S_4Cl_2(py)_4]\cdot 2py$ (py = pyridine)[19] and $[W_2S_4Br_2(PPh_3)_2]$[23] these atoms are six-co-ordinate.

The values of the two terminal bond lengths, W(1)–O(1) 1.699(6) and W(2)–O(2) 1.709(6) Å are in good agreement with those usually reported for W=O double bonds, showing that in the selected crystal the sites were fully occupied by oxygen. The difference observed in the results of the chemical analysis of **1** between calculated and observed data for sulfur is a consequence of the statistical replacement of sulfur by oxygen at the terminal site of the W=S double bond. This replacement is clearly evidenced by the IR spectra which show both absorptions at 951 and 937 cm^{-1} (W=O) and 503 cm^{-1} (W=S).

The angles in the W–S–W–S ring, 74.64(6)° at S(1), 74.19(6)° at S(2), 101.67(7)° at W(1) and 101.72(7)° at W(2), are similar to those observed in the closely related compounds $[W_2S_4Cl_2(py)_4]\cdot 2py$[19] and $[W_2S_4Br_2(PPh_3)_3]$.[23] The average length of the W–S bridging bonds [2.331(2) Å] is comparable to that observed in $[W_4S_{12}]^{2-}$,[7] [2.328(2) Å], and somewhat longer than reported for $[W_2S_4Cl_2(py)_4]\cdot 2py$, [2.30(2) Å] and [2.30(1)].[19]

The W–W distance of 2.8179(4) Å is quite similar to that observed for $[W_2S_4\{S_2P(OEt)_2\}_2]$ [2.819(1)] and $[W_2S_4(S_2CNEt_2)_2]$ [2.795(2)] but significantly shorter than for $[W_4S_{12}]^{2-}$ [2.912(6) Å] and $[W_2S_4(S_2C_2H_4)_2]^{2-}$ [2.862(1) Å]. Such a short W–W distance agrees with a strong spin coupling between the two formal W^V atoms since the complex was found to be diamagnetic at room temperature ($\chi_M = -316 \times 10^{-6}$ cm^3 mol^{-1}). In **1**, the two tungsten atoms are displaced from the equatorial plane towards the terminal oxygen by distances of 0.34 and 0.35 Å respectively, being comparable to the 0.33 Å observed in $[W_2S_4\{S_2P(OEt)_2\}_2]$, but significantly less than for $[W_4S_{12}]^{2-}$ (0.65 Å) and

Table 4 Selected bond lengths (Å) and angles (°) for complexes **1** (X = Cl) and **2** (X = Br)

	1	**2**
W(1)–W(2)	2.8179(4)	2.822(2)
W(1)–S(1)	2.338(2)	2.33(1)
W(1)–S(2)	2.323(2)	2.32(1)
W(1)–X(1)	2.479(2)	2.623(5)
W(1)–O(1)	1.699(6)	1.83(2)
W(1)–N(1)	2.227(7)	2.20(3)
W(1)–N(2)	2.341(7)	2.33(3)
W(2)–S(1)	2.310(2)	2.32(1)
W(2)–S(2)	2.349(2)	2.33(1)
W(2)–X(2)	2.467(2)	2.639(5)
W(2)–O(2)	1.709(6)	1.75(2)
W(2)–N(3)	2.347(6)	2.35(3)
W(2)–N(4)	2.207(6)	2.25(3)
S(2)–W(1)–S(1)	101.67(7)	101.4(4)
O(1)–W(1)–S(1)	102.9(2)	103.8(9)
O(1)–W(1)–S(2)	106.3(2)	105.2(8)
N(1)–W(1)–S(1)	83.3(2)	84.5(9)
N(1)–W(1)–S(2)	162.3(2)	160.6(8)
N(1)–W(1)–O(1)	88.9(3)	90.9(11)
N(2)–W(1)–S(1)	85.0(2)	84.1(8)
N(2)–W(1)–S(2)	93.0(2)	92.7(7)
N(2)–W(1)–O(1)	156.8(3)	158.2(10)
N(2)–W(1)–N(1)	70.3(2)	69.4(10)
X(1)–W(1)–S(1)	159.12(7)	159.4(3)
X(1)–W(1)–S(2)	88.04(7)	86.8(3)
X(1)–W(1)–N(1)	82.3(2)	82.0(8)
X(1)–W(1)–N(2)	75.9(2)	76.6(8)
W(2)–S(1)–W(1)	74.64(6)	74.7(3)
W(2)–S(2)–W(1)	74.19(6)	74.7(3)
S(2)–W(2)–S(1)	101.72(7)	101.3(3)
O(2)–W(2)–S(1)	106.8(2)	106.9(8)
O(2)–W(2)–S(2)	102.6(2)	104.7(9)
N(3)–W(2)–S(1)	92.1(2)	91.4(9)
N(3)–W(2)–S(2)	83.9(2)	84.7(8)
N(3)–W(2)–O(2)	158.0(3)	157.0(11)
N(4)–W(2)–S(1)	161.5(2)	162.3(9)
N(4)–W(2)–S(2)	83.7(2)	84.5(8)
N(4)–W(2)–O(2)	89.0(3)	87.5(12)
N(4)–W(2)–N(3)	70.7(2)	72.3(12)
X(2)–W(2)–S(1)	86.53(7)	88.2(3)
X(2)–W(2)–S(2)	159.14(8)	159.4(3)
X(2)–W(2)–N(3)	76.7(2)	76.8(8)
X(2)–W(2)–N(4)	82.9(2)	81.3(8)

$[W_2S_4(S_2C_2H_4)_2]^{2-}$ (0.72 Å). This difference is related to the presence in **1** and $[W_2S_4\{S_2P(OEt)_2\}_2]$ of a ligand *trans* to the W=E (E = O or S) double bond. As expected, the equatorial tungsten–nitrogen bonds, W(1)–N(1) 2.227(7), W(2)–N(4) 2.207(7) Å are shorter than the axial W–N bonds *trans* to the double bond, W(1)–N(2) 2.341(7), W(2)–N(3) 2.347(7) Å.

The two terminal Cl(1) and Cl(2) atoms, one bound to each tungsten atom, are located *trans* to each other, W(1)–Cl(1) 2.479(2), W(2)–Cl(2) 2.467(2) Å. X-Ray crystallography could not distinguish between a chloro ligand Cl^- and a hydrosulfido ligand SH^-; thus, an ambiguity remained about the occupancy of these two terminal sites. However, the single-crystal structure of the bromo analogue **2** obtained from the acidification of $[WS_4]^{2-}$ in the presence of bromide solved this problem, revealing that **2** contains two *trans* bromines instead of the two corresponding chlorines of **1**. This point, together with the elemental analysis for chlorine, indicated that the formulation with two chloride ligands is correct for **1**.

Structure Determination of Complex **2**.—Compound **2** was found to be isostructural with **1**. The complete structural data for **2** are given in the supplementary data. A view of the molecular dinuclear complex **2** is shown in Fig. 3.

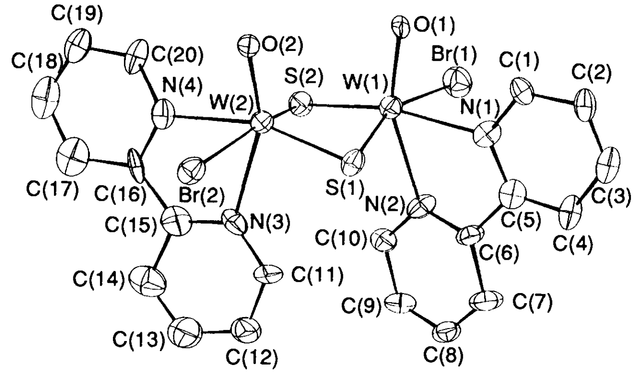


Fig. 3 An ORTEP representation of compound **2**, 30% ellipsoids shown

Preparation.—The complete characterizations of **1** and **2** clearly indicate that between the starting material $[WS_4]^{2-}$, and the final product WS_3, intermediates exist whose structures are dependent on the nature of the acid used. With HCl or HBr (or H_2SO_4 + Br^-), the two transient species **1** or **2** trapped by addition of 2,2′-bipyridine contain a chloro or bromo ligand, whereas these structures were not isolated in the absence of halides.

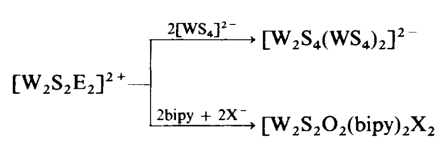
The redox process leading to the formation of the $[W_2S_4]^{2+}$ fragment is given in equations (1) and (2), assuming that the S^{2-} ligand is the reducing agent.

$$2[WS_4]^{2-} + 8H^+ + 2e^- + 2H_2O \longrightarrow W_2S_2O_2{}^{2+} + 6H_2S \quad (1)$$

$$2H_2S \longrightarrow S_2{}^{2-} + 2e^- + 4H^+ \quad (2)$$

Such a redox reaction is comparable to the reaction leading to the formation of dimeric $[W_2S_4\{S_2P(OEt)_2\}_2]$ obtained by reduction of $[WS_4]^{2-}$, the thio ligand $HS_2P(OEt)_2$ acting as the reducing agent.[21]

The structure of $[W_4S_{12}]^{2-}$ can be formulated as $[(WS_4)(W_2S_4)(WS_4)]^{2-}$ with two WS_4 groups acting as terminal bidentate ligands to the central W_2S_4 core. The formation of compounds **1** and **2** can be understood as resulting in the bonding to the central W_2S_4 (or $W_2S_2O_2$) core of the strongly chelating bipy ligand instead of the two WS_4 groups as represented in Scheme 1.



Scheme 1 E = O or S, X = Cl or Br

The anion $[W_4S_{12}]^{2-}$ slowly decomposes in acetonitrile to form the well characterized trinuclear complex $[W_3S_9]^{2-}$, and in the presence of water $[W_3S_8O]^{2-}$, confirming the better stabilization of W^{IV} in a sulfur environment than of W^V. Addition of 2,2′-bipyridine in the presence of halides to $[W_4S_{12}]^{2-}$ in acetonitrile prevents the formation of $[W_3S_9]^{2-}$, yielding after several days black crystals of compound **2**, together with $[WO(S_2)_2(bipy)]$[12] as a minor by-product.

These data show that the central $[W_2S_2E_2]^{2+}$ (E = O or S) core can be stabilized by 2,2′-bipyridine, either by direct condensation of $[WS_4]^{2-}$ in acidic medium, or by decomposition of $[W_4S_{12}]^{2-}$ which already contains the central W_2S_4 fragment.

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