

[1.722 (3) and 1.704 (5) Å] can be attributed to the thermal motion of F(3) although it is noteworthy that the average bond length (1.716 Å av.) is very similar to that of 1.719 (3) Å found in KAsF_6 (Gafner & Kruger, 1974), indicative of the strength of the coordination. The average As–F distance after application of a riding correction is 1.737 (3) Å. In the *N*-methyl-*S,S*-difluorosulphoximine adduct the As–F distances are shorter than those in KAsF_6 and this along with the long As–N distance is considered to be evidence for a fractional bond order for the As–N bond. An even longer, weaker As–N bond of 2.29 (2) Å is found in the adduct $\text{Cl}_3\text{As}\cdot\text{NMe}_3$, although in this case As^{III} is involved (Webster & Keats, 1971).

There are no intermolecular contacts of note. The chemistry of the reactions producing this adduct will be discussed elsewhere (Gillespie, Kent & Sawyer, 1980).

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Caesium Lithium Tungstate: A Stuffed *H*-Cristobalite Structure

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Abstract. CsLiWO_4 , cubic, $F\bar{4}3m$, $a = 8.350(1)$ Å, $Z = 4$, $D_x = 4.42$ Mg m⁻³. The crystals were prepared by heating a mixture of Cs_2CO_3 , Li_2CO_3 and WO_3 at 1173 K for 3 h in a platinum crucible. Colourless and transparent prismatic crystals were obtained. The substance is a stuffed derivative of the *H*-cristobalite structure, with W–O and Li–O distances of 1.78 (3) and 1.87 (3), and Cs–O distances of 3.22 (3) and 3.60 (3) Å.

Introduction. A preliminary X-ray study with Weissenberg photographs revealed that the crystals were cubic with Laue symmetry $m\bar{3}m$. As the hkl reflexions were systematically missing for $h + k$, $k + l$ and $l + h$ odd, the possible space groups were restricted to $F\bar{4}3m$, $F432$ and $Fm\bar{3}m$. $F\bar{4}3m$ gave a satisfactory result for the structure refinement. A prismatic crystal with approximate dimensions 0.15 × 0.05 × 0.05 mm was used for intensity collection. With the ω – 2θ scan tech-

nique, intensities were measured on a Philips PW1100 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The scan speed was 4° min⁻¹ in ω and scanning was repeated twice when the total counts were less than 10 000. The scan width was determined according to $(1.2 + 0.3 \tan \theta)^\circ$. Intensities were corrected for the Lorentz–polarization and absorption effects ($\mu = 27.18$ mm⁻¹). Corrections for isotropic secondary extinction were carried out in the final stage of the structure refinement (the crystal was assumed to be a sphere 0.1 mm in diameter). Intensities of 187 independent reflexions, with $|F| > 3\sigma(|F|)$, were obtained and used for the structure determination.

The positions of the Cs and W atoms were obtained from the Patterson map and those of the Li and O atoms were then found on Fourier and difference Fourier maps synthesized with phases derived from the Cs and W atoms. The structure was refined with the

Table 1. Final atomic parameters of CsLiWO₄

	x	y	z	B (Å ²)
Cs	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.55 (3)
Li	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.2 (13)
W	$\frac{1}{4}$	$\frac{1}{4}$	0	1.37 (2)
O	0.390 (3)	0.390	0.147 (4)	3.7 (8)

Table 2. Interatomic distances (Å) of CsLiWO₄

W—O	1.78 (3) × 4	Li—O	1.87 (3) × 4
Cs—O	3.22 (3) × 4	Cs—O	3.60 (3) × 8

full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) to an $R = 0.073$, but the temperature factor of the O atom became very large ($B = 10.0 \text{ \AA}^2$). Thus, the O atom was assumed to be disordered, and its position was considered to be randomly distributed on the $48(h)$ position instead of the $16(e)$ position. A further refinement of this disordered structure model converged to give the final value of $R = 0.050$ after correction for secondary extinction. The extinction parameter (G) was $0.05 (1) \times 10^{-4}$. The weighting scheme of Hughes (1941) was adopted: $w = 1.0$ if $F_o < 131.6$ and $w = (131.6/F_o)^2$ if $131.6 \leq F_o$. The atomic scattering factors for neutral atoms and the dispersion-correction factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are listed in Table 1.* Interatomic distances are given in Table 2.

Discussion. It had been reported by many workers (Muller & Roy, 1974) that the crystal structures of $ACBO_4$ compounds were stuffed derivatives of tridymite when A is large in size and both B and C are small. It is of interest to obtain further knowledge on the crystal chemistry of the stuffed derivatives of the silica structures. However, no crystallographic and structural investigations of $A^+LiB^{6+}O_4$ compounds ($A = K, Rb, Cs$; $B = Mo, W$) have yet been made. The structure determination of CsLiWO₄ by means of single-crystal X-ray diffraction was, therefore, undertaken.

The structure viewed along the $[001]$ axis is shown in Fig. 1. The W and Li atoms are each tetrahedrally surrounded by four O atoms. These WO_4 and LiO_4 tetrahedra are joined together to form a cristobalite-like framework. The O atoms at the assumed disordered positions are separated by $0.44 (4) \text{ \AA}$. The W—O and

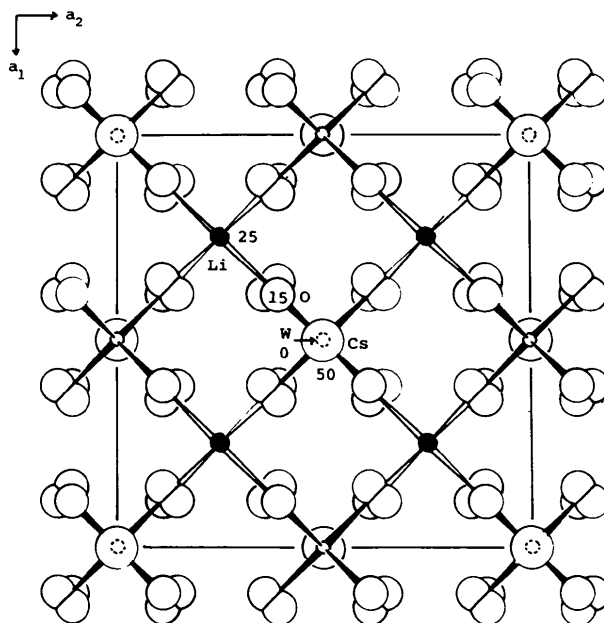


Fig. 1. Projection of the structure of CsLiWO₄ along the $[001]$ axis; numbers give, in decimal fractions of the $[001]$ length, the heights of the atoms ($\times 10^2$). Large open circles denote Cs, medium open circles O, small open circles W, and small solid circles Li.

Table 3. Crystal data of $A^+LiB^{6+}O_4$

Compound	CsLiWO ₄	CsLiMoO ₄	RbLiWO ₄	RbLiMoO ₄
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	$F\bar{4}3m$	$F\bar{4}3m$	$F\bar{4}3m$	$F\bar{4}3m$
a (Å)	8.350 (1)	8.320 (1)	8.141 (1)	8.113 (2)
M_r	387.69	299.78	340.26	252.35
Z	4	4	4	4
D_x (Mg m ⁻³)	4.42	3.46	4.19	3.14
Temperature (K)	298	298	423*	423*

* Data were taken at 423 K because these two specimens were highly hygroscopic.

Li—O distances are $1.78 (3)$ and $1.87 (3) \text{ \AA}$ respectively. The Li—O distance is a little shorter than the reported average value of 1.95 \AA (Brown & Shannon, 1973). The Cs atom is surrounded by 12 O atoms and located in the large cavities of the framework. Four Cs—O distances are $3.22 (3) \text{ \AA}$ and the remaining eight are $3.60 (3) \text{ \AA}$. An electrostatic valence balance, computed according to the method of Brown & Wu (1976), gave the following results: O 2.02, W 5.97, Li 1.16, Cs 0.94. The balance is satisfactory for all the atoms with the exception of Li.

Crystals of several $A^+LiB^{6+}O_4$ compounds ($A = Rb, Cs$; $B = Mo, W$) were synthesized and studied with X-rays, giving the crystal data listed in Table 3. All of these compounds are isostructural with CsLiWO₄, *i.e.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34875 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

stuffed derivatives of the *H*-cristobalite structure. Almost all of the stuffed derivatives of silica-structure-type compounds are reported to be of the tridymite type and cristobalite-type compounds are rather uncommon.

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Hydrazinium(2+) Difluoride Hexafluorotitanate(IV)

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Abstract. $(\text{N}_2\text{H}_6)_2\text{F}_2[\text{TiF}_6]$, orthorhombic, *Pccn*, $a = 5.481$ (1), $b = 13.588$ (3), $c = 10.937$ (2) Å, $Z = 4$, $D_o = 2.17$ (3), $D_c = 2.185$ Mg m⁻³, $V = 814.54$ Å³; $R = 0.023$, $R_w = 0.021$ for 625 observed reflections. The structure consists of $\text{N}_2\text{H}_6^{2+}$ cations, discrete $[\text{TiF}_6]^{2-}$ octahedral anions and F^- anions. These units are connected by $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds.

Introduction. Some hydrazinium(1+) and hydrazinium(2+) fluoro complexes of transition metals have been prepared at the Institute 'Jožef Stefan', Ljubljana, Yugoslavia (Slivnik & Volavšek, 1968; Slivnik, Šmalc, Sedej & Vilhar, 1964). The structures of $\text{N}_2\text{H}_6[\text{TiF}_6]$ (Kojić-Prodić, Matković & Ščavničar, 1971) and $\text{N}_2\text{H}_6[\text{ZrF}_6]$ (Kojić-Prodić, Ščavničar & Matković, 1971) have been solved. For the compound with the stoichiometry $(\text{N}_2\text{H}_6)_2\text{TiF}_8$ two different formulae, $(\text{N}_2\text{H}_5)_2\text{F}_2[\text{TiF}_6]$ and $(\text{N}_2\text{H}_6)_2[\text{TiF}_8]$, were postulated (Slivnik, Maček, Orel & Sedej, 1973; Slivnik & Volavšek, 1968). The structure determination of this compound was carried out in order to determine the coordination polyhedron around Ti, as well as the presence of N_2H_5^+ or $\text{N}_2\text{H}_6^{2+}$ cations in the structure. The analysis clearly shows that the correct structural formula for the compound is $(\text{N}_2\text{H}_6)_2\text{F}_2[\text{TiF}_6]$.

Oscillation, Weissenberg (Cu *Kα* radiation) and precession photographs (Mo *Kα* radiation) gave preliminary cell dimensions and showed *mmm* symmetry. Systematic absences indicated the space group *Pccn*. Cell dimensions were determined from a least-squares fit of fifteen reflections. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer in the ω - 2θ mode, with a graphite monochromator and Mo *Kα* radiation.

One quarter of the sphere of reflections (2431 intensities in all) in the range $1.5 < \theta < 30.0^\circ$ was measured. Symmetry-equivalent reflections (*hkl* and $h\bar{k}l$) were averaged (mean discrepancy on *I* was 2.1%) to yield 1186 independent reflections of which 625 with $I_o \geq 3\sigma(I_o)$ (calculated from counting statistics) were considered as observed and used for the analysis. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the heavy-atom method and refined by full-matrix least squares with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). A difference map revealed the coordinates of all H atoms, which were included in the refinement as invariants with isotropic thermal parameters ($B = 1.5$ Å²). Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms terminated at $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.023$

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