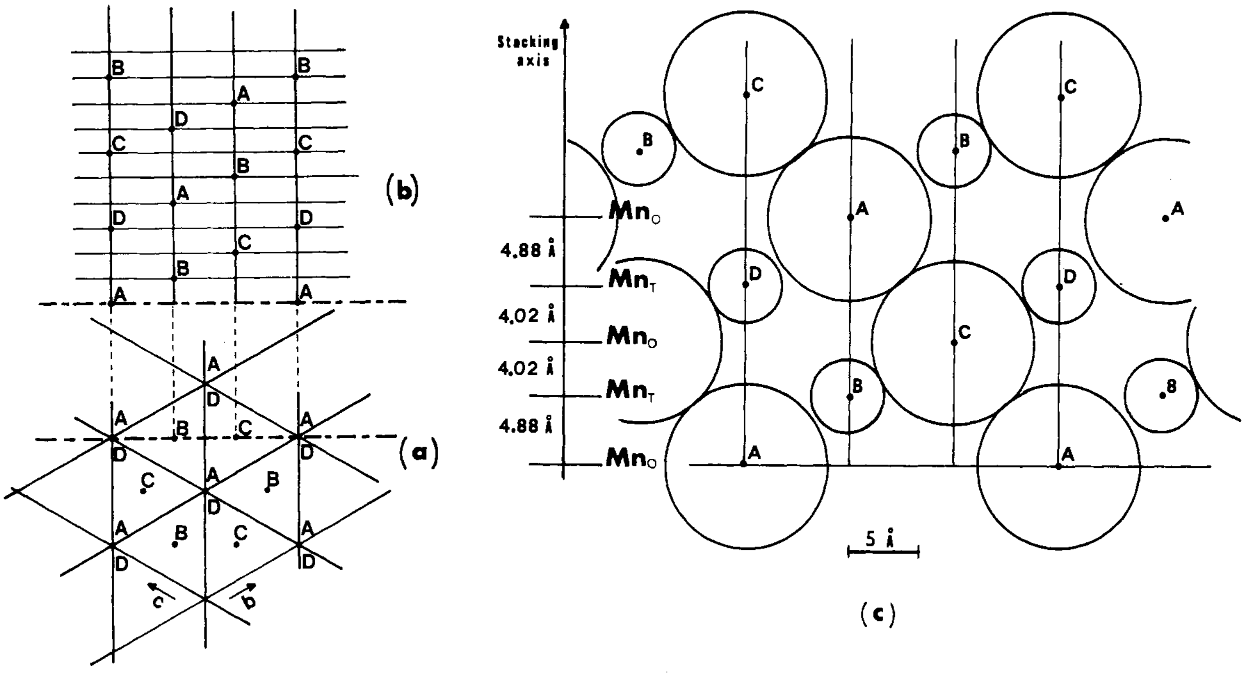

**Figure 2.** (a) Projection on the ($\vec{b},\vec{c}$) plane of centers of octahedral and tetrahedral spheres showing a like close-packed cubic arrangement (four successive levels only): (A and C) $Mn_O$, centers of octahedral spheres; (B and D) $Mn_T$, centers of tetrahedral spheres. (b) Elevation showing the layers (horizontal lines) viewed in the stacking direction. (c) Scale drawing of sphere layers along the stacking axis.

structure thermal parameter *B* (especially for ethyl carbons).

Moreover, considering the tetrahedral and octahedral groups as two kinds of spheres (with radii of about 2.5 and 6 Å, respectively), we studied the stacking of this ionic structure. From a projection on the ($\vec{b},\vec{c}$) plane of the central manganese atoms (of any sort), it can be described as a close-packed cubic structure, with staggered octahedral ($Mn_O$) and tetrahedral $Mn_T$) sphere layers. These are schematized in Figure 2a,b. It is worth noting that the densest possible packing is carried out, as sequences of bulky ACAC spheres in contact on the one hand and alternative bulky cations and smaller anions ABCD on the other hand. Octahedral and tetrahedral sphere layers along the stacking axis are separated by 4.88 and 4.02 Å, as shown in Figure 2c.

In conclusion, we have confirmation of a rare mixed tetrahedral–octahedral structure, which, to our knowledge, has not been previously reported in Mn(II) complexes. From powder patterns, the complex $[Mn(deu)_6][MnCl_4]$ is assumed to be isostructural.

Various conformations in the same complex have only been reported for Co(II) and Ni(II).[25,26] Hitherto, geometrical data on the tetrahedral $[MnBr_4]^{2-}$ anion were unknown, as in other transition-metal tetrabromides; in contrast, several were known for $[MCl_4]^{2-}$ (M = Ni(II), Co(II), Zn(II), Cu(II)[27-33] and the Mn–Cl distance in $[MnCl_4]^{2-}$ was just approximately given.[34] From all these structural results and thermodynamic ones,[35] we could attribute to Mn–Br a bond energy of ca. 560 kJ $mol^{-1}$.[3]

On the other hand, the destruction of planarity in deu molecules (when two $CH_3$ groups are added in chain ends of dmu) seems to hinder a trigonal-bipyramidal environment,[1] and moreover the bulkier $[Mn(deu)_6]^{2+}$ cation stabilizes the $[MnBr_4]^{2-}$ anion whereas $[Mn(dmu)_6]^{2+}$ does not;[3] however, these two octahedral cations exist, associated with iodide and perchlorate anions.[2,36]

**Acknowledgment.** We thank Dr Cl. Pascard (Gif-Sur-Yvette, France) for the use of the automated diffractometer and Dr J. Guilhem (Gif-sur-Yvette, France) for assistance in structure refinement.

**Registry No.** $[Mn(deu)_6]^{2+}[MnBr_4]^{2-}$, 41586-60-1.

**Supplementary Material Available:** A perspective view of packing in the unit cell and tables of all crystal data and collection parameters, anisotropic thermal parameters and root-mean-square displacements of heavy atoms, fractional coordinates of hydrogen atoms, hydrogen bonds and intermolecular contacts with principal angles between $[Mn(deu)_6][MnBr_4]$ asymmetric units, least-squares planes of the OCNN urea skeleton, dihedral angles giving *N,N'*-diethylurea conformations, and lattice spacings for $[Mn(deu)_6][MnX_4]$ (X = Br, Cl) (8 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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## Synthesis and Structural Characterization of a New Polymorph of Tungsten(VI) Sulfide Tetrachloride, $WSCl_4$

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Interest in tungsten(VI) tetrahalide oxides and chalcogenides stems in part from their versatility as starting materials for synthesis[1] as well as from curiosity concerning the diverse structural forms that they adopt. Infrared data indicate that the

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[1] (a) Drew, M. G. B.; Page, E. M.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1983**, 61. (b) Britnell, D.; Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A. *J. Chem. Soc., Chem. Commun.* **1972**, 462.

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**Table I.** Crystal Data for $WSCl_4$

| | |
|---|---|
| formula | $Cl_4SW$ |
| fw | 357.72 |
| space group | $P2_1/n$ |
| syst abs | $h0l$: $h + l = 2n + 1$<br>$0k0$: $k = 2n + 1$ |
| $a$, Å | 8.898 (3) |
| $b$, Å | 12.434 (4) |
| $c$, Å | 12.080 (3) |
| $\alpha$, deg | 90.0 |
| $\beta$, deg | 111.40 (2) |
| $\gamma$, deg | 90.0 |
| $V$, Å$^3$ | 1244 (1) |
| $Z$ | 8 |
| $d_{calc}$, g/cm$^3$ | 3.819 |
| cryst size, mm | 0.35 × 0.25 × 0.10 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 208.90 |
| data collecn instrument | Rigaku AFC5R |
| radiation (monochromated in incident beam) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| orientation reflecns: no.; range ($2\theta$), deg | 25; $20 < 2\theta < 30$ |
| temp, °C | 21 |
| scan method | $\omega-2\theta$ |
| data colcn range ($2\theta$), deg. | $4 \leq 2\theta \leq 45$ |
| no. of unique data; tot. with $F_o^2 > 3\sigma(F_o^2)$ | 1299; 696 |
| no. of params refined | 110 |
| transmissn factors: max; min | 1.000; 0.586 |
| $R^a$ | 0.05143 |
| $R_w{}^b$ | 0.05793 |
| quality-of-fit indicator$^c$ | 0.975 |
| largest shift/esd, final cycle | 0.00 |
| largest peak, e/Å$^3$ | 1.751 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

$WX_4$ units found in tungsten oxide tetrachloride and tetrabromide are joined into infinite chains by –W–O–W– bonds[2] while the corresponding sulfide complexes form dimeric units via weak W–X bonds.[3] This behavior is rationalized by recognizing that the individual molecules are coordinatively unsaturated, which also explains why they react with a great variety of ligands and donor molecules to form six-coordinate adducts. We inadvertently prepared $WSCl_4$ in a new way, and when we attempted to confirm its identity by comparative X-ray crystallography, we found that we had a new polymorph. We present here the synthesis and single-crystal X-ray structure of this new polymorph of tungsten(VI) sulfide tetrachloride.

## Experimental Section

A Pyrex tube evacuated to $2 \times 10^{-4}$ Torr, containing W (2.00 g, 11.0 mmol), $S_2Cl_2$ (0.6 ml, 7.5 mmol), and S (0.36 g, 11.0 mmol) was heated at 425 °C for 48 h. When the tube was slowly cooled, a mass of ruby red $WSCl_4$ crystals formed. Yield: 1.2 g, 89% based on $S_2Cl_2$. The compound rapidly decomposes in air. Therefore, the tube was opened in an inert atmosphere and the crystals handled in degassed mineral oil.

A crystal selected from the product was shown to be of excellent quality by polarized light microscopy. The crystal was sealed with epoxy cement in a glass capillary and mounted on the goniometer head of a Rigaku diffractometer. The crystal parameters and basic information relating to data collection and structure refinement are summarized in Table I. Data for a unique quadrant ($+h,+k,\pm l$) were collected in the range 4–45° in $2\theta$. Periodically monitored check reflections displayed an average decrease in intensity of 80.7% during the data collection. This was corrected for by use of an isotropic decay correction. After data collection, six azimuthal scans were collected and used to correct for absorption. The tungsten atoms were located by direct methods,[4] and the remainder of the atoms were located and refined by alternating difference Fourier maps and least-squares cycles employing the Enraf-Nonius Structure Determination Package (SDP).[5] All atoms were refined anisotropically. An observed systematic dependence of $w[|F_o| - |F_c|]^2$ on $(\sin \theta)/\lambda$ implied the need for a secondary extinction correction, $g$, of the form $F_c = |F_c|/(1 + gI_c)$. The refined extinction coefficient was $6.033 \times 10^{-8}$. The final difference Fourier map had randomly located peaks with heights of <1.751 e/Å$^3$. Atomic scattering factors were those of the SDP.

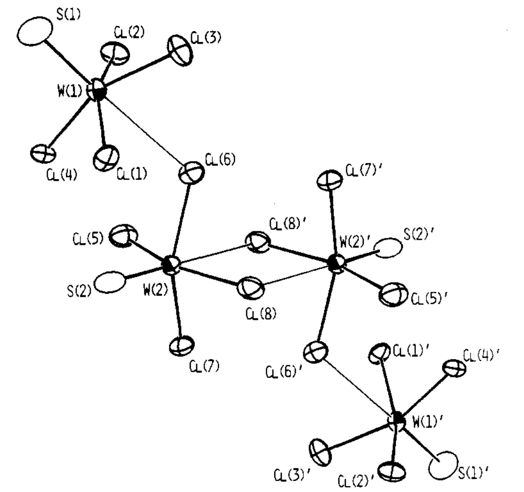

**Figure 1.** ORTEP drawing of four $WSCl_4$ molecules. Atoms are represented by their ellipsoids at the 50% probability level.

**Table II.** Bond Distances (Å) and Angles (deg) for $WSCl_4$[a]

| | | | |
|---|---|---|---|
| | Distances | | |
| W(1)–Cl(1) | 2.296 (9) | W(2)–Cl(5) | 2.251 (12) |
| W(1)–Cl(2) | 2.282 (9) | W(2)–Cl(6) | 2.341 (12) |
| W(1)–Cl(3) | 2.265 (12) | W(2)–Cl(7) | 2.243 (13) |
| W(1)–Cl(4) | 2.280 (12) | W(2)–Cl(8) | 2.433 (12) |
| W(1)–S(1) | 2.076 (13) | W(2)–Cl(8)′ | 2.908 (10) |
| W(1)–Cl(6) | 3.233 (11) | W(2)–S(2) | 2.076 (11) |
| | Angles | | |
| Cl(1)–W(1)–Cl(2) | 155.1 (4) | Cl(5)–W(2)–Cl(8) | 160.9 (3) |
| Cl(1)–W(1)–Cl(3) | 87.5 (4) | Cl(5)–W(2)–S(2) | 101.7 (4) |
| Cl(1)–W(1)–Cl(4) | 87.7 (4) | Cl(6)–W(2)–Cl(7) | 157.7 (4) |
| Cl(1)–W(1)–S(1) | 102.5 (4) | Cl(6)–W(2)–Cl(8)′ | 77.5 (4) |
| Cl(2)–W(1)–Cl(3) | 87.4 (4) | Cl(6)–W(2)–Cl(8) | 84.8 (4) |
| Cl(2)–W(1)–Cl(4) | 86.9 (4) | Cl(6)–W(2)–S(2) | 99.9 (5) |
| Cl(2)–W(1)–S(1) | 102.4 (4) | Cl(7)–W(2)–C6(8)′ | 80.4 (4) |
| Cl(3)–W(1)–Cl(4) | 155.6 (4) | Cl(7)–W(2)–Cl(8) | 87.1 (4) |
| Cl(3)–W(1)–S(1) | 102.2 (5) | Cl(7)–W(2)–S(2) | 101.7 (5) |
| Cl(4)–W(1)–S(1) | 102.2 (5) | Cl(8)–W(2)–Cl(8)′ | 77.0 (3) |
| Cl(5)–W(2)–Cl(6) | 89.1 (4) | Cl(8)′–W(2)–S(2) | 173.8 (5) |
| Cl(5)–W(2)–Cl(7) | 91.8 (5) | Cl(8)–W(2)–S(2) | 97.2 (4) |
| Cl(5)–W(2)–Cl(8)′ | 84.0 (4) | W(2)–Cl(8)–W(2)′ | 103.0 (3) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

## Discussion

An ORTEP drawing showing the atom numbering scheme is depicted in Figure 1. A unit cell diagram is shown in Figure 2. Table II presents selected important interatomic distances and angles.

The single-crystal X-ray structure of a triclinic modification of $WSCl_4$ was determined in 1970 by Drew and Mandyczewsky.[3] These authors described the geometry about tungsten as either five-coordinate square pyramidal or six-coordinate distorted octahedral. In that polymorph the W–S bond distance was found to be 2.098 (8) Å. Three of the four W–Cl distances were shown to be equivalent within experimental error (2.277 [7] Å). However, the fourth W–Cl distance is significantly longer, 2.366 (10) Å. This lengthening is due to a 3.049 (11) Å interaction with a tungsten atom on a neighboring $WSCl_4$ unit which is trans to

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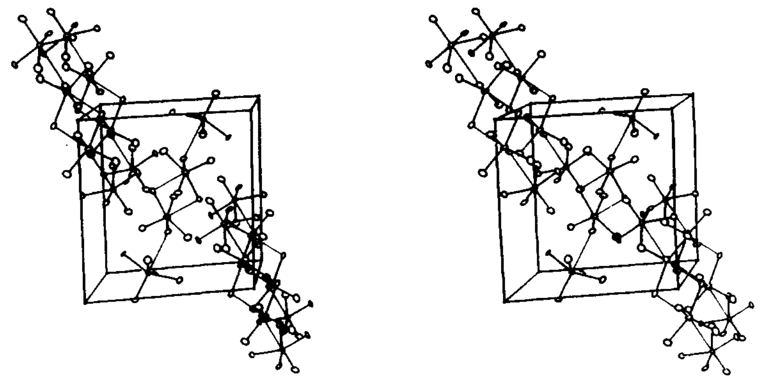

**Figure 2.** Unit cell diagram for $WSCl_4$. Axes orientation: *b*, down; *c*, across; *a*, toward viewer.

**Table III.** Least-Squares Planes[a]

| atom | *x* | *y* | *z* | dist, Å | esd |
|---|---|---|---|---|---|
| Plane 1: $A = 0.3937$; $B = 0.8175$; $C = -0.4203$; $D = -1.0231$ | | | | | |
| | | Atoms in Plane | | | |
| Cl(1) | −2.4218 | 3.8192 | 7.6101 | −0.006 | 0.011 |
| Cl(2) | −1.6804 | 5.5469 | 11.6659 | −0.006 | 0.011 |
| Cl(3) | −0.0412 | 3.7507 | 9.6770 | 0.006 | 0.012 |
| Cl(4) | −4.0550 | 5.6528 | 9.6167 | 0.006 | 0.011 |
| | | $\chi^2 = 1$ | | | |
| | | Other Atom | | | |
| W(1) | −1.8531 | 5.0883 | 9.4376 | 0.487 | 0.002 |
| Plane 2: $A = 0.1217$; $B = 0.2492$; $C = -0.9608$; $D = -3.8532$ | | | | | |
| | | Atoms in Plane | | | |
| Cl(5) | −5.1864 | 9.6004 | 5.0359 | 0.776 | 0.010 |
| Cl(6) | −8.0662 | 8.6010 | 6.0782 | −0.825 | 0.010 |
| Cl(7) | −3.9291 | 6.8359 | 6.1315 | −0.812 | 0.010 |
| Cl(8) | −6.5073 | 6.5494 | 3.9898 | 0.860 | 0.010 |
| | | $\chi^2 = 27940$ | | | |
| | | Other Atom | | | |
| W(2) | −5.8415 | 7.9671 | 6.4397 | −1.059 | 0.002 |

[a] The equation of the plane is of the form $Ax + By + Cz - D = 0$, where *A*, *B*, *C*, and *D* are constants and *x*, *y*, and *z* are orthogonalized coordinates.

sulfur, the Cl′–W–S angle being 176.4°. The weak tungsten-chlorine interaction occurs across a center of symmetry and results in the formation of dimeric $W_2S_2Cl_8$ units. These dimers are similar in structure to the isomorphous $W_2Cl_{10}$[6] and $Mo_2Cl_{10}$.[7]

In the new polymorph, we report here there are two $WSCl_4$ groups in the asymmetric unit. One of the $WSCl_4$ entities (A) relates to its symmetry equivalent across a center of inversion, giving dimeric units of the type just described, while the other $WSCl_4$ molecule (B) relieves its nascent coordinative unsaturation by a longer, unreciprocated W(1)–Cl(6) interaction. We will first contrast the dimeric unit in the present compound with that of the triclinic modification.

In the dimeric unit of the present modification, one of the tungsten chlorine distances, W(2)–Cl(8), is much longer than the other three, 2.433 (12) Å. This lengthening is due to a 2.908 (9) Å interaction between this chlorine atom and the tungsten atom of a symmetry-related (A)-$WSCl_4$ unit. Furthermore, the W(2)–Cl(8)′ distance is 0.14 Å shorter than the analogous interaction in the triclinic modification and the Cl(8)′–W(2)–S(2) angle is 173.8 (5)°. Simultaneously, (A)-$WSCl_4$ units approach the (B)-$WSCl_4$ units via a W(1)–Cl(6) contact of 3.233 (11) Å. This contact causes a slight lengthening of the W(2)–Cl(6) bond, which is 2.341 (12) Å. The average W–Cl bond distance for chlorine atoms that do not interact with tungsten atoms is 2.247 [4] Å. The remaining bond distances and angles are normal for this type of distorted-square-pyramidal structure, but they differ considerably from those of the triclinic modification. One manifestation of these differences is that in the triclinic modification the chlorine atoms were found to be planar with the tungsten atom 0.45 Å above the plane. However, in the present compound the chlorine atoms are far from planar (see Table III).

The five ligands around the tungsten atom in the (B)-$WSCl_4$ unit form a nearly regular square pyramid. The W–Cl bond lengths and mutually cis Cl–W–Cl and S–W–Cl bond angles are equivalent within experimental error. The four chlorine atoms of the B unit are planar and the tungsten atom sits 0.487 (2) Å above the plane.

The chlorine atoms on the B units do not interact with any other tungsten atoms; hence, tetrameric entities are formed that are internally linked by weak W–Cl bonds. The W(1)–W(2) and W(2)–W(2)′ distances are 4.844 (3) and 4.189 (3) Å, respectively, indicating that there is no electronic interaction between the metal centers. Other than the aforementioned contacts, there are no other <4.0 Å contacts between chlorine and sulfur atoms and tungsten atoms on adjacent molecules.

The crystal structure presented here displays a previously unknown mode of association for transition metal oxide/sulfide tetrahalides. The electron deficient and coordinatively unsaturated tungsten atoms of this modification exhibit stabilizing weak W–Cl interactions, which contrasts with the existence of monomeric molecules of $WOX_4$ and $WSX_4$ in the vapor phase.[8]

**Acknowledgment.** We thank the Robert A. Welch Foundation for support under Grant No. A494.

**Registry No.** W, 7440-33-7; $S_2Cl_2$, 10025-67-9; S, 7704-34-9; $WSCl_4$, 25127-53-1.

**Supplementary Material Available:** Full listings of bond distances, bond angles, and positional and isotropic equivalent displacement parameters for $WSCl_4$ (4 pages); a listing of observed and calculated structure factors for $WSCl_4$ (6 pages). Ordering information is given on any current masthead page.

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## Assignment of the Intense UV Bands in the Solution Electronic Spectrum of $Ni(CN)_4^{2-}$. MCD Spectra for the 3.7- and 5.0-$\mu m^{-1}$ Bands

W. Roy Mason

*Received November 28, 1988*

The intense bands in the region 3.0–4.5 $\mu m^{-1}$ exhibited by the planar $Ni(CN)_4^{2-}$ ion in solutions and in crystalline environments have been investigated by a variety of spectroscopic methods including low-temperature absorption,[1] magnetic circular di-