Refinement of the Structure of Trilanthanum Trichlorohexaoxotungstate, La₃WO₆Cl₃, from Neutron Powder Diffraction Data

By J. B. Parise and L. H. Brixner

Central Research and Development Department,* E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, DE 19898, *USA*

and E. Prince

National Measurements Laboratory, National Bureau of Standards, Washington, DC 20234, *USA*

Abstract. $M_r = 802.9$, $P6_3/m$, $a = 9.4092$ (2), $c = 5.4276$ (2) Å, $V = 416.15$ (2) Å³, $Z = 2$, high-resolution neutron powder diffraction data ($\lambda = 1.5416$ (3) Å, $T = 295$ K), collected from 10 to 122° in 2θ with a 0.05° step size; final weighted profile $R = 9.16\%$ was compared to an expected $R_E = 7.41\%$ (conventional R based on integrated intensities = 6.00%). The refinement confirms the unusual trigonal prismatic coordination found for the WO₆ group in the X-ray study [Brixner, Chen & Foris (1982). *J. Solid State Chem.* **44**, 99–107]. The W–O and La–Cl bond lengths determined in this study are slightly shorter, by 0.006 (2)–0.014 (4) Å, than those found in the X-ray determination.

Introduction. We have recently published (Brixner, Chen & Foris, 1982) the structure of the new compound La₃WO₆Cl₃, where W⁶⁺ finds itself in a highly unusual trigonal prismatic coordination, surrounded by six equidistant O²⁻ atoms. An extended Hückel molecular-orbital calculation (Pensak & McKinney, 1979), comparing the D_{3h} environment for W⁶⁺ in La₃WO₆Cl₃ with the more common O_h symmetry in Ba₂CaWO₆ indicated a 146 kJ difference in favor of the octahedral arrangement. A calculation of the Madelung energy contribution (Hoppe, 1982) to the lattice energy also showed that W–O bonds do not contribute their normal share of energy in this D_{3h} environment. These facts raised some doubt about the structure of La₃WO₆Cl₃ and prompted us to undertake a neutron diffraction study and unambiguously establish the correct symmetry of the WO₆ group.

Experimental. Preparation followed procedures previously described (Brixner, Chen & Foris, 1982); 10 g sample in vanadium can, ~10 mm diameter, high-resolution five-detector diffractometer (Prince & Santoro, 1980) at the National Bureau of Standards Reactor; monochromator: 220 reflection of Cu;

horizontal divergences: 10′ in-pile collimator, 20° monochromatic beam collimator, 10′ diffracted beam collimator; monochromator mosaic spread: ~15′; angular ranges scanned by detectors: 10–42, 30–62, 50–82, 70–102, 10–122°. Data analyzed with the Rietveld technique (Rietveld, 1969*a*,*b*) as modified by Prince (1980) for data collected from the multi-detector neutron powder diffractometer; Fourier and bond length/bond angle calculations performed using a package of programs described by Finger & Prince (1975); $b(O) = 5.803$, $b(La) = 8.27$, $b(W) = 4.77$, $b(Cl) = 9.5792$ fm (Koester, 1977); background fitted by assuming a straight line, and the two parameters describing it were refined for each of the five counters; a common polynomial curve to describe halfwidths and a common zero point was assumed for the counters; corrections for counter efficiency carried out by comparison to an Al₂O₃ standard prior to Rietveld analysis; peak shape considered to be strictly Gaussian with no corrections made for either low-angle peak asymmetry or preferred orientation effects; no corrections for absorption; peaks due to unreacted LaOCl starting material in the sample excluded from refinement; unit-cell constants and symmetry checked using the program of Visser (1969) and were found to be in agreement with the single-crystal analysis; in particular, no evidence of a superlattice was detected.

Using the atomic parameters of Brixner, Chen & Foris (1982), refinement of all positional parameters, individual isotropic thermal parameters, cell constants, three half-width parameters, and diffractometer zero point led to the final discrepancy factors listed in Table 1. Fig. 1 shows the final fit between observed and calculated neutron powder diffraction patterns for La₃WO₆Cl₃.† No significant details were observed in the final difference Fourier map which was calculated

† Numerical data corresponding to all 5 counters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38697 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results of the Rietveld refinement of the structure of* $La_3WO_6Cl_3$

	x	y	z	B (Å^2)
La	0·0896 (3)	0·6843 (3)	$\frac{3}{4}$	0·50 (5)
W	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1·42 (21)
Cl	0·2399 (2)	0·0474 (3)	$\frac{1}{4}$	0·42 (4)
O	0·3627 (3)	0·8370 (3)	0·0231 (5)	0·56 (5)

Function minimized: $\chi^2 = \sum_i w_i [y_i(\text{obs}) - (1/c) y_i(\text{calc})]^2$

$R_N = 100 \, [\sum | I(\text{obs}) - I(\text{calc}) | / \sum I(\text{obs})] = 6·00$
$R_P = 100 \, [\sum | y(\text{obs}) - y(\text{calc}) | / \sum y(\text{obs})] = 7·00$
$R_W = 100 \, \{\sum w [y(\text{obs}) - y(\text{calc})]^2 / \sum w y^2(\text{obs})\}^{1/2} = 9·16$
$R_E = 100 \, [(N-P)/\sum w y^2(\text{obs})]^{1/2} = 7·41$

In the above formulas, N is the number of statistically independent observations, P the number of parameters refined, I the integrated intensities, $y(\text{obs})$ and $y(\text{calc})$ the observed and calculated intensities, and $w = 1/y(\text{obs})$ the weights associated with the data points $y(\text{obs})$.

using structure factors derived from the integrated intensities determined according to the approximation of Rietveld (1969a,b).

Table 2. *Comparison of interatomic distances* (Å) *for the structure of* $La_3WO_6Cl_3$

Derived from (a) neutron and (b) X-ray data (Brixner, Chen & Foris, 1982).

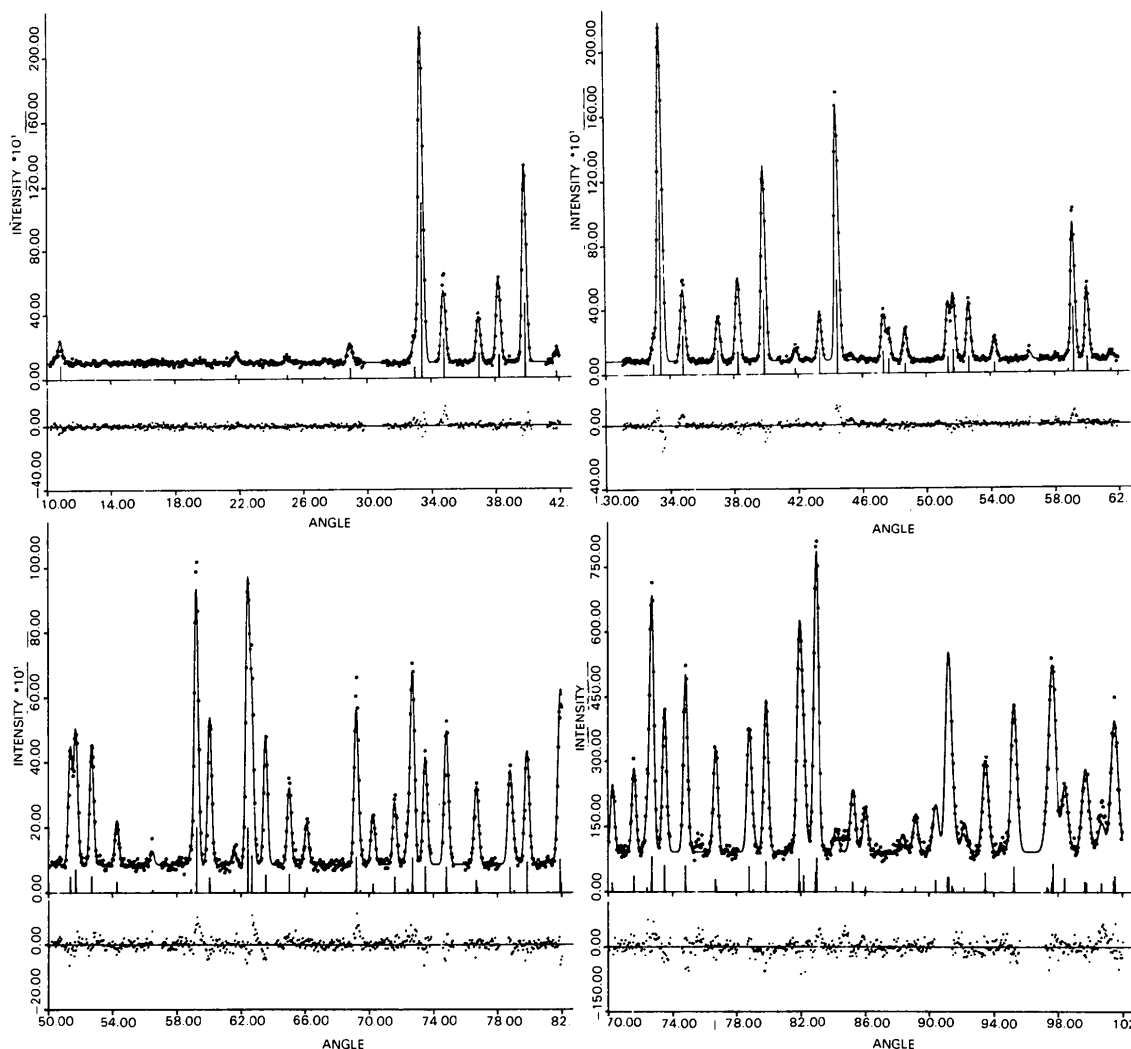|	(a)	(b)
W–O	1·928 (2)	1·940 (2)
La–O	2·435 (3)	2·436 (2)
	2·525 (3)	2·534 (3)
	2·678 (3)	2·672 (2)
La–Cl	2·973 (4)	2·965 (1)
	3·054 (1)	3·048 (1)
	3·075 (3)	3·061 (1)

Fig. 1. Observed (dots) and calculated (full line) intensity profile for $La_3WO_6Cl_3$. Vertical lines indicate the positions and relative calculated intensity for reflections contributing to the pattern. Data from four of the five counters are shown. The difference (obs–calc) profile is shown beneath the pattern for each counter.
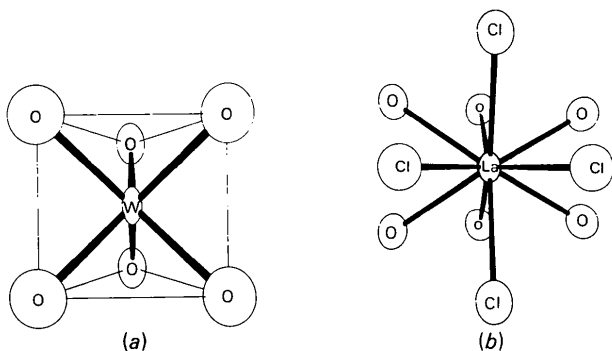
Fig. 2. Coordination about the (a) W and (b) La atoms in $LaWO_6Cl_3$.

Discussion. Table 1 lists the final refined atomic parameters, and Table 2 contains the pertinent bond lengths compared to those obtained previously. This refinement confirms the trigonal prismatic coordination of the WO_6 group in $La_3WO_6Cl_3$ as well as the other aspects of the structure.

Although the precision of the two structural refinements are comparable (Table 2), the W—O and La—Cl

bond lengths determined from the neutron data are somewhat shorter. Computation of the bond lengths based on the cell dimensions determined from Guinier-camera data only decreases these distances by 0·001 Å. The La–O distances are in generally good agreement considering their associated e.s.d.

The WO_6 group and the coordination sphere of the La atom are shown in Fig. 2.

References

BRIXNER, L. H., CHEN, H. Y. & FORIS, C. M. (1982). *J. Solid State Chem.* **44**, 99–107.
FINGER, L. W. & PRINCE, E. (1975). *Natl Bur. Stand. US Tech. Note*, No. 854.
HOPPE, R. (1982). Private communication.
KOESTER, L. (1977). *Springer Tracts Mod. Phys.* **80**, 1–55.
PENSAK, D. A. & MCKINNEY, R. J. (1979). *Inorg. Chem.* **18**, 3407–3413.
PRINCE, E. (1980). *Natl Bur. Stand. US Tech. Note*, No. 1117, edited by F. SHORTEN.
PRINCE, E. & SANTORO, A. (1980). *Natl Bur. Stand. US Tech. Note*, No. 1117, edited by F. SHORTEN.
RIETVELD, H. M. (1969a). Research Report RCN 104. Reactor Centrum Nederland. (Unpublished.)
RIETVELD, H. M. (1969b). *J. Appl. Cryst.* **2**, 65–67.
VISSER, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.

Lead Indium Bismuth Chalcogenides. I. Structure of $Pb_{1.6}In_8Bi_4S_{19}$

BY VOLKER KRÄMER

Kristallographisches Institut der Universität, Hebelstrasse. 25, D-7800 Freiburg, Federal Republic of Germany

Abstract. $M_r = 2695·2$, monoclinic, $C2/m$, $a = 29·167$ (5), $b = 3·872$ (2), $c = 15·554$ (5) Å, $\beta = 121·6$ (1)°, $V = 1496·1$ Å³, $Z = 2$, $D_x = 5·983$ g cm⁻³, $\lambda(Mo K\alpha) = 0·71069$ Å, $\mu = 40·24$ cm⁻¹, $F(000) = 2384$, room temperature; reflection condition hkl: $h + k = 2n$; final $R = 0·062$ for 3560 independent reflections. The structure consists of distorted In–S octahedra, and mono- and bicapped triangular prisms of Bi–S as well as bicapped triangular prisms of Pb–S (site occupancy of Pb~0·8), all forming chains along y.

Introduction. The present paper is part of a series on the study of lead indium bismuth chalcogenides.

Experimental. Needle-shaped crystals up to $20 \times 0·5 \times 0·5$ mm grown by chemical vapour transport with iodine in a two-zone furnace adjusted to 923–873 K; charge consisted of Pb+4In+2Bi+10S. Black crystals

with high metallic lustre, elongated along y, pinacoids {100}, {001}, {20$\bar{1}$}, and {010}; D_m not measured; crystal $20 \times 1500 \times 20$ µm, automatic four-circle diffractometer (Enraf–Nonius CAD-4), graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from refinement of 20 reflections, scan width 1·2°, ω–2θ scan mode, $2\theta < 70°$, h 0 to 46, k 0 to 6, $l \pm 21$; *SHELX* (Sheldrick, 1976) and XRAY systems (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); two standard reflections: no significant variation; 7296 total reflections, 3560 independent, 3038 with $I > 3\sigma(I)$; $R_{int} = 5·0\%$; corrections for Lorentz–polarization, absorption (A^* 1·973 to 2·345), and extinction effects [$g = 2·43$ (8) $\times 10^{-4}$]. A starting set of heavy atoms was selected from an E map calculated with direct methods (*SHELX*); remaining atoms from successive Fourier syntheses; $\sum w(\Delta F^2)$ minimized, unit weights. Refinement of positional and