

83681-34-9; [Pt₂(μ-SPPPh₂)₂(PPh₃)₂], 67275-91-6; [Pt₂(μ-SPEt₂)₂(PPh₃)₂], 54020-36-9; [Pt₂(μ-SPCy₂)₂(PPh₃)₂], 74353-71-2; [Pd₂(μ-SPPPh₂)₂(PPh₃)₂], 67275-92-7; [Pt₂(μ-SPOEt₂)₂(PPh₃)₂], 83666-30-2.

Supplementary Material Available: The ³¹P{¹H} NMR spectrum

of [Pt₂(μ-SPEt₂)(P(OPh)₃)₂] and listings of all interatomic distances and angles, hydrogen positional parameters, anisotropic thermal parameters for non-hydrogen atoms, least-squares planes, and observed and calculated structure amplitudes (×10) (30 pages). Ordering information is given on any current masthead page.

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Substitution Derivatives of the Mixed-Valence [W₄O₈Cl₈(H₂O)₄]²⁻ Ion. Crystal and Molecular Structure of Cs₅NH₄[W₄O₈(NCS)₁₂]·6H₂O

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Mixed-valence complexes containing the W₄O₈⁶⁺ core have been prepared from [W₄O₈Cl₈(H₂O)₄]²⁻. These include [W₄O₈Cl₆(DMF)₆], [W₄O₈(NCS)₁₂]⁶⁻, and [W₄O₈(NCS)₄(C₂O₄)₄]⁶⁻. The cesium ammonium salt Cs₅NH₄[W₄O₈(NCS)₁₂]·6H₂O crystallizes in the orthorhombic space group *Pna*2₁ with *a* = 17.938 (3) Å, *b* = 13.395 (6) Å, *c* = 21.448 (9) Å, and *Z* = 4. The structure has been solved from 2354 observed reflections. Full-matrix least-squares refinements led to the final agreement factors *R* = 0.073 and *R*_w = 0.080. The [W₄O₈(NCS)₁₂]⁶⁻ anion exhibits a planar W₄O₄ ring. The terminal (unshared) oxygen atoms are found in a "chair" arrangement, which differs from the case of [W₄O₈Cl₈(H₂O)₄]²⁻. This could be explained by an interaction with Cs⁺ cations in the solid state. No crystallographic evidence for valence trapping has been observed.

Introduction

In the framework of a general study of mixed-valence compounds on an experimental¹ as well as a theoretical basis,² we have tried to prepare some new compounds containing a tetranuclear arrangement. In a previous paper, we described the structure and properties of the mixed-valence [W₄O₈Cl₈(H₂O)₄]²⁻ ion.³ This species is obtained by an equilibrated reaction between W^{VI}O₂Cl₄²⁻ and W^VOCl₅²⁻ in concentrated hydrochloric acid. Its crystal structure shows a nearly planar square of four tungsten atoms linked by linear oxygen bridges. In addition, each tungsten atom is linked to a terminal unshared oxygen atom so that the actual mixed-valence moiety is W₄O₈⁶⁺. This square arrangement can be considered as a fragment of the perovskite structure of tungsten bronzes. The main interest of this compound resides in its electronic structure: owing to the presence of two tungsten(VI) and two tungsten(V) ions, it can exhibit both mixed-valence and exchange-interaction properties. This is the subject of a detailed treatment that will be published elsewhere.⁴

In order to develop the chemistry of this unique compound, we have prepared several substitution derivatives. Although the [W₄O₈Cl₈(H₂O)₄]²⁻ ion does not present great thermodynamic stability since it equilibrates in solution with the monomeric W^V and W^{VI} complexes, it can be used as a starting material to prepare other compounds containing the mixed-valence W₄O₈⁶⁺ core. We have thus prepared the species [W₄O₈Cl₆(DMF)₆], [W₄O₈(NCS)₁₂]⁶⁻, and [W₄O₈(NCS)₄(C₂O₄)₄]⁶⁻ and solved the structure of the thiocyanate complex. This complex was the only one that gave crystals suitable for an X-ray study. The structure showed an unexpected stereochemical change of the W₄O₈⁶⁺ geometry, due to a different disposition of unshared oxygen atoms.

Experimental Section

Synthesis from [W₄O₈Cl₈(H₂O)₄]²⁻. All experiments were performed under a nitrogen or argon atmosphere.

[W₄O₈Cl₆(DMF)₆]·2DMF. A 1.41-g sample of (HNMe₂)₂[W₄O₈Cl₈(H₂O)₄]·2H₂O³ (1.02 mmol) was dissolved in 100 mL of *N,N*-dimethylformamide. The resulting deep blue solution was filtered off to eliminate a small residue and then precipitated by 750 mL of ethyl acetate. The precipitate was filtered off, dried under vacuum for 2 days, and finally ground. Anal. Calcd: W, 44.28; Cl, 12.81; N, 6.75; C, 17.36; H, 3.40. Found: W, 44.66; Cl, 13.31; N, 6.43; C, 15.82; H, 3.53.

Cs₅NH₄[W₄O₈(NCS)₁₂]·6H₂O. To 500 mL of an aqueous solution of NH₄SCN (5 mol dm⁻³) and HCl (0.05 mol dm⁻³) was added 4.16 g of (HNMe₂)₂[W₄O₈Cl₈(H₂O)₄]·2H₂O (3 mmol). The solution was filtered to remove a trace of undissolved chloride complex, and 20 g of cesium chloride was slowly added under stirring. Very small crystals appeared after 2 days at 0 °C and were washed with absolute ethanol and ether. Crystals for X-ray work were obtained by a modified procedure, using 50 mL of a solution of NH₄SCN (3 mol dm⁻³) and HCl (0.1 mol dm⁻³), 0.412 g of the chloride complex, and 2 g of CsCl. The solution was heated to 60 °C until the precipitate redissolved and then slowly cooled down first to 35 °C and then from 35 to 20 °C at a rate of 3 °C/day. Beautiful blue crystals with an orange metallic luster were obtained after several days. Anal. Calcd: W, 31.28; Cs, 28.26; S, 16.36; C, 6.13; N, 7.75; H, 0.69. Found: W, 32.44; Cs, 29.09; S, 16.68; C, 6.62; N, 7.83; H, 0.72. The presence of NH₄⁺ was confirmed by IR spectroscopy (bands at 3120 and 1400 cm⁻¹). The number of crystallization water molecules was determined by NMR⁵ as follows. The thiocyanate complex was dissolved in (C²H₅)₂SO to a concentration of 5.2 × 10⁻² mol dm⁻³ and the spectrum recorded. A triplet with *J* = 50 Hz was observed at 6.95 ppm (with respect to hexamethyldisiloxane), corresponding to the NH₄⁺ protons interacting with the ¹⁴N nucleus, while the signal corresponding to crystallization water molecules was observed at 3.20 ppm. After taking into account the residual water of the solvent, we used this peak to determine the number of water molecules by comparison with a reference peak provided by a known amount of CHCl₃. This procedure yielded six molecules of crystallization water per formula unit.

(C₉H₇N)₅(NMe₄)[W₄O₈(NCS)₄(C₂O₄)₄]·3H₂O. The preceding preparation was repeated, but the precipitation of [W₄O₈(NCS)₁₂]⁶⁻ was carried out by NMe₄⁺ instead of Cs⁺. A 600-mg sample of the tetramethylammonium salt was dissolved in 50 mL of H₂C₂O₄ (1 mol dm⁻³), and the solution was precipitated by 400 mg of quinoline

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Table I. Crystal Data

$a = 17.938 (3) \text{ \AA}^a$	fw: 2351
$b = 13.395 (6) \text{ \AA}$	$d_{\text{calcd}} = 3.03 \text{ g cm}^{-3}$
$c = 21.448 (9) \text{ \AA}$	$d_{\text{measd}} = 2.98^b \text{ g cm}^{-3}$
cryst system: orthorhombic	$Z = 4$
space group: $Pna2_1$	$F(000) = 612$

radiation: Mo K α ($\lambda = 0.71069 \text{ \AA}$)
 scan mode: $\theta-2\theta$
 Bragg range: $0-21^\circ$
 scan range: 1.2° in Bragg angle
 scan rate: $0.8^\circ/\text{min}$ in Bragg angle
 bkgd: 18 s before and after each reflcn in fixed positions
 no. of measd reflns: 2490 at room temp
 no. of reflns kept for refinement ($F > 3\sigma$): 2354
 std check reflns: 060, 026, monitored every 50 reflns cor for decrease in intens found necessary
 cryst dimens: $0.14 \times 0.26 \times 0.50 \text{ mm}$
 abs coeff: 13.95 mm^{-1}
 transmission factor range: 0.033-0.178

^a Unit cell parameters were obtained from a least-squares refinement based upon the setting angles of 10 intense reflections.
^b Flotation; mixture of $\text{C}_2\text{H}_4\text{I}_2$ and $\text{C}_2\text{H}_2\text{Br}_4$.

hydrochloride. The blue precipitate was filtered off and washed with cold water, alcohol, and finally acetone. Anal. Calcd: W, 33.02; S, 5.76; N, 6.29; C, 32.90; H, 2.60. Found: W, 32.94; S, 5.36; N, 5.82; C, 33.23; H, 2.51; $\text{C}_2\text{O}_4^{2-}/\text{W}$ by gravimetry of CaC_2O_4 : 0.91.

Crystal Structure Solution of $\text{Cs}_5\text{NH}_4[\text{W}_4\text{O}_8(\text{NCS})_{12}]\cdot 6\text{H}_2\text{O}$

A crystal of the thiocyanate compound was mounted in a Pyrex tube under argon. The parameters relevant to the space group determination and data collection are gathered on Table I. Computations were performed with use of standard programs.⁶ Scattering factors were taken from ref 7, including $\Delta f'$ and $\Delta f''$ for tungsten and cesium. Full-matrix least-squares methods were used to minimize $\sum (w||F_o| - |F_c||^2)$, where $w = 1/\sigma$. Before the completion of the structure, since the intensity diffracted by the crystal was rather weak, another set of data was collected with a second crystal. However, the results of least-squares refinements were poorer so that the results presented here are those obtained from the first crystal.

The structure was solved by the Patterson method. Systematic extinctions were consistent with either the centrosymmetric $Pnma$ or the noncentrosymmetric $Pna2_1$ space group. The analysis of the Patterson map ruled out the first possibility so that the $Pna2_1$ group was chosen. The four tungsten atoms were then found crystallographically independent in general positions. Least-squares refinement of their coordinates yielded $R_w = 0.37$. A tungsten-phased Fourier series then showed six main peaks corresponding to the Cs^+ cations. Since there were only five Cs^+ in the formula, a statistical disorder was assumed. Upon refinement with a Cs^+ cation located on each peak position, the R_w factor dropped to 0.21. However, two of the six positions gave large thermal parameter values. If all thermal parameters were fixed at a same reasonable value and the occupancy factors refined, then these two positions gave occupancy factors near 0.6. It was thus considered that four positions were fully occupied by Cs^+ ions, and the remaining two by a statistical mixture of Cs^+ and NH_4^+ ions in a 50/50 ratio. At this stage, R_w was 0.18. Then all remaining atoms were found on a Fourier map. After absorption correction and anisotropic refinement of the tungsten, cesium, and sulfur atoms, the final agreement factors were $R = 0.073$ and $R_w = 0.08$. Atomic parameters with their standard deviations are given in Table II, and chemically significant interatomic distances and angles in Tables III and IV.

Results and Discussion

Conservation of the Mixed-Valence $\text{W}_4\text{O}_8^{6+}$ Moiety. Several compounds have been obtained from the $[\text{W}_4\text{O}_8\text{Cl}_8(\text{H}_2\text{O})_4]^{2-}$ ion. They display analogous properties, suggesting that the mixed-valence moiety has been preserved during the reaction.

In the strongly donor solvent DMF, substitution of the water molecules and of some chloride ligands occurs. Several species

Table II. Fractional Atomic Coordinates^a

atom	x	y	z
W(1)	0.2653 (1)	-0.0453 (2)	0.1862 (1)
W(2)	0.0863 (1)	0.0430 (2)	0 ^b
W(3)	0.1558 (1)	0.1785 (2)	0.1394 (2)
W(4)	0.1965 (1)	-0.1811 (2)	0.0456 (2)
O(1)	0.350 (2)	0.000 (3)	0.162 (2)
O(2)	0.004 (2)	0.024 (2)	0.032 (2)
O(3)	0.065 (2)	0.168 (3)	0.179 (2)
O(4)	0.265 (2)	-0.171 (3)	0.004 (2)
O(5)	0.136 (2)	-0.069 (2)	0.024 (1)
O(6)	0.234 (2)	-0.114 (2)	0.116 (1)
O(7)	0.200 (2)	0.065 (3)	0.168 (2)
O(8)	0.127 (2)	0.115 (3)	0.066 (1)
O(9) ^c	0.122 (3)	-0.087 (4)	0.445 (2)
O(10) ^c	0.485 (4)	-0.074 (5)	0.262 (3)
S(1)	0.415 (1)	0.258 (2)	0.087 (1)
S(2)	-0.0534 (9)	-0.266 (1)	0.1225 (9)
S(3)	-0.023 (1)	-0.106 (1)	-0.1801 (8)
S(4)	0.030 (1)	0.368 (1)	-0.0788 (8)
S(5)	0.0135 (9)	-0.352 (1)	-0.077 (1)
S(6)	0.070 (1)	0.508 (1)	0.096 (1)
S(7)	0.292 (1)	-0.507 (1)	0.105 (1)
S(8)	0.321 (2)	0.369 (1)	0.274 (1)
S(9)	0.352 (1)	-0.336 (1)	0.295 (1)
S(10)	0.325 (1)	0.137 (3)	-0.100 (1)
S(11)	0.057 (1)	-0.181 (2)	0.308 (1)
S(12)	0.277 (2)	0.098 (3)	0.392 (1)
N(1)	0.267 (4)	0.207 (5)	0.099 (3)
N(2)	0.099 (2)	-0.226 (3)	0.107 (2)
N(3)	0.060 (2)	-0.022 (3)	-0.082 (2)
N(4)	0.044 (4)	0.174 (6)	-0.038 (3)
N(5)	0.131 (2)	-0.264 (3)	-0.014 (2)
N(6)	0.130 (3)	0.320 (4)	0.103 (2)
N(7)	0.235 (2)	-0.318 (3)	0.077 (2)
N(8)	0.199 (4)	0.260 (6)	0.215 (4)
N(9)	0.304 (3)	-0.173 (4)	0.229 (2)
N(10)	0.191 (3)	0.090 (4)	-0.049 (3)
N(11)	0.156 (4)	-0.114 (5)	0.236 (3)
N(12)	0.290 (3)	0.009 (5)	0.276 (3)
C(1)	0.327 (5)	0.232 (7)	0.091 (4)
C(2)	0.038 (3)	-0.241 (4)	0.117 (2)
C(3)	0.028 (3)	-0.062 (4)	-0.120 (2)
C(4)	0.043 (3)	0.254 (5)	-0.056 (3)
C(5)	0.081 (2)	-0.305 (3)	-0.041 (2)
C(6)	0.102 (3)	0.403 (4)	0.095 (2)
C(7)	0.262 (3)	-0.403 (4)	0.086 (3)
C(8)	0.265 (4)	0.291 (6)	0.242 (3)
C(9)	0.334 (3)	-0.245 (4)	0.260 (2)
C(10)	0.245 (3)	0.102 (4)	-0.073 (3)
C(11)	0.110 (4)	-0.134 (5)	0.265 (3)
C(12)	0.276 (4)	0.051 (5)	0.326 (3)
Cs(1)	-0.0303 (3)	-0.0161 (3)	0.1810 (2)
Cs(2)	0.1083 (3)	0.1483 (4)	0.4717 (3)
Cs(3)	0.3935 (3)	-0.0001 (4)	0.0257 (3)
Cs(4)	0.3390 (3)	0.1100 (5)	0.7311 (3)
CsN(1)	0.4504 (5)	0.1526 (5)	0.2449 (4)
CsN(2)	0.2812 (4)	-0.1524 (6)	0.4624 (4)

^a Estimated standard deviations in parentheses refer to the last digit. ^b Since the space group was polar in z, this coordinate was arbitrarily fixed to zero. ^c Crystallization water molecules.

may exist in the solution, but the precipitation with a weakly polar solvent (diethyl ether, ethyl acetate) selectively yields the uncharged compound $[\text{W}_4\text{O}_8\text{Cl}_6(\text{DMF})_6]$.

The thiocyanate complex can be obtained in aqueous solution. The starting chloride complex hydrolyzes in pure water with precipitation of blue hydrated oxides. However, this reaction is avoided in the presence of NCS^- ions in acid medium and a stable solution is obtained. A spectrophotometric study then shows that its composition is rather complicated. Besides the mixed-valence complex, the mononuclear $[\text{W}^{\text{VO}}(\text{NCS})_5]^{2-}$ ion can be identified by its intense band at 400 nm .⁸ However, the precipitation with Cs^+ selectively yields

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Table III. Interatomic Distances (Å) with Estimated Standard Deviations in Parentheses

	Coordination around Tungsten Atoms							
	W(1)		W(2)		W(3)		W(4)	
oxygen atoms								
terminal	O(1)	1.72 (4)	O(2)	1.65 (3)	O(3)	1.83 (4)	O(4)	1.53 (4)
equatorial (bridging)	O(6)	1.84 (3)	O(5)	1.82 (3)	O(7)	1.82 (3)	O(6)	1.89 (3)
	O(7)	1.93 (3)	O(8)	1.86 (3)	O(8)	1.87 (3)	O(5)	1.91 (3)
nitrogen atoms								
axial	N(11)	2.41 (7)	N(10)	2.24 (6)	N(1)	2.21 (7)	N(2)	2.28 (4)
equatorial	N(9)	2.07 (5)	N(3)	2.01 (4)	N(6)	2.10 (5)	N(5)	2.07 (4)
	N(12)	2.11 (6)	N(4)	2.08 (8)	N(8)	2.10 (8)	N(7)	2.07 (4)
tungsten displacement ^a	0.25		0.18		0.27		0.16	
	Tungsten-Tungsten Distances							
W(1)-W(3)	3.72 (4)	W(3)-W(2)	3.71 (3)	W(2)-W(4)	3.72 (2)	W(4)-W(1)	3.73 (3)	
	Distances in the Thiocyanate Ligands							
	W(1)		W(2)		W(3)		W(4)	
nitrogen-carbon								
axial	N(11)-C(11)	1.08 (7)	N(10)-C(10)	1.11 (7)	N(1)-C(1)	1.1 (1)	N(2)-C(2)	1.12 (6)
equatorial	N(9)-C(9)	1.29 (7)	N(3)-C(3)	1.13 (6)	N(6)-C(6)	1.22 (7)	N(5)-C(5)	1.20 (6)
	N(12)-C(12)	1.23 (9)	N(4)-C(4)	1.13 (8)	N(8)-C(8)	1.4 (1)	N(7)-C(7)	1.25 (7)
carbon-sulfur								
axial	C(11)-S(11)	1.47 (7)	C(10)-S(10)	1.61 (6)	C(1)-S(1)	1.6 (1)	C(2)-S(2)	1.68 (5)
equatorial	C(9)-S(9)	1.46 (6)	C(3)-S(3)	1.70 (6)	C(6)-S(6)	1.53 (6)	C(5)-S(5)	1.57 (5)
	C(12)-S(12)	1.55 (7)	C(4)-S(4)	1.63 (7)	C(8)-S(8)	1.62 (8)	C(7)-S(7)	1.55 (6)

^a Distance with respect to the mean plane defined by the two bridging oxygens and the two equatorial nitrogen ligands.

Table IV. Bond Angles (deg)

Angles around Tungsten Atoms								
O(1)-W(1)-O(6)	101 (2)	O(2)-W(2)-O(5)	101 (2)	O(3)-W(3)-O(7)	100 (2)	O(4)-W(4)-W(5)	105 (2)	
O(1)-W(1)-O(7)	102 (2)	O(2)-W(2)-O(8)	97 (2)	O(3)-W(3)-O(8)	97 (2)	O(4)-W(4)-O(6)	98 (2)	
O(6)-W(1)-O(7)	92 (1)	O(5)-W(2)-O(8)	91 (1)	O(7)-W(3)-O(8)	91 (1)	O(5)-W(4)-O(6)	91 (1)	
N(9)-W(1)-N(1)	76 (2)	N(3)-W(2)-N(4)	87 (2)	N(1)-W(3)-N(6)	84 (2)	N(2)-W(4)-N(5)	77 (1)	
N(9)-W(1)-N(12)	79 (2)	N(3)-W(2)-N(10)	85 (2)	N(1)-W(3)-N(8)	83 (3)	N(2)-W(4)-N(7)	80 (1)	
N(11)-W(1)-N(12)	84 (2)	N(4)-W(2)-N(10)	83 (2)	N(6)-W(3)-N(8)	84 (3)	N(5)-W(4)-N(7)	85 (2)	
O(1)-W(1)-N(9)	98 (2)	O(2)-W(2)-N(3)	95 (2)	O(3)-W(3)-N(6)	92 (2)	O(4)-W(4)-N(5)	98 (2)	
O(1)-W(1)-N(12)	88 (2)	O(2)-W(2)-N(4)	89 (2)	O(3)-W(3)-N(8)	90 (2)	O(4)-W(4)-N(7)	90 (2)	
O(6)-W(1)-N(9)	93 (2)	O(5)-W(2)-N(3)	91 (1)	O(7)-W(3)-N(1)	83 (2)	O(5)-W(4)-N(2)	85 (1)	
O(6)-W(1)-N(11)	86 (2)	O(5)-W(2)-N(10)	88 (2)	O(7)-W(3)-N(8)	91 (2)	O(5)-W(4)-N(5)	87 (1)	
O(7)-W(1)-N(11)	84 (2)	O(8)-W(2)-N(4)	90 (2)	O(8)-W(3)-N(1)	90 (2)	O(6)-W(4)-N(2)	86 (1)	
O(7)-W(1)-N(12)	93 (2)	O(8)-W(2)-N(10)	83 (2)	O(8)-W(3)-N(6)	92 (2)	O(6)-W(4)-N(7)	92 (2)	
O(1)-W(1)-N(11)	171 (2)	O(2)-W(2)-N(10)	171 (2)	O(3)-W(3)-N(1)	173 (2)	O(4)-W(4)-N(2)	169 (2)	
O(6)-W(1)-N(12)	168 (2)	O(5)-W(2)-N(4)	170 (2)	O(7)-W(3)-N(6)	167 (2)	O(5)-W(4)-N(7)	164 (2)	
O(7)-W(1)-N(9)	159 (2)	O(8)-W(2)-N(3)	168 (2)	O(8)-W(3)-N(8)	172 (2)	O(6)-W(4)-N(5)	164 (1)	
	Angles around Bridging Oxygen Atoms							
W(2)-O(5)-W(4)	175 (2)	W(1)-O(6)-W(4)	176 (2)	W(1)-O(7)-W(3)	167 (2)	W(2)-O(8)-W(3)	171 (2)	
	Angles around Nitrogen Atoms							
C(11)-N(11)-W(1)	168 (6)	C(10)-N(10)-W(2)	172 (5)	C(1)-N(1)-W(3)	165 (7)	C(2)-N(2)-W(4)	154 (4)	
C(9)-N(9)-W(9)	173 (4)	C(3)-N(3)-W(2)	162 (4)	C(6)-N(6)-W(3)	164 (4)	C(5)-N(5)-W(4)	167 (3)	
C(12)-N(12)-W(1)	155 (5)	C(4)-N(4)-W(2)	160 (6)	C(8)-N(8)-W(3)	143 (6)	C(7)-N(7)-W(4)	169 (4)	
	Angles around Carbon Atoms							
S(11)-C(11)-N(11)	168 (7)	S(10)-C(10)-N(10)	170 (6)	S(1)-C(1)-N(1)	172 (9)	S(2)-C(2)-N(2)	173 (5)	
S(9)-C(9)-N(9)	168 (5)	S(3)-C(3)-N(3)	172 (5)	S(6)-C(6)-N(6)	171 (5)	S(5)-C(5)-N(5)	176 (4)	
S(12)-C(12)-N(12)	167 (6)	S(4)-C(4)-N(4)	174 (7)	S(8)-C(8)-N(8)	156 (7)	S(7)-C(7)-N(7)	174 (5)	

the mixed-valence compound, which can then be used to prepare the last complex $[W_4O_8(NCS)_4(C_2O_4)]^{6-}$.

For all four complexes, a characteristic UV-visible spectrum is observed with two intense bands near 550 and 700 nm (Figure 1). The analogy of these spectra strongly suggests the presence of the same $W_4O_8^{6+}$ chromophore in the studied compounds. The high values of the extinction coefficients are characteristic of intervalence transitions for strongly delocalized systems. A detailed discussion of the optical spectrum of $[W_4O_8Cl_8(H_2O)_4]^{2-}$ will be published elsewhere. Herein, we will only point out the particularly high extinction coefficients for the thiocyanate complex ($\epsilon \approx 40\,000$, i.e., about

twice the value of the three others). This can be qualitatively explained by some delocalization in the thiocyanate π system. The intensity of an intervalence transition depends on the distance R between metal orbitals centered on different sites. Thus, any delocalization in an extended π system such as NCS^- increases the effective R distance and consequently the intensity.

Of the three new complexes presented here, only the thiocyanate compound could be obtained as single crystals. The structure, which is discussed below, effectively shows that it contains a $W_4O_8^{6+}$ moiety. However, its geometry was found slightly different from the case of $[W_4O_8Cl_8(H_2O)_4]^{2-}$.

Crystal Structure of $[W_4O_8(NCS)_{12}]^{6-}$. The crystal structure is made of $[W_4O_8(NCS)_{12}]^{6-}$ anions, Cs^+ and NH_4^+ cations, and crystallization water molecules. Only two out of the six

(8) Sabat, H.; Rudolf, M. F.; Jezowska-Trzebiatowska, B. *Inorg. Chim. Acta* 1973, 7, 365.

Table V. Nearest-Neighbor Distances (Å) for Cs(1) and Cs(3)^a

	Cs(1)				Cs(3)			
	O(3)	O(2)	S(2)	S(11)	O(1)	O(4)	S(10)	S(1)
neighbors belonging to the same molecule (equiv position x, y, z)	3.01	3.29	3.60	3.84	3.02	3.28	3.49	3.72
neighbors belonging to other molecules	S(3) ^a 3.53	S(7) ^b 3.59	S(9) ^b 3.84	S(8) ^c 3.87	S(6) ^d 3.51	S(5) ^e 3.65	S(4) ^d 3.75	S(2) ^e 3.87

^a Symmetry codes: (a) $\bar{x}, \bar{y}, 1/2 + z$; (b) $-1/2 + x, -1/2 - y, z$; (c) $-1/2 + x, 1/2 - y, z$; (d) $1/2 + x, 1/2 - y, z$; (e) $1/2 + x, -1/2 - y, z$.

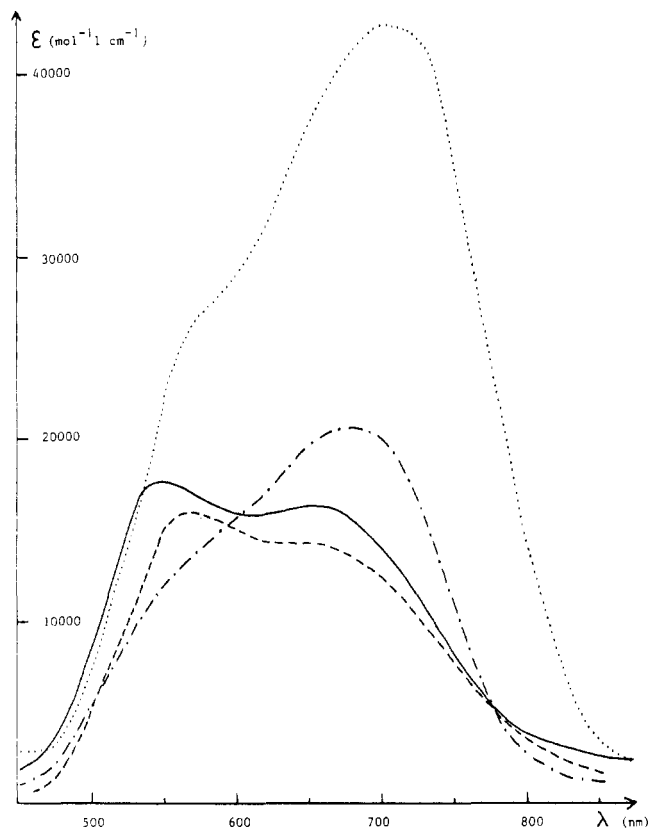


Figure 1. Electronic spectra of $[W_4O_8Cl_8(H_2O)_4]^{2-}$ (—), $[W_4O_8Cl_8(DMF)_6]$ (---), $[W_4O_8(NCS)_{12}]^{6-}$ (····), and $[W_4O_8(NCS)_4(C_2O_4)_4]^{6-}$ (— · — · —).

water molecules could be clearly seen on Fourier difference maps, suggesting that the remaining four are statistically disordered.

The unit cell is drawn in Figure 2, which shows the arrangement of the four $[W_4O_8(NCS)_{12}]^{6-}$ anions. Each anion is built around a square of four tungsten atoms. The anions are related by glide planes and helicoidal axes. Since the W_4

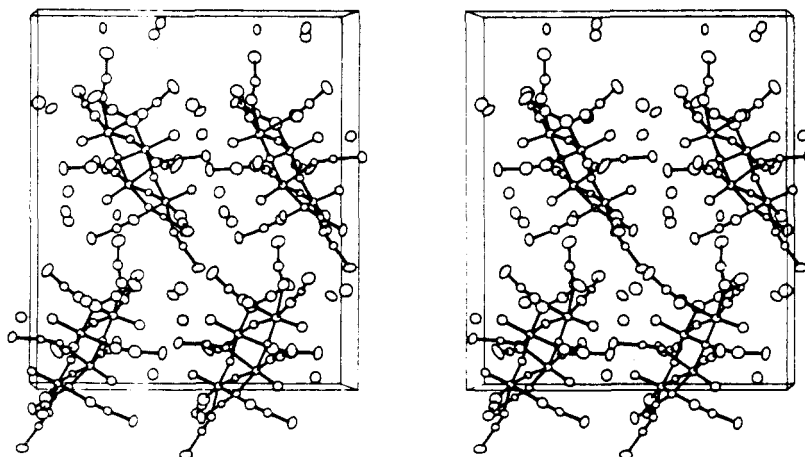


Figure 2. Stereoscopic view of the unit cell along the b axis.

square planes are not parallel to the crystallographic axes, a complicated disposition results where no privileged orientation can be recognized.

The $[W_4O_8(NCS)_{12}]^{6-}$ anion is drawn in Figure 3. It can be considered as the association of four $WO_3(NCS)_3$ octahedra sharing corners. Contrary to the case of $[W_4O_8Cl_8(H_2O)_4]^{2-}$, the four tungsten atoms are very close to their mean plane, the deviations not exceeding 0.05 Å. Each tungsten atom is coordinated to two bridging oxygens, one unshared (oxo type) oxygen, and two "equatorial" and one "axial" N-bonded thiocyanate ligands. As usual for oxo complexes of tungsten, the metal atom is not found at the center of the coordination octahedron but is shifted toward the terminal unshared oxygen atom. The deviations with respect to the mean plane defined by the two bridging oxygens and the two equatorial nitrogen atoms range from 0.16 to 0.27 Å (see Table III). This displacement is also clearly apparent when the equatorial W–N distances (average value 2.08 Å) and the axial ones (2.28 Å) are compared. This is a consequence of the existence of a strong tungsten-unshared oxygen bond with a double-bond character that weakens the trans W–N bond.

The disposition of the terminal oxygen atoms is different from the case of $[W_4O_8Cl_8(H_2O)_4]^{2-}$. While in this latter compound they were found alternately above and below the molecular plane, in the present case they exhibit a "chair" arrangement (see Figure 4). It follows that the displacements of the tungsten atoms in the direction of the unshared oxygens do not oppose the planarity of the W_4 square.

The remaining distances have normal values. In particular, the tungsten-bridging oxygen distances (average 1.87 Å) show the occurrence of a π character as in the chloride complex.

A question now arises: Why do the terminal oxygen atoms adopt different arrangements in the two complexes? No obvious explanation can be derived from the electronic structures. We think that a partial answer can be found for the thiocyanate complex by inspection of the crystal structure and particularly the cation-anion interactions. Of the four sites occupied by Cs^+ cations, two (Cs(1) and Cs(3)) are in a remarkable disposition with respect to the anion. For instance Cs(1) is found above the W_4 square, in contact with two

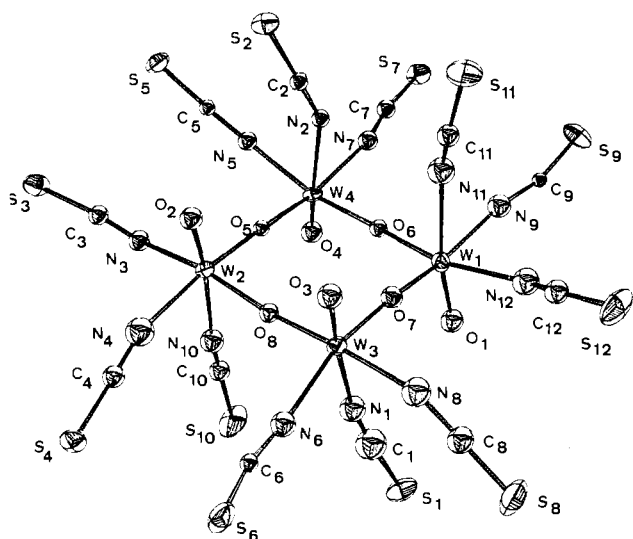


Figure 3. Structure of the $[\text{W}_4\text{O}_8(\text{NCS})_{12}]^{6-}$ anion.

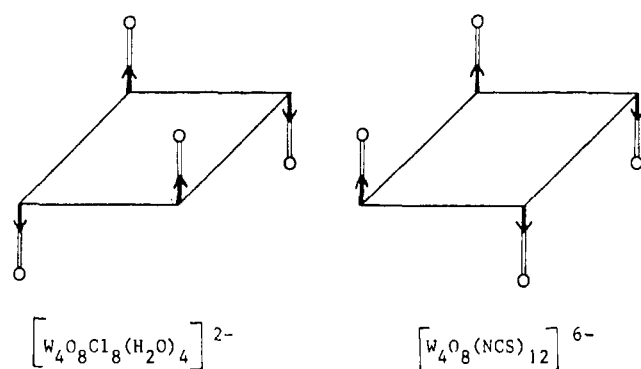


Figure 4. Sketch of the two possible configurations of the $\text{W}_4\text{O}_8^{6+}$ core. The arrows show the displacements of the tungsten atoms with respect to a regular octahedral coordination.

unshared oxygens O(2) and O(3) and also with the two terminal sulfurs S(2) and S(11) belonging to axial thiocyanate ligands (see Figure 5 and Table V where the cesium nearest-neighbor distances are given). This geometry is reminiscent of the perovskite structure of tungsten bronzes, where the alkaline cation projects on the center of a W_4 square. However, in the present case, owing to its size, the Cs^+ cation cannot be found exactly above the center of the square. Instead it is shifted toward the W(2)–W(3) edge (see Figure 5). This disposition where the Cs^+ cation is in contact with four atoms of the same anion could stabilize the “chair” arrangement in the solid state since an analogous interaction is impossible for the “alternate” configuration. Of course, no conclusion can be drawn for the species in solution where interconversion of the two forms could take place.

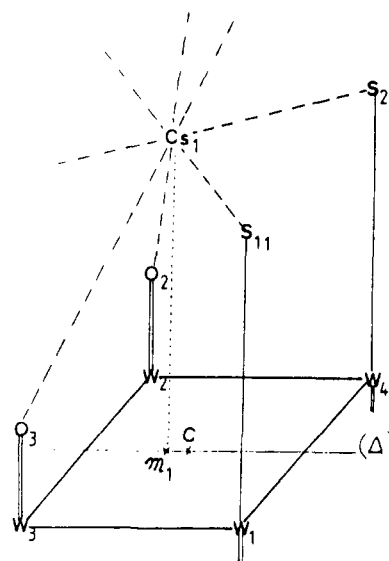


Figure 5. Coordination around the $\text{Cs}(1)^+$ cation. Δ is the common mediatrix of the W(3)–W(2) and W(4)–W(1) edges. The projection m_1 of Cs(1) on the W(1)W(2)W(3)W(4) plane is located at 1.0 Å from the center of the square.

Finally, the question of electron localization or delocalization in this mixed-valence complex can be discussed. Since the four tungsten atoms are crystallographically independent, one could observe differences in bond lengths in the case of a trapped-valence (class II) system. These differences should concern the tungsten–bridging oxygen and tungsten–equatorial nitrogen distances, because W^{V} has an extra electron in a d_{xy} orbital perpendicular to the tungsten–terminal oxygen direction. Inspection of Table III shows that this is not observed: In view of the standard deviations, no significant and systematic variation in the bond lengths around two tungsten atoms can be detected. This cannot be used as proof of a class III (delocalized) character since this effect could be buried by a static or dynamic disorder. At present, there is no simple experiment that could definitely prove the localized or delocalized character. However, the structure shows that a good overlap between tungsten d_{xy} orbitals and bridging oxygen 2p orbitals is possible so that the electronic interaction must be important. Furthermore, the intensity of the intervalence band is very high in all these complexes. This leads us to describe them rather as delocalized systems.

Registry No. $[\text{W}_4\text{O}_8\text{Cl}_6(\text{dmf})_6]$, 83781-16-2; $(\text{HNMe}_3)_2[\text{W}_4\text{O}_8\text{Cl}_8(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, 65027-46-5; $\text{Cs}_5\text{NH}_4[\text{W}_4\text{O}_8(\text{NCS})_{12}] \cdot 6\text{H}_2\text{O}$, 83781-17-3; $(\text{C}_9\text{H}_8\text{N})_5(\text{NMe}_4)[\text{W}_4\text{O}_8(\text{NCS})_4(\text{C}_2\text{O}_4)_4]$, 83781-20-8.

Supplementary Material Available: Listings of anisotropic and isotropic thermal parameters and observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.