bonds occurs in the median Mo_3 triangle [2·680 (4) Å in $In_2Mo_{15}Se_{19}$]. Nevertheless, the overall effect is again a contraction of the cluster as reflected by the interplane distance $\Delta(2)$—$\Delta(3)$ which decreases from 2·280 to 2·263 Å. This trend is analogous to that reported for the series $In_xMo_{15}Se_{19}$ ($2{\cdot}9 \leq x \leq 3.4$) when the indium content x increases (Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber, 1979; Potel, 1981). The latter compound also contains Mo_6Se_8 and Mo_9Se_{11} units but arranged in a different way. The Mo—Se distances are nearly unaffected by the cationic charge and range between 2·5395 (7) and 2·710 (2) Å as usual.

The Ba atoms, located in channels running along the a axis of the rhombohedral unit cell, are each surrounded by 11 Se atoms. The five closest Se atoms at distances ranging from 3·2424 (7) to 3·4761 (5) Å form a trigonal bipyramid, with Se(4) and Se(5) located on the threefold axis in axial positions and three related Se(2) in the equatorial sites. The other six [three Se(1) and three Se(3)] cap the faces of the bipyramid with Ba–Se distances between 3·7235 (7) and 3·8659 (5) Å (Fig. 2). Whereas in the title compound the Ba atom is nearly equidistant from the two axial Se atoms, in $In_2Mo_{15}Se_{19}$ the In is slightly displaced towards the Se(4) atoms [In—Se(4) 3·468 (6) and In—Se(5) 3·593 (6) Å] probably owing to the presence of the lone pair. This effect is still more evident in $Tl_2Mo_{15}Se_{19}$ (Potel & Gougeon, 1987) where the Tl—Se(4) and Tl—Se(5) distances are 3·379 and 3·684 Å respectively.

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Structural Characterization of $WCl_6.S_8$

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Abstract. Tungsten hexachloride-*cyclo*-octasulfur, (1), $M_r = 653{\cdot}08$, triclinic, $P\overline{1}$, $a = 7{\cdot}901$ (1), $b = 7{\cdot}923$ (1), $c = 12{\cdot}696$ (2) Å, $\alpha = 97{\cdot}08$ (1), $\beta = 100{\cdot}50$ (1), $\gamma = 90{\cdot}26$ (1)°, $V = 775{\cdot}2$ (4) Å^3, $Z = 2$, $D_x = 2{\cdot}798$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 96{\cdot}65$ cm^{-1}, $F(000) = 608$, $T = 294$ K, $R = 0{\cdot}028$ for 1337 observed reflections. The asymmetric unit is composed of one molecule of WCl_6 in which the W atom sits at the center of a nearly perfect octahedron of Cl atoms, and one molecule of S_8 which adopts the crown ring structure. The average W—Cl distance is 2·276 (2) Å, the average S—S distance 2·044 (1) Å, and the average S—S—S angle 107·9 (1)°.

Introduction. During the course of a synthetic program directed towards the preparation of mixed metal chalcogenide halide clusters we have inadvertently prepared WCl_6S_8. The structure determination we report here complements that for WCl_6 (Ketelaar & van Oosterhout, 1943).

Experimental. A Pyrex tube evacuated to 2×10^{-4} torr ($2{\cdot}67 \times 10^{-2}$ Pa), containing Ti (0·30 g,

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Table 1. *Crystallographic data for* $WCl_6.S_8$

Systematic absences	None
Crystal size (mm)	0·50 × 0·45 × 0·30
Data-collection instrument	Syntex *P*3
Orientation reflections:	
No., range (°)	25, $20 < 2\theta < 30$
Scan method	ω–2θ
Data-collection range (°)	$4 \leq 2\theta \leq 45$
h,k,l, ranges	$0 \leq h \leq 8$ $-8 \leq k \leq 8$ $-13 \leq l \leq 13$
No. of unique data: total,	1436
with $F_o^2 > 3\sigma(F_o^2)$	1337
No. of parameters refined	137
Transmission factors: max., min.	0·998, 0·620
R	0·0278
*wR**	0·0457
Quality-of-fit indicator	1·185
Largest shift/e.s.d., final cycle	0·01
Largest peak (e Å^{-3})	−0·61

* $w = 1/\sigma^2(|F_o|)$.

Table 2. *Positional and equivalent isotropic displacement parameters and their estimated standard deviations for* $WCl_6.S_8$

The equivalent isotropic displacement parameter is:

$$\tfrac{1}{3}[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*b^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}].$$

	x	*y*	*z*	B_{eq}(Å^2)
W(1)	0·28711 (4)	0.77666 (5)	0·10660 (3)	2·203 (9)
Cl(1)	0·2052 (4)	1·0523 (3)	0·1072 (2)	4·16 (7)
Cl(2)	0·0092 (3)	0·6949 (4)	0·1016 (2)	4·12 (7)
Cl(3)	0·3650 (3)	0·4997 (3)	0·1055 (2)	3·78 (6)
Cl(4)	0·5648 (3)	0·8580 (4)	0·1102 (2)	3·94 (6)
Cl(5)	0·3380 (3)	0·8110 (3)	0·2905 (2)	3·33 (6)
Cl(6)	0·2418 (4)	0·7452 (4)	−0·0764 (2)	4·25 (7)
S(1)	−0·3784 (3)	0·4898 (3)	0·4027 (2)	3·32 (6)
S(2)	−0·2405 (3)	0·5912 (3)	0·3030 (2)	3·11 (6)
S(3)	0·0141 (3)	0·5838 (3)	0·3711 (2)	2·77 (6)
S(4)	0·1147 (3)	0·3756 (3)	0·2953 (2)	3·07 (6)
S(5)	0·1206 (3)	0·1842 (3)	0·3903 (2)	3·16 (6)
S(6)	−0·0886 (3)	0·0262 (3)	0·3308 (3)	3·68 (7)
S(7)	−0·2743 (3)	0·0892 (4)	0·4200 (3)	3·59 (6)
S(8)	−0·4446 (3)	0·2434 (4)	0·3385 (3)	3·77 (7)

6·3 mmol), W (0·38 g, 2·1 mmol), S_2Cl_2 (1·6 ml, 12·6 mmol) and S (0·54 g, 16·8 mmol), was heated at 698 K for 48 h. Upon slow cooling a mass of black WCl_6S_8 crystals formed in the tube.

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 Syntex *P*3 diffractometer. The crystal parameters and basic information relating to data collection and structure refinement are summarized in Table 1. Periodically monitored check reflections displayed an average decrease of 8·7% during the data collection. This decay was corrected for by the use of an isotropic decay correction. At the end of the data collection six azimuthal scans were collected and used to correct for absorption. The W atom was located by direct methods (*SHELXS*86; Sheldrick, 1986) and the remainder of the atoms were located and refined by alternating difference Fourier maps and least-squares cycles employing the Enraf–Nonius (1979) *Structure Determination Package*. 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 of the form $F_c = |F_c|/(1 + gI_c)$. The refined extinction coefficient, *g*, was $5{\cdot}45 \times 10^{-7}$. The final difference Fourier map showed two peaks near W of height 0·900 and 0·857 e Å^{-3}. The remaining peaks were randomly located and had heights of <0·550 e Å^{-3}. No disorder or other non-routine problems arose. Atomic scattering factors were those of *SDP*.

Discussion. The positional parameters and equivalent isotropic displacement parameters are given in Table 2.* The asymmetric unit, consisting of one WCl_6 and

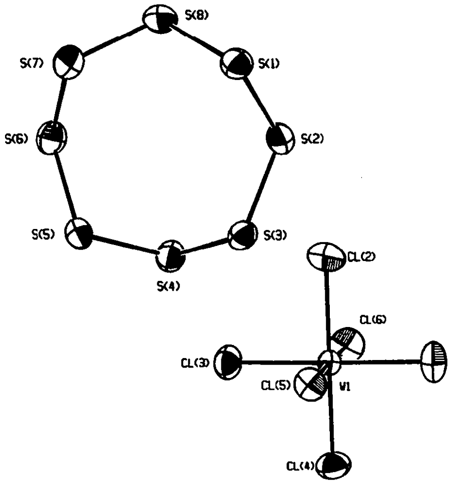

Fig. 1. *ORTEP* (Johnson, 1965) drawing of compound (1). Atoms are represented by displacement ellipsoids at the 50% level.

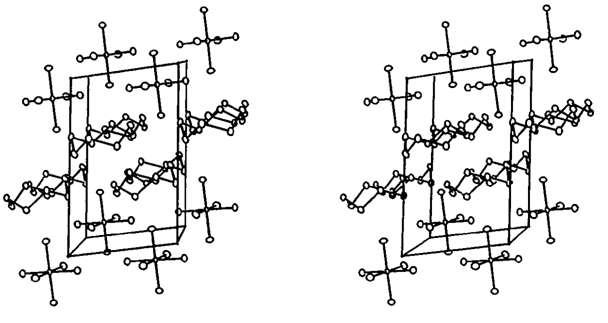

Fig. 2. Unit-cell diagram for (1). Atoms are represented by displacement ellipsoids at the 20% level. Axes orientation: *b* across, *c* down, *a* toward viewer.

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51882 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

one S_8 molecule, is depicted in Fig. 1 where the atom-numbering scheme is also defined. A unit-cell diagram is shown in Fig. 2.

Ewens & Lister (1938) studied tungsten hexachloride in the vapor phase by electron diffraction. They concluded that in the vapor, WCl_6 exists as regular octahedra with a W—Cl distance of 2·26 (2) Å. The single-crystal X-ray structure of WCl_6 was determined in 1942 and was shown to comprise a distorted hexagonal close-packed array of Cl atoms with W atoms in the octahedral holes. The W atoms are surrounded by a nearly regular octahedron of Cl atoms with an average W—Cl distance of 2·24 Å.

In the compound we report here, the W atom is in the center of a nearly regular octahedron of Cl atoms with an averge W—Cl distance of 2·276 (2) Å. The greatest deviation from regular octahedral angles is 90·8 (1)° for the Cl(2)—W(1)—Cl(5) angle. The S_8 unit assumes the crown ring structure. the average S—S—S angle is 107·9 (1)° and the average S—S bond length is 2·044 (1) Å. These values compare well with those found in naturally occurring orthorhombic sulfur (Caron & Donohue, 1965). The three-dimensional structure is composed of alternating layers of WC_6 and S_8 molecules which are parallel to the *ab* plane.

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Note added in proof: A prior example of S_8 molecules in a crystal of another substance recently came to our attention [A. Müller, M. Römer, H. Bögge, E. Krickemayer & M. Zimmermann (1986). *Z. Anorg. Allg. Chem.* **534**, 69–76].

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trans-(Dimethyl sulfoxide-*O*)(dimethyl sulfoxide-*S*)bis(trifluoroacetato)palladium(II); Alternative Ligation Modes of an Ambidentate Ligand

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Abstract. $[Pd(C_2F_3O_2)_2(C_2H_6OS)_2]$, $M_r = 488{\cdot}69$, monoclinic, $P2_1/c$, $a = 20{\cdot}159$ (3), $b = 7{\cdot}498$ (8), $c = 23{\cdot}926$ (8) Å, $\beta = 101{\cdot}64$ (7)°, $V = 3542$ (2) Å^3, $Z = 8$, $D_x = 1{\cdot}833$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 13{\cdot}36$ cm^{-1}, $F(000) = 1920$, $T = 293$ K, $R = 0{\cdot}0582$ for 2836 observed reflections. The two crystallographically independent molecules are substantially identical. Each square complex has a *trans* structure with one S-bonded and one O-bonded dimethyl sulfoxide molecule. Mean dimensions for the S-bonded ligands: Pd—S = 2·205 (4), C—S = 1·78 (1), S—O = 1·45 (1) Å. Mean dimensions for the O-bonded ligands: Pd—O = 2·06 (3), C—S = 1·81 (1), S—O = 1·54 (2) Å. The average of the four Pd—O(CF_3CO_2) distances is 2·011 (9) Å.

Introduction. Dimethyl sulfoxide (dmso), like sulfoxides generally, is an ambidentate ligand, as first discussed nearly thirty years ago (Cotton, Francis & Horrocks, 1960). The factors that determine which way an ambidentate ligand will be found are both steric (not easily evaluated) and electronic (subject to debate). Perhaps the most interesting problem is posed by those rare cases in which two of the same ligand occupy what could be identical sites, sterically and electronically, but adopt opposite modes of attachment. Relatively few are known and only with sulfoxides have they previously been supported by crystallographic proof. We report here one that we encountered recently by chance, *viz.*, $[Pd(OCOCF_3)_2\{Me_2(O)S\}(Me_2SO)]$.

Experimental. The compound was prepared by a modification of the method of Stephenson,

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