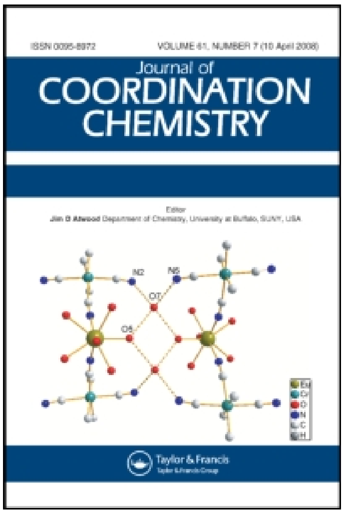

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SYNTHESIS AND MOLECULAR STRUCTURE OF BIS(TETRATHIOTUNGSTATO(VI)-S,S′) OXOTUNGSTATE(IV), $((C_6H_5)_4P)_2(WO(WS_4)_2)^{-2}$

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The mixed valence complex $(P(C_6H_5)_4)_2$ $(WO(WS_4)_2)$ was prepared by acidification of Na_2WS_4 by ion exchange in a protonated resin, and isolated as tetraphenylphosphonium salt. It was characterized by X-ray structure determination. The lattice enclosed the two equivalent ions $(WO(WS_4)_2)^{2-}$ and $(WS(WS_4)_2)^{2-}$ with a sulfido replacing an oxo group. Crystals are monoclinic, space group $P2_1/c$: $a = 10.287(5)$, $b = 11.791(5)$, $c = 22.428(6)$ Å, $\beta = 108.37(1)°$. The structure was solved by the heavy atom method. Anisotropic least-squares refinement (except hydrogen atoms) of 2706 independant data led to the final R = 0.070. The tetranuclear unit consists in a central WXS_4 (X = O or S) tetragonal pyramid sharing edges with two WS_4 tetrahedra. The apical position of the pyramid is occupied by a terminal oxo or sulfido group. A disordered packing of the unit is observed : the WX moiety is statistically distributed over two positions related to the crystallographic center. The trinuclear species is a class (1) mixed valence compound with two tetrahedral W(VI) and one pyramidal W(IV).

INTRODUCTION

In recent years, considerable interest has grown in sulfur containing compounds of molybdenum with respect to the biochemical implications of their redox behaviour.[1] Synthesis and structure of mononuclear and polynuclear molybdenum complexes were previously reported.[2-8] Tungsten often presents very close properties to molybdenum, but such sulfurated compounds are not so numerous in tungsten chemistry. We herein report the synthesis of one of the first highly sulfurated polynuclear diamagnetic complexes with a central pyramidal oxothiotungsten(IV). The described anion is a mixed valence group. The complex indeed involves two different formal valence states with two different coordination geometries. A structural comparison with molybdenum(IV) complexes is carried out.

EXPERIMENTAL SECTION

Synthesis and physical measurements

Excess of hydrogen sulfide was bubbled into an aqueous solution (250 ml) of Na_2WO_4 (25 mmol) up to pH = 5.5, yielding a mixture of 80% $(WOS_3)^{2-}$ and 20% $(WS_4)^{2-}$. This solution was kept at 60°C under H_2S atmosphere for about four days which gives only $(WS_4)^{2-}$. After cooling at 0°C, the solution was mixed with an equal volume of dimethylformamide. The aqueous-organic mixture was poured onto a cooled 50W-X_2 100-200 mesh Dowex resin. The Na^+/H^+ exchange led to a red solution which was precipitated by adding tetraphenylphosphonium bromide $2P(C_6H_5)_4^+/W$. The red powder was filtered off washed with alcohol and recrystallized using dichloromethane.

Tungsten analyses were performed by oxidation to the hexavalent state using hydrogen peroxide. Excess of hydrogen peroxide was removed by boiling the solution with sodium hydroxide. The solution was diluted in 6 M hydrochloric acid, reduced to pentavalent state by hydrochloric solution of $SnCl_2$ and $TiCl_3$, and colorimetrically titrated as thiocyanate complex, at 400 nm. Carbon and sulfur were determined by standard microanalytical method.

IR spectra were recorded on Perkin-Elmer 457 spectrophotometer. $(P(C_6H_5)_4)$ Br and complex were sampled as KBr pellets.

Electronic spectra were recorded on Beckman

Acta V spectrophotometer for DMF solutions, and on Beckman DK 2A spectrophotometer for solids.

Magnetic susceptibilities of solids were measured by the Faraday method at room temperature.

X-ray Diffraction Study – Intensity Data

The crystal selected for X-ray analysis was shaped as a truncated square pyramid (0.32 x 0.14 x 0.08 mm). Laue and precession photographs indicated monoclinic symmetry, with systematic absences consistent with space group $P2_1/c$. The crystal was mounted on an automatic three circles diffractometer. Unit cell parameters were obtained by a least-squares procedure using 9 reflections.

$a = 10.287(5)$ Å
$b = 11.791(5)$ Å
$c = 22.428(6)$ Å
$\beta = 108.37(1)$ Å

Data collection was carried out with the following conditions:

take off angle: 3°
scan type: θ-2θ
scan length in θ: $0.8° + 0.35 \text{ tg}\theta$
scan speed: $1°/\text{mn}(\theta)$

The MoK_α peak was selected by a graphite monochromator set on the diffracted beam path. The scintillation counter was associated with a pulse-height analyser adjusted to MoK_α radiation in such a way that 90% of the diffracted intensity was counted. 3591 reflections were collected at room temperature, up to $\sin\theta/\lambda = 0.55$.

Standards 0 2 0 and 3 0 $\overline{10}$ were monitored every 100 reflections. A linear intensity decay of 21% for the whole data set was found and corrected.

Treatment of Intensity Data

Intensities were first corrected for Lorentz and polarization factors. Absorption corrections were carried out, ($\mu = 74.6 \text{ cm}^{-1}$);[9] minimum and maximum transmission factors were respectively 0.168 and 0.506). Each structure factor was assigned a standard deviation $\sigma = (F \times \Delta I)/2I$, where I was the integrated intensity and ΔI the error. Atomic form factors were taken from Cromer and Mann,[10] including the real and imaginary components of anomalous dispersion for all non hydrogen atoms.

Full matrix least squares procedure was used in refinement. The minimized quantity was $w^2(|Fo|-|Fc|)^2$. The weighting scheme based on counting statistics was $w = 2F/\sigma$. The agreement indices were defined as:

$$R_w = (\Sigma w^2(|Fo|-|Fc|)^2/\Sigma w^2|Fo|^2)^{1/2}$$
$$R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$$

STRUCTURE SOLUTION

The structure was solved by the heavy atom method. A tridimensional Patterson map was consistent with the presence of two tungsten atoms in general positions. The occurrence of a short metal-metal vector (1.62 Å) led us to expect a statistical distribution between two sites related through the inversion center. Then, this atom was introduced with an occupancy factor equal to 0.5. Refinement with isotropic thermal parameters gave R equal to 0.35. Subsequent phased Fourier syntheses led to location of all atoms. Refinement of coordinates and anisotropic thermal components led to $R = 0.11$. The introduction of absorption corrections gave a significant improvement in the R factor which dropped to $R = 0.07$. Phenyl hydrogen atoms were introduced in calculated positions but not refined. Their temperature factors were taken 1 Å^2 greater than those of the carbon atoms to which they are attached. The final refinement of 289 variables using 2706 observations ($Fo > 4\sigma$) led to the R value:

$R = 0.07$
$R_w = 0.071$

The terminal W(1)O distance of 1.83(2)Å (vide infra) is longer than that usually reported for W and Mo oxocompounds (1.7 Å). Moreover, the terminal oxygen has a very close isotrope temperature factor value (2.4 Å^2) to that of the tungsten to which it is attached (2.5 Å^2). These unexpected data are very similar to the results reported by Enemark *et al.* for the structure of $Mo_2OS(\mu\text{-}S)_2(dtc)_2$.[11] They showed that an oxygen–sulfur disorder in the central site led to a long MoO distance (1.82(2) Å). Because of disorder the oxygen temperature factor they measured (1.8 Å^2) was very low in front of that of the heavy atom (2.7 Å^2). These data led us to expect a similar oxygen–sulphur disorder. A new scattering table was built mixing oxygen and sulfur ones and assigned to the terminal disordered oxygen atom. The best refinement was obtained for a 50% oxygen–50% sulfur trial (for clarity this terminal "mixed" atom was called Ost). The equivalent Ost B-factor became much more reliable (6.8 Å^2) than that one observed with oxygen (3.2 Å^2). This new value was now comparable with that of the terminal sulfurs: respectively 6.6 and 7.9 Å^2 for S(3) and S(4) atoms (vide infra). Atomic coordinates are listed in Table I, equivalent thermal parameters in Table II, interatomic distances and bond angles in Table III. A list of structure factors is available as supplementary material upon request.

TABLE I

Final atomic coordinates in $[(C_6H_5)_4P]_2[W_3OstS_8]$ with esd's in parentheses (A)

W_1	−0.03341 (1)	0.0465 (2)	−0.00396 (6)
W_2	0.14021 (7)	0.04162 (9)	0.13244 (3)
S_1	−0.06126 (5)	−0.0475 (6)	0.0885 (2)
S_2	0.2114 (5)	0.0822 (5)	0.0497 (2)
S_3	0.1057 (7)	0.1949 (6)	0.1752 (3)
S_4	0.2799 (7)	−0.653 (7)	0.2012 (3)
O	−0.117 (2)	0.184 (2)	−0.0939 (9)
P	0.2346 (4)	0.0285 (5)	0.3962 (2)
C_1	0.337 (2)	0.150 (2)	0.3913 (9)
C_2	0.399 (2)	0.216 (2)	0.4433 (9)
C_3	0.477 (2)	0.309 (2)	0.439 (1)
C_4	0.491 (2)	0.335 (3)	0.380 (1)
C_5	0.429 (3)	0.269 (2)	0.330 (1)
C_6	0.352 (2)	0.178 (2)	0.333 (1)
C_{11}	0.749 (2)	0.408 (2)	0.334 (1)
C_{12}	0.001 (2)	0.137 (2)	0.326 (1)
C_{13}	−0.129 (3)	0.144 (3)	0.280 (1)
C_{14}	−0.178 (2)	0.476 (4)	0.246 (1)
C_{15}	−0.105 (2)	−0.052 (2)	0.250 (1)
C_{16}	0.021 (2)	−0.055 (2)	0.294 (1)
C_{21}	0.318 (2)	−0.102 (1)	0.389 (1)
C_{22}	0.261 (2)	−0.204 (2)	0.396 (1)
C_{23}	0.321 (2)	−0.306 (2)	0.392 (1)
C_{24}	0.444 (3)	−0.308 (2)	0.382 (1)
C_{25}	0.500 (2)	−0.207 (2)	0.371 (1)
C_{26}	0.441 (2)	−0.104 (2)	0.374 (1)
C_{31}	0.208 (2)	0.276 (2)	0.473 (1)
C_{32}	0.129 (2)	0.113 (2)	0.485 (1)
C_{33}	0.116 (2)	0.114 (2)	0.545 (1)
C_{34}	0.174 (2)	0.035 (3)	0.589 (1)
C_{35}	0.247 (2)	−0.054 (2)	0.574 (1)
C_{36}	0.268 (2)	−0.053 (2)	0.516 (1)

TABLE II

Equivalent thermal parameters in $[(C_6H_5)_4P]_2[W_3\ Ost\ S_8]$

W_1	4.38(4)	C_{13}	7.0 (1)
W_2	3.82(6)	C_{14}	7.0 (1)
S_1	5.7 (1)	C_{15}	5.8 (9)
S_2	5.2 (2)	C_{16}	4.6 (7)
S_3	6.6 (2)	C_{21}	4.4 (5)
S_4	7.9 (4)	C_{22}	4.3 (7)
O	3.2 (9)	C_{23}	5.2 (7)
Ost	6.8 (4)	C_{24}	7.2 (7)
P	4.0 (2)	C_{25}	5.8 (9)
C_1	4.0 (1)	C_{26}	5.1 (8)
C_2	4.9 (1)	C_{31}	4.9 (8)
C_3	6.0 (1)	C_{32}	5.3 (8)
C_4	7.0 (1)	C_{33}	5.0 (1)
C_5	6.0 (1)	C_{34}	6.0 (9)
C_6	5.1 (9)	C_{35}	5.9 (8)
C_{11}	4.9 (8)	C_{36}	4.9 (8)
C_{12}	5.9 (9)		

Ost = statistical O or S

RESULTS AND DISCUSSION

Crystal structure

A perspective view of the anion is given in Figure 1 and indicates that it consists of a central square pyramid sharing edges with two WS_4 tetrahedra. The $(WS_4)^{2-}$ ion can be considered as a bidentate ligand toward the WOst group. The four bridging sulfur atoms form the basal square pyramidal plane while the doubly Ost atom is in apical positions (for Ost see structure solution).

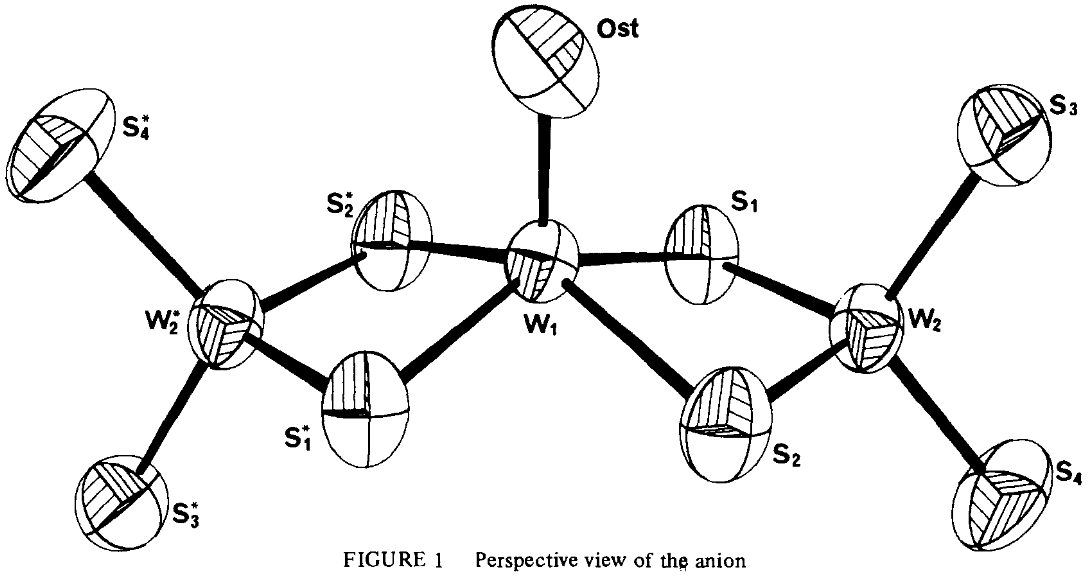

FIGURE 1 Perspective view of the anion

TABLE III

Interatomic distances (A) and principal bond angles (°) with esd's in parentheses

Metal-metal distances							
$W_1 \ldots W_2$	3.018 (2)						
$W_1 \ldots W_2^b$	2.932 (2)						
$W_1 \ldots W_1$	1.277 (4)	(distance from the two disordered sites).					
Bonds involving sulfur bridge							
W_1-S_1	2.448 (5)	W_1-S_2	2.462 (5)	W_2-S_1	2.254 (6)	S_1---S_2	3.54 (1)
W_1-S_1^b	2.390 (5)	W_1-S_2^b	2.351 (5)	W_2-S_2	2.250 (6)	S_1---S_2^b	3.03 (1)
S_1-W_1-S_2^b	78.2 (2)	S_1-W_2-S_2	103.5 (2)	S_1-W_1-S_2	92.1 (2)		
S_1^b-W_1-S_2	77.2 (2)	W_1-S_1-W_2	79.76 (2)	S_1^b-W_1-S_2	78.18 (2)		
S_1^b-W_1-S_2^b	96.4 (2)	W_1-S_2-W_2	79.52 (1)	S_2^b-W_1-S_1	78.18 (2)		
Bond involving sulfur terminal[a] atoms							
W_2-S_3	2.129 (5)	S_2-W_2-S_3	109.4 (3)	S_1-W_2-S_4	110.7 (3)	S_3-W_2-S_4	110.0 (3)
W_2-S_4	2.154 (6)	S_1-W_2-S_3	109.6 (2)	S_2-W_2-S_4	113.5 (2)	S_1-W_2-S_2	103.5 (2)
Oxygen surrounding angles							
W_1-Ost	1.83 (2)						
O-W_1-S_1	106.2 (6)	O-W_1-S_1^b	104.3 (6)	S_1-W_1-O^b	73.2 (4)	O^b-W_1-S_1^b	76.3 (4)
O-W_1-S_2	105.8 (7)	O-W_1-S_2^b	104.8 (7)	S_2-W_1-O_2^b	72.4 (4)	O^b-W_1-S_2^b	76.9 (4)
Tetraphenylphosphonium bonds and angles							
P-C_1	1.80 (2)	C_1-P-C_{11}	107. (1)	P-C_1-C_6	119. (1)	P-C_{21}-C_{26}	121. (2)
P-C_{11}	1.79 (2)	C_1-P-C_{21}	112.1(9)	P-C_1-C_2	121. (1)	P-C_{21}-C_{22}	121. (1)
P-C_{21}	1.79 (2)	C_{11}-P-C_{21}	110. (1)	P-C_{11}-C_{12}	120. (2)	P-C_{31}-C_{36}	121. (2)
P-C_{31}	1.82 (2)	C_{21}-P-C_{31}	107. (1)	P-C_{11}-C_{16}	120. (2)	P-C_{31}-C_{32}	118. (2)
C_1-C_2	1.38 (3)	C_1-C_1-C_6	118. (2)	C_{11}-C_{12}	1.25 (3)	C_{12}-C_{11}-C_{16}	119. (2)
C_2-C_3	1.37 (3)	C_1-C_2-C_3	121. (2)	C_{12}-C_{13}	1.41 (4)	C_{11}-C_{12}-C_{12}	121. (2)
C_3-C_4	1.40 (4)	C_2-C_3-C_4	119. (2)	C_{13}-C_{14}	1.38 (4)	C_{12}-C_{13}-C_{14}	117. (2)
C_4-C_5	1.36 (4)	C_3-C_4-C_5	119. (2)	C_{14}-C_{15}	1.39 (4)	C_{13}-C_{14}-C_{15}	125. (2)
C_5-C_6	1.34 (3)	C_4-C_5-C_6	123. (2)	C_{15}-C_{16}	1.36 (3)	C_{14}-C_{15}-C_{16}	116. (2)
C_6-C_1	1.40 (3)	C_5-C_6-C_1	119. (2)	C_{11}-C_{16}	1.44 (3)	C_{15}-C_{16}-C_{11}	122. (2)
C_{21}-C_{22}	1.37 (3)	C_{22}-C_{21}-C_{26}	118. (2)	C_{31}-C_{32}	1.38 (3)	C_{32}-C_{31}-C_{36}	121. (2)
C_{22}-C_{23}	1.37 (3)	C_{21}-C_{22}-C_{23}	123. (2)	C_{32}-C_{33}	1.38 (3)	C_{31}-C_{32}-C_{33}	117. (2)
C_{32}-C_{24}	1.36 (4)	C_{22}-C_{23}-C_{24}	119. (2)	C_{33}-C_{34}	1.36 (3)	C_{32}-C_{33}-C_{34}	123. (2)
C_{24}-C_{25}	1.39 (4)	C_{23}-C_{24}-C_{25}	119. (2)	C_{34}-C_{35}	1.39 (4)	C_{33}-C_{34}-C_{35}	119. (2)
C_{25}-C_{26}	1.37 (3)	C_{24}-C_{25}-C_{26}	122. (2)	C_{35}-C_{36}	1.38 (3)	C_{34}-C_{35}-C_{36}	118. (2)
C_{26}-C_{21}	1.41 (3)	C_{25}-C_{26}-C_{21}	118. (2)	C_{36}-C_{31}	1.36 (3)	C_{35}-C_{36}-C_{31}	121. (2)

[a] terminal = atom bonded to only one metallic center.

[b] atom in symmetric position through the inversion center.

Ost = statistical O or S.

A characteristic feature of this structure is the statistical distribution of the W(1)Ost moiety between two positions related through the crystallographic inversion center. This can be interpreted as a disordered packing of the non-centrosymmetric $(W_3OstS_8)^{2-}$ anion, leading to an overall arrangement which then looks centrosymmetric. A similar example of disorder has been briefly reported[12] for the structure of triclinic $(P(C_6H_5)_4)_2(W_3S_9)$.

The tetrahedral environment of W(2) is very slightly distorted. As a consequence of bonding, the terminal bonds (2.14(2)Å) are shorter than the chelating ones (2.25(2)Å). Both mean values are very close to those reported for the free $(WS_4)^{2-}$ ion[13] and for bis(tetrathiotungstato)complex.[14,15,16] The average value of the four bonds in the WS_4 group (2.195 Å) is in good agreement with the data published by Paulat-Boshen *et al.* for the $(Zn(WS_4)_2)^{2-}$ ion (2.195 Å). These first data show that the tetrahedral coordination of the tungsten(VI) is retained in the WS_4 ligand. Thus a (+VI) valence state is expected for the W(2) atom since tetrahedral coordination geometry is unambiguously characteristic of hexavalent tungsten.

The geometry about the W(1) atom is described as a distorted square pyramid. The four sulfur atoms form the basal plane and the Ost atom occupies the apical position. The central W(1) tungsten is displaced 0.615 Å from the basal plane toward the axial atom. The W(1)–W(2) and W(1)–W(2)^b distances are very short, so that steric interactions exist in the anion (respectively 3.018(2) and 2.932(2) Å). This feature leads to four asymmetric equatorial bond distances as shown in Table III. The dihedral angle between the S(1) W(1) S(2) and S(1) W(2) S(2) planes (153.8°) and the bond angles at the bridging sulfido ligands (79.76(2)° and 79.52(2)°) are in the range observed previously in Mo_2S_2 bridges.[3,4,11] The W–W interactions could explain why the W(2) atom lies 0.106 Å above the sulfur basal plane. For symmetry reasons, the W(2)^b atom is 0.106 Å under the basal plane.

The charge of the anion (determined by chemical titrations) and evidence of two hexavalent tungstens are consistent with a (+IV) formal valence state for the central pyramidal tungsten. Further, the complex is diamagnetic in solid state ($X = -360 \pm 30 \times 10^{-6}$ cgs) as well as in DMF or DMSO solution (no ESR signal). This diamagnetism is in agreement with a d^2 metal in a square pyramidal environment.[17] The absence of a ligand trans to the Ost atom and the position of the W(1) above the basal plane are consistent with π character for the W(1)Ost bond as usually found for d^2 square pyramidal oxocompounds. The apparent W(1)O distance of 1.83(2) Å was attributed to a crystallograpic oxygen–sulfur disorder. So, chemically, the studied species would be composed of the two equivalent ions $(WO(WS_4)_2)^{2-}$ and $(WS(WS_4)_2)^{2-}$ with sulfide replacing an oxo group. (The crystal might be considered as a partial solid solution of the two species.) The first step of the acidification of $(WS_4)^{2-}$ ion was the formation of $(WS(WS_4)_2)^{2-}$. In aqueous solution this reaction was followed by the formation of $(WO(WS_4)_2)^{2-}$.[18] So the occurrence of mixed species in crystals could be reasonably considered.

The P–C and C–C distances (1.80(2), 1.38(2) Å) in the $(P(C_6H_5)_4)^+$ ion are in the range reported for this cation in other compounds.[15] No deviation from planarity is observed in the phenyl rings.

IR Spectrum

Band assignments were made using three different cations $(P(C_6H_5)_4)^+$, $(N(C_2H_5)_4)^+$ and $(N(CH_3)_4)^+$ to avoid any cation–anion band overlap.

The presence of the W(1)O group is shown by a strong IR band at 972 cm^{-1}, characteristic of the terminal W–O stretching vibration.[19] No bands exist in the 700–800 cm^{-1} range which could be assigned to bridging oxygens.

The presence of the terminal tungsten sulfur W(2)-St is shown by a strong band at 495 cm^{-1}, whereas the 465 and 453 cm^{-1} bands are assigned to the W(1)-S-W(2) bridges.[19] As revealed by IR spectra, the $(N(CH_3)_4)^+$ and $(N(C_2H_5)_4)^+$ salts are free of $(WS(WS_4)_2)^{2-}$. No bands which could be assigned to the W(1)S vibration (about 525 cm^{-1})[12] is observed. (Presence of $(W_3S_9)^{2-}$ in $(P(C_6H_5)_4)^+$ structure crystal cannot be proved because of the strong cation band about 515 cm^{-1}.)

Electronic Spectrum

Electronic spectra were recorded from $((CH_3)_4N_2(WO(WS_4)_2)$. No intervalence transition is observed in the 2000–700nm range. This is consistent with a mixed valence complex belonging to the first class system.[20] The structure bonding shows that the W(1) and the W(2) atoms are located in two sites of different symmetry : the W(1) atom is in pyramidal ligand field with low spin (d^2 diamagnetic) whereas the W(2) atom is in a tetrahedral ligand field. The valence electrons are firmly trapped on each site, so no or little delocalization can occur. Moreover, the electronic exchange between the W(1) and W(2) tungsten atoms is not easy because of the very weak π character of the W(1)–S(1)–W(2) bond.

In the 700–200 nm range, four intense bands are observed in the $(W_3OS_8)^{2-}$ spectrum respectively at 445 nm ($\epsilon = 3.30\ 10^3$ 1 mol^{-1} cm^{-1}), 385 nm ($\epsilon = 7.35\ 10^3$ 1 mol^{-1} cm^{-1}), 275 nm (1.88 10^4 1 mol^{-1} cm^{-1}), 260 nm, whereas the free $(WS_4)^{2-}$ ion exhibits only two bands at 397 nm ($\epsilon = 1.80\ 10^4$ 1 mol^{-1} cm^{-1}) and 285 nm ($\epsilon = 2.65\ 10^4$ 1 mol^{-1} cm^{-1}). To assign the polyanion bands, complexes having the same bidentate chelating WS_4 group were prepared by the Muller *et al.* method,[13,16] and their spectra recorded. In all these last compounds, a central divalent cation is bonded to WS_4 groups as in $(WO(WS_4)_2)^{2-}$. Their spectra are very close to that of $WO(WS_4)_2{}^{2-}$ as shown in Table IV. From Table IV it appears that $WS_4{}^{2-}$ bands (395 and 283 nm) are systematically split by the central cation (Zn^{++}, Sn^{++}, WO^{++}). The four WS_4 equivalent sulfur atoms are separated into two groups, so two different charge transfer bands (S → W(VI)) can be observed.

TABLE IV

Complexes	λ_1(nm)	λ_2(nm)	λ_3(nm)	λ_4(nm)	ϵ_2
$(WS_4)^{2-}$	–	397	285	–	$1.8\ 10^4$
$(Zn(WS_4)_2)^{2-}$	455	385	275	270	$1.05\ 10^4$
$(Sn_2(WS_4)_4)^{4-}$	435	365	276	260	$3.95\ 10^3$
$(WO(WS_4)_2)^{2-}$	445	385	275	260	$7.35\ 10^3$

The terminal oxygen charge transfer (O → W(IV)) is located as a shoulder at 300 nm, in agreement with square pyramidal oxocompounds with a d^2 configuration.[21]

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