The Crystal Structure of $Cs_6W_{11}O_{36}$

BY K. OKADA, F. MARUMO AND S. IWAI

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

The crystal structure of $Cs_6W_{11}O_{36}$ has been determined from three-dimensional X-ray diffractometer data and refined to an R value of 0·057 for 2321 observed reflexions. $Cs_6W_{11}O_{36}$ crystallizes in the monoclinic space group Aa with $a = 37·800$ (5), $b = 7·261$ (1), $c = 12·577$ (2) Å, $\beta = 102·81$ (1)°, $Z = 4$ and $D_x = 6·70$ g cm^{-3}. The structure is built up of distorted WO_6 octahedra, and CsO_{15} and CsO_{18} coordination polyhedra. WO_6 octahedra are linked by sharing corners to form layers of $|(W_{11}O_{36})^6\,|$ anions parallel to (001). The W–O bond lengths vary from 1·57 (7) to 2·30 (7) Å, with a mean value of 1·93 Å. Four crystallographically independent Cs atoms occupy large tunnel sites in the $|(W_{11}O_{36})^6\,|$ layer and each is coordinated by 18 O atoms. The remaining two Cs atoms are situated between the neighbouring layers and coordinated by 15 O atoms. The Cs–O bond lengths vary from 2·94 (7) to 3·93 (8) Å. The mean values are 3·49 Å for CsO_{15} and 3·54 Å for CsO_{18}.

Introduction

In the Cs_2WO_4–WO_3 system the existence of three compounds, $Cs_2W_2O_7$, $Cs_2W_3O_{10}$ and $Cs_2W_6O_{19}$, was reported on the basis of synthesis from the melts (Chang & Sachdev, 1975). On the other hand, crystals of $Cs_{22}W_{32}O_{107}$ (W/Cs = 1·455), close to $Cs_2W_3O_{10}$ (W/Cs = 1·5), were synthesized, and found to be isostructural with $Rb_{22}W_{32}O_{107}$ (Okada, Marumo & Iwai, 1977).

The phase relation of the Cs_2WO_4–WO_3 system was investigated to settle the disagreement between these two reports. Crystals of $Cs_6W_{11}O_{36}$, which had not been reported, were synthesized during the investigation. It is of interest to compare the structure of $Cs_6W_{11}O_{36}$ with that of $Cs_{22}W_{32}O_{107}$ to obtain further knowledge on the crystal chemistry of the isopoly-tungstate anions. The structure determination of $Cs_6W_{11}O_{36}$ was, therefore, undertaken by means of single-crystal X-ray diffraction.

Experimental

Crystals of $Cs_6W_{11}O_{36}$ were synthesized by heating an intimate mixture of Cs_2CO_3 and WO_3, in molar ratio 1:4, in a platinum crucible at 1100°C for 3 h and by

cooling at the rate 20–30°C h^{-1}. They are colourless, transparent thin plates with rhombic shapes.

From Weissenberg and precession photographs, the crystal was found to have monoclinic symmetry. Systematic absences of hkl for $k + l$ odd and $h0l$ for h odd restricted possible space groups to Aa (non-centrosymmetric) and $A2/a$ (centrosymmetric). Crystallographic data are given in Table 1.

Intensities were collected on a four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation reflected from a graphite monochromator. The dimensions of the crystal are about $0·13 \times 0·13 \times 0·02$ mm. The ω–2θ scan technique was employed with a scanning speed of 4° min^{-1} in ω. Because of the large cell dimensions, narrow scan widths determined with the formula $(0·8 + 0·1 \tan \theta)$° were employed. In all, 2321 independent reflexion data, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained within the range $2\theta < 60°$. Here, the $\sigma(|F|)$'s are the standard deviations of the structure amplitudes due to counting statistics. Intensities were corrected for Lorentz and polarization factors. Absorption corrections were also made by a local version of the program *ACACA* (Wuensch & Prewitt, 1965), the maximum and minimum transmission factors being 0·2633 and 0·0095 respectively. Corrections for isotropic secondary extinction were carried out in the course of the structure refinement with a sphere 0·08 mm in diameter assumed for the crystal shape.

Structure determination

The structure was solved by the heavy-atom method. The arrangement of metal atoms was derived from the

Table 2. *Final positional and isotropic thermal parameters for* $Cs_6W_{11}O_{36}$

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
W(1)	0·5	0·2342 (10)	0·75	0·80*	O(11)	0·664 (3)	0·168 (15)	0·382 (9)	5·0 (23)
W(2)	0·5000 (1)	0·2354 (9)	0·2192 (3)	0·77*	O(12)	0·648 (2)	0·326 (11)	0·628 (6)	2·2 (15)
W(3)	0·6653 (3)	0·2476 (9)	0·5170 (7)	0·84*	O(13)	0·653 (2)	0·691 (7)	0·641 (5)	0·5 (8)
W(4)	0·3346 (3)	0·2318 (10)	0·9619 (8)	0·67*	O(14)	0·709 (2)	0·303 (9)	0·568 (5)	0·5 (9)
W(5)	0·3352 (3)	0·2461 (11)	0·4447 (7)	1·07*	O(15)	0·716 (2)	0·702 (12)	0·547 (7)	2·6 (16)
W(6)	0·6651 (3)	0·2447 (10)	0·0022 (9)	1·23*	O(16)	0·488 (2)	0·200 (9)	0·360 (5)	0·9 (11)
W(7)	0·5841 (3)	0·0051 (13)	0·3675 (7)	0·90*	O(17)	0·494 (2)	0·814 (12)	0·373 (7)	1·6 (15)
W(8)	0·4165 (2)	−0·0050 (13)	0·5894 (7)	0·67*	O(18)	0·514 (2)	0·664 (8)	0·086 (5)	0·7 (10)
W(9)	0·6659 (3)	0·5229 (9)	0·7572 (8)	1·09*	O(19)	0·513 (2)	0·313 (9)	0·093 (6)	0·8 (11)
W(10)	0·3356 (3)	0·5128 (10)	0·2087 (7)	0·68*	O(20)	0·333 (2)	0·313 (9)	0·089 (6)	1·2 (11)
W(11)	0·5000 (3)	0·0298 (4)	0·4834 (10)	0·89*	O(21)	0·332 (2)	0·685 (8)	0·104 (4)	0·2 (8)
Cs(1)	0·2794 (3)	−0·0001 (17)	0·1690 (9)	1·70*	O(22)	0·348 (2)	0·326 (7)	0·315 (5)	0·2 (9)
Cs(2)	0·7214 (4)	0·0017 (24)	0·7971 (12)	3·21*	O(23)	0·354 (2)	0·688 (11)	0·311 (7)	2·8 (15)
Cs(3)	0·4013 (4)	−0·0026 (25)	0·2518 (12)	3·21*	O(24)	0·287 (2)	0·285 (13)	0·409 (7)	2·2 (17)
Cs(4)	0·6008 (4)	0·0025 (18)	0·7183 (10)	1·79*	O(25)	0·293 (2)	0·693 (10)	0·421 (6)	1·1 (11)
Cs(5)	0·5638 (4)	0·4942 (22)	0·5252 (11)	2·38*	O(26)	0·456 (3)	0·323 (14)	0·196 (7)	3·3 (18)
Cs(6)	0·4375 (3)	0·5037 (18)	0·4420 (10)	1·77*	O(27)	0·452 (2)	0·672 (9)	0·183 (6)	0·6 (10)
O(1)	0·544 (2)	0·010 (10)	0·472 (5)	1·0 (10)	O(28)	0·389 (3)	0·812 (14)	0·513 (8)	2·5 (19)
O(2)	0·333 (2)	0·020 (9)	0·418 (5)	1·0 (10)	O(29)	0·393 (2)	0·170 (8)	0·513 (5)	0·9 (10)
O(3)	0·608 (2)	0·007 (12)	0·269 (6)	1·1 (11)	O(30)	0·514 (2)	0·504 (12)	0·281 (5)	0·7 (10)
O(4)	0·709 (2)	0·520 (12)	0·751 (7)	2·5 (16)	O(31)	0·668 (2)	−0·022 (9)	0·557 (5)	0·7 (10)
O(5)	0·493 (3)	0·009 (15)	0·186 (6)	2·3 (15)	O(32)	0·654 (2)	0·467 (10)	0·463 (6)	2·1 (14)
O(6)	0·548 (2)	0·824 (10)	0·293 (6)	0·7 (12)	O(33)	0·288 (2)	0·503 (11)	0·203 (5)	1·0 (10)
O(7)	0·548 (2)	0·203 (10)	0·299 (6)	1·2 (13)	O(34)	0·391 (3)	0·484 (15)	0·208 (8)	3·2 (20)
O(8)	0·606 (2)	0·811 (9)	0·447 (6)	0·6 (11)	O(35)	0·351 (2)	0·502 (11)	0·505 (5)	0·8 (9)
O(9)	0·612 (2)	0·202 (12)	0·439 (7)	3·1 (17)	O(36)	0·450 (2)	0·013 (11)	0·498 (5)	1·3 (11)
O(10)	0·668 (2)	0·818 (8)	0·348 (5)	1·2 (9)					

* Calculated from anisotropic thermal parameters according to the expression: $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)/3$.

Table 3. *Bond lengths* (Å) *for* $Cs_6W_{11}O_{36}$

Symmetry code

(0)	x,	y,	z	(v)	x,	$-\frac{1}{2} + y$,	$-\frac{1}{2} + z$
(i)	x,	$1 + y$,	z	(vi)	$\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$\frac{1}{2} + z$
(ii)	x,	$-1 + y$,	z	(vii)	$-\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$-\frac{1}{2} + z$
(iii)	x,	$\frac{1}{2} + y$,	$\frac{1}{2} + z$	(viii)	x,	y,	$1 + z$
(iv)	x,	$-\frac{1}{2} + y$,	$\frac{1}{2} + z$	(ix)	x	$\frac{1}{2} + y$,	$-\frac{1}{2} + z$

W(1)O$_6$ (mean)	1·93	W(2)O$_6$ (mean)	1·89	W(3)O$_6$ (mean)	1·84
W(1)–O(5^{iii})	2·02 (10)	W(2)–O(5^0)	1·83 (11)	W(3)–O(9^0)	2·06 (7)
W(1)–O(6^{iv})	1·89 (7)	W(2)–O(7^{ii})	1·88 (7)	W(3)–O(11^0)	1·78 (11)
W(1)–O(17^{iv})	1·71 (9)	W(2)–O(16^0)	1·94 (7)	W(3)–O(12^0)	1·76 (8)
W(1)–O(18^{iv})	2·30 (7)	W(2)–O(19^0)	1·85 (8)	W(3)–O(14^0)	1·68 (6)
W(1)–O(27^{iv})	1·88 (7)	W(2)–O(26^0)	1·74 (10)	W(3)–O(31^0)	2·02 (7)
W(1)–O(30^{iv})	1·77 (8)	W(2)–O(30^0)	2·12 (8)	W(3)–O(32^0)	1·75 (7)
W(4)O$_6$ (mean)	1·93	W(5)O$_6$ (mean)	1·95	W(6)O$_6$ (mean)	2·01
W(4)–O(2^{iii})	2·16 (7)	W(5)–O(2^0)	1·67 (7)	W(6)–O(8^v)	2·24 (7)
W(4) O(20^{viii})	1·72 (7)	W(5)–O(21^{iv})	2·08 (5)	W(6)–O(10^v)	2·04 (7)
W(4)–O(23^{iv})	2·20 (9)	W(5)–O(22^0)	1·89 (7)	W(6) O(13^v)	1·94 (6)
W(4)–O(25^{iv})	1·57 (7)	W(5)–O(24^0)	1·80 (7)	W(6)–O(15^v)	1·91 (7)
W(4)–O(28^{iv})	2·10 (10)	W(5)–O(29^0)	2·23 (6)	W(6)–O(31^{ix})	1·82 (7)
W(4)–O(35^{iv})	1·82 (7)	W(5)–O(35^0)	2·05 (7)	W(6)–O(32^v)	2·10 (7)
W(7)O$_6$ (mean)	1·94	W(8)O$_6$ (mean)	1·93	W(9)O$_6$ (mean)	1·95
W(7) –O(1^0)	2·22 (7)	W(8)–O(26^{iv})	2·17 (9)	W(9)–O(3^{iii})	2·23 (8)
W(7)–O(3^0)	1·69 (8)	W(8)–O(27^{iv})	2·03 (6)	W(9)–O(4^0)	1·65 (8)
W(7)–O(6^{ii})	1·98 (7)	W(8)–O(28^{ii})	1·82 (9)	W(9)–O(10^{ix})	1·87 (6)
W(7) –O(7^0)	2·04 (7)	W(8)–O(29^0)	1·72 (6)	W(9)–O(11^{iii})	1·90 (11)
W(7)–O(8^{ii})	1·82 (7)	W(8)–O(34^{iv})	1·95 (11)	W(9)–O(12^0)	2·16 (7)
W(7) - O(9^0)	1·88 (8)	W(8)–O(36^0)	1·89 (7)	W(9) O(13^0)	1·88 (5)

Table 3 (cont.)

W(10)O$_6$ (mean)	1·92	W(11)O$_6$ (mean)	1·90		
W(10)–O(20^0)	2·08 (7)	W(11)–O(1^0)	1·71 (7)		
W(10)–O(21^0)	1·80 (5)	W(11)–O(16^0)	1·96 (6)		
W(10)–O(22^0)	1·89 (6)	W(11)–O(17^{ii})	2·07 (9)		
W(10)–O(23^0)	1·83 (8)	W(11)–O(18^{iv})	1·61 (6)		
W(10)–O(33^0)	1·79 (7)	W(11)–O(19^{iv})	2·08 (7)		
W(10)–O(34^0)	2·11 (11)	W(11)–O(36^0)	1·94 (7)		
Cs(1)O$_{15}$ (mean)	3·48	Cs(2)O$_{15}$ (mean)	3·50	Cs(3)O$_{18}$ (mean)	3·54
Cs(1)–O(2^0)	3·33 (6)	Cs(2)–O(4^0)	3·82 (9)	Cs(3)–O(2^0)	3·67 (7)
Cs(1)–O(4^{vii})	3·06 (9)	Cs(2)–O(4^{ii})	3·56 (9)	Cs(3)–O(5^0)	3·74 (8)
Cs(1)–O(14^{vii})	3·04 (6)	Cs(2)–O(10^{iv})	3·21 (6)	Cs(3)–O(16^0)	3·57 (7)
Cs(1)–O(15^{vii})	2·94 (7)	Cs(2)–O(11^{iv})	3·57 (11)	Cs(3)–O(17^{ii})	3·74 (7)
Cs(1)–O(20^0)	3·35 (7)	Cs(2)–O(12^0)	3·89 (7)	Cs(3)–O(20^0)	3·71 (6)
Cs(1)–O(21^{ii})	3·25 (6)	Cs(2)–O(13^{ii})	3·66 (5)	Cs(3)–O(21^{ii})	3·65 (6)
Cs(1)–O(22^0)	3·69 (5)	Cs(2)–O(14^0)	3·57 (6)	Cs(3)–O(22^0)	3·33 (6)
Cs(1)–O(23^{ii})	3·75 (7)	Cs(2)–O(14^{iv})	3·82 (7)	Cs(3)–O(23^{ii})	3·06 (8)
Cs(1)–O(24^0)	3·62 (7)	Cs(2)–O(15^{ii})	3·79 (9)	Cs(3)–O(26^0)	3·32 (10)
Cs(1)–O(24^v)	3·69 (8)	Cs(2)–O(15^{iv})	3·51 (9)	Cs(3)–O(27^{ii})	3·28 (7)
Cs(1)–O(25^{ii})	3·81 (7)	Cs(2)–O(24^{vi})	3·00 (6)	Cs(3)–O(28^{ii})	3·67 (11)
Cs(1)–O(25^v)	3·56 (8)	Cs(2)–O(25^{vi})	3·14 (6)	Cs(3)–O(28^v)	3·72 (10)
Cs(1)–O(33^0)	3·68 (8)	Cs(2)–O(31^0)	3·24 (6)	Cs(3)–O(29^0)	3·59 (7)
Cs(1)–O(33^{ii})	3·64 (8)	Cs(2)–O(32^{iv})	3·64 (9)	Cs(3)–O(29^v)	3·79 (6)
Cs(1)–O(35^v)	3·75 (7)	Cs(2)–O(33^{vi})	3·01 (7)	Cs(3)–O(34^0)	3·58 (11)
				Cs(3)–O(34^{ii})	3·78 (11)
				Cs(3)–O(35^v)	3·26 (6)
				Cs(3)–O(36^0)	3·23 (6)
Cs(4)O$_{18}$ (mean)	3·53	Cs(5)O$_{18}$ (mean)	3·52	Cs(6)O$_{18}$ (mean)	3·55
Cs(4)–O(1^0)	3·36 (6)	Cs(5)–O(1^0)	3·63 (7)	Cs(6)–O(5^{iii})	3·31 (7)
Cs(4)–O(3^{iii})	3·72 (9)	Cs(5)–O(1^i)	3·85 (7)	Cs(6)–O(16^0)	3·23 (7)
Cs(4)–O(3^{iv})	3·65 (9)	Cs(5)–O(3^{iii})	3·15 (7)	Cs(6)–O(17^0)	3·35 (9)
Cs(4)–O(6^{iv})	3·34 (8)	Cs(5)–O(5^{iii})	3·69 (8)	Cs(6)–O(18^{iv})	3·92 (6)
Cs(4)–O(7^{iv})	3·26 (8)	Cs(5)–O(6^0)	3·72 (7)	Cs(6)–O(19^{iii})	3·79 (7)
Cs(4)–O(8^{ii})	3·73 (7)	Cs(5)–O(6^{iv})	3·76 (8)	Cs(6)–O(22^0)	3·64 (6)
Cs(4)–O(8^{iv})	3·62 (7)	Cs(5)–O(7^0)	3·49 (7)	Cs(6)–O(23^0)	3·49 (7)
Cs(4)–O(9^0)	3·91 (9)	Cs(5)–O(7^{iii})	3·93 (8)	Cs(6)–O(26^0)	3·57 (10)
Cs(4)–O(9^{iv})	3·48 (9)	Cs(5)–O(8^0)	3·08 (7)	Cs(6)–O(26^{iii})	3·88 (9)
Cs(4)–O(10^{iv})	3·54 (6)	Cs(5)–O(9^0)	3·14 (9)	Cs(6)–O(27^0)	3·63 (7)
Cs(4)–O(11^{iv})	3·70 (10)	Cs(5)–O(12^0)	3·39 (7)	Cs(6)–O(27^{iv})	3·81 (7)
Cs(4)–O(12^0)	3·30 (8)	Cs(5)–O(13^0)	3·65 (6)	Cs(6)–O(28^0)	3·15 (11)
Cs(4)–O(13^{ii})	3·29 (6)	Cs(5)–O(16^0)	3·80 (6)	Cs(6)–O(29^0)	3·19 (6)
Cs(4)–O(18^{iv})	3·53 (6)	Cs(5)–O(17^0)	3·71 (8)	Cs(6)–O(30^0)	3·88 (7)
Cs(4)–O(19^{iv})	3·62 (7)	Cs(5)–O(18^{iv})	3·24 (7)	Cs(6)–O(34^0)	3·08 (9)
Cs(4)–O(30^{iv})	3·54 (7)	Cs(5)–O(19^{iii})	3·24 (8)	Cs(6)–O(35^0)	3·53 (7)
Cs(4)–O(31^0)	3·59 (7)	Cs(5)–O(30^0)	3·23 (6)	Cs(6)–O(36^0)	3·64 (8)
Cs(4)–O(32^{iv})	3·29 (7)	Cs(5)–O(32^0)	3·67 (8)	Cs(6)–O(36^i)	3·77 (8)

three-dimensional Patterson function with space group Aa assumed, and the trial structure was refined to give an R value of 0·100. No reasonable model was derived for the space group $A2/a$. Therefore, the non-centrosymmetric space group Aa was adopted as the correct one. All O atoms were found on the Fourier and difference Fourier maps synthesized with phases derived from the metal atoms. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assigning anisotropic temperature factors to W and Cs and isotropic factors to O. After correction for secondary extinction, the calculation converged to an R value of 0·057 for the 2321 observed reflexions; the extinction parameter (G) was 0·12 (1) × 10^{-4} and the largest correction was about 19% of F. In the least-squares refinements, the x and z parameters of W(1) were fixed at 0·5 and 0·75 respectively, since the origin can be taken at any point along the a and c axes in the space group Aa. The weighting scheme of Hughes (1941) was adopted: $w = 1·0$ if $F_o < 580·0$, and $w = (580·0/F_o)^2$ if $580·0 \leq F_o$. The atomic scattering factors for W^{6+} and Cs$^+$ were taken from *International Tables for X-ray Crystallography* (1974) and those for O^{2-} given by Tokonami (1965) were used. The dispersion correction factors for all the atoms were also taken from *Inter-*

national Tables for X-ray Crystallography (1974). The final positional and thermal parameters are listed in Table 2.*

Discussion

The W—O and Cs—O bond lengths in WO_6, CsO_{15} and CsO_{18} coordination polyhedra and their mean values are given in Table 3 with their estimated standard deviations in parentheses. The standard deviations are rather large because of the lower accuracy of the O positions. The structure viewed along **b** is shown in Fig. 1. There are eleven crystallographically independent W atoms in the unit cell, each being octahedrally surrounded by six O atoms. The WO_6 octahedra are largely distorted. The W—O bond lengths range from 1·57 (7) to 2·30 (7) Å with the mean value of 1·93 Å. The

* Lists of structure factors and anisotropic temperature factors for W and Cs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32957 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
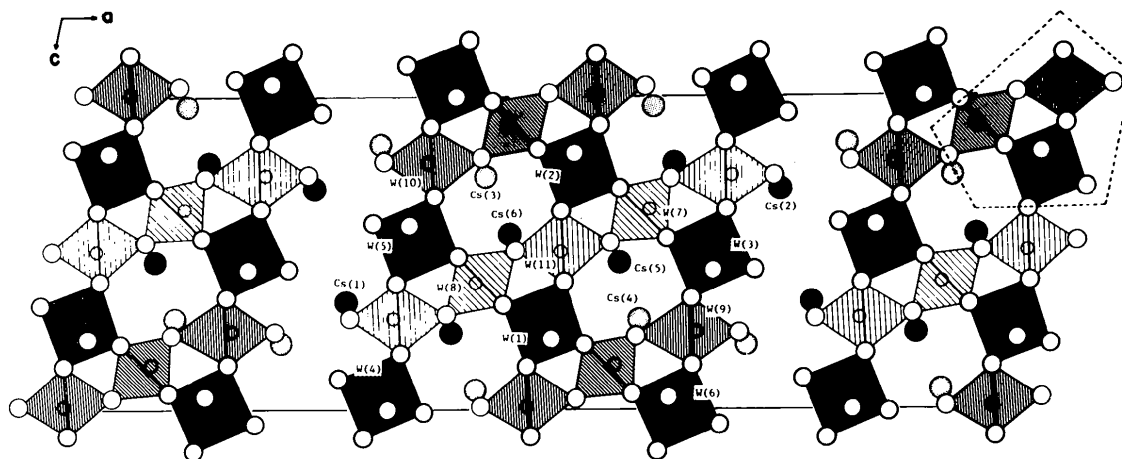
O—W—O angles between neighbouring W—O bonds range from 71 (4) to 106 (3)° and those between W—O bonds extending on the opposite sides from a W atom range from 155 (4) to 177 (3)°. There are six crystallographically independent Cs atoms in the unit cell. Cs(1) and Cs(2) are surrounded by 15 O atoms, and Cs(3), Cs(4), Cs(5) and Cs(6) are surrounded by 18 O atoms. The Cs—O bond lengths in the CsO_{15} polyhedra range from 2·94 (7) to 3·89 (7) Å with a mean value of 3·49 Å. The Cs—O bond lengths in the CsO_{18} polyhedra range from 3·06 (8) to 3·93 (8) Å with a mean value of 3·54 Å.

As shown in Table 4, each of the eleven WO_6 octahedra shares corners with five or six neighbouring WO_6 octahedra. Six W atoms [W(1) to W(6)] and their crystallographic equivalents are situated nearly on the planes $y = 0·25$ and 0·75. The coordination octahedra around these W atoms form three crystallographically independent $[(W_2O_{10})^{8-}]_\alpha$ anion chains, parallel to **b**, by sharing corners. The remaining five independent octahedra [W(7)O_6 to W(11)O_6], whose central metal atoms are situated nearly on the planes $y = 0$ or 0·5, are linked to form a chain parallel to the (010) plane and combine the $[(W_2O_{10})^{8-}]_\alpha$ anion chains laterally to

Fig. 1. The crystal structure of $Cs_6W_{11}O_{36}$ viewed along **b**. The levels of the WO_6 octahedra are shown by shading. The darkly shaded octahedra are approximately at the level $y = 0·25$. The finely striped ones are at about $y = 0·5$ and the widely striped at $y = 0$. The WO_6 octahedra at the level $y = 0·75$, which are crystallographically related to those at $y = 0·25$, are omitted to avoid complexity.

Table 4. *Corner-sharing scheme between the* WO_6 *octahedra*

	W(1)O_6	W(2)O_6	W(3)O_6	W(4)O_6	W(5)O_6	W(6)O_6	W(7)O_6	W(8)O_6	W(9)O_6	W(10)O_6	W(11)O_6
W(1)O_6	–	2	–	–	–	–	1	1	–	–	2
W(2)O_6	2	–	–	–	–	–	1	1	–	–	2
W(3)O_6	–	–	–	–	–	2	1	–	2	–	–
W(4)O_6	–	–	–	–	2	–	–	1	–	2	–
W(5)O_6	–	–	–	2	–	–	–	1	–	2	–
W(6)O_6	–	–	2	–	–	–	1	–	2	–	–
W(7)O_6	1	1	1	–	–	1	–	–	1	–	1
W(8)O_6	1	1	–	1	1	–	–	–	–	1	1
W(9)O_6	–	–	2	–	–	2	1	–	–	–	–
W(10)O_6	–	–	–	2	2	–	–	1	–	–	–
W(11)O_6	2	2	–	–	–	–	1	1	–	–	–
Total	6	6	5	5	5	5	6	6	5	5	6

form a complex layer of $[(W_{11}O_{36})^{6-}]_\infty$ parallel to (001). There are large tunnels along **b** within the layers and Cs(3), Cs(4), Cs(5) and Cs(6) are located in them. Cs(1) and Cs(2) are located between the layers and connect neighbouring layers.

It is of interest to compare the structure of $Cs_6W_{11}O_{36}$ (W/Cs = 1·833) with that of $Cs_{22}W_{32}O_{107}$ (W/Cs = 1·455), which is isostructural with $Rb_{22}W_{32}O_{107}$ (Okada *et al.*, 1977), in order to examine the structural change accompanying the change in W/Cs ratio. The structure of $Cs_{22}W_{32}O_{107}$ is constructed by the three-dimensional framework of $[(W_{32}O_{107})^{22-}]_\infty$ built up of corner-shared W_4O_{18} groups. On the other hand, the structure of $Cs_6W_{11}O_{36}$ is constructed by complex layers of WO_6 octahedra by sharing corners. Apparently, there is little similarity between these two structures. However, W_4O_{18} groups are also observed in the $Cs_6W_{11}O_{36}$ structure, as shown in the area enclosed by dashed lines in Fig. 1. In fact, the complex layers in $Cs_6W_{11}O_{36}$ can be considered to be built up of W_4O_{18} groups. Accordingly, the three-dimensional framework of $[(W_{32}O_{107})^{22-}]_\infty$ changes to

complex layers of $[(W_{11}O_{36})^{6-}]_\infty$ retaining the W_4O_{18} units, with increasing molar ratio W/Cs.

We are very grateful to Professor Y. Iitaka for his kindness in allowing us to use an automated four-circle diffractometer. Computations were carried out on HITAC 8700 and M-180 computers at the Computer Center of Tokyo Institute of Technology.

References

CHANG, L. L. Y. & SACHDEV, S. (1975). *J. Am. Ceram. Soc.* **58**, 267–270.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
OKADA, K., MARUMO, F. & IWAI, S. (1977). *Acta Cryst.* **B33**, 3345–3349.
TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

Refinement of the Molecular Charge Distribution in Decaborane(14)

BY HANS DIETRICH AND CHRISTIAN SCHERINGER*

Fritz-Haber-Institut der Max-Planck-Gesellschaft, 1000 *Berlin-Dahlem, Federal Republic of Germany*

The model published by Brill, Dietrich & Dierks [*Acta Cryst.* (1971), B27, 2003–2018] has been further developed and refined by least-squares methods after improving the data reduction of the original measurements. The diffuse charge density spread within the boron framework of the molecule has been accounted for in two different ways, yielding about the same total description of the molecular charge distribution. $F_o - F_c$ syntheses do not indicate further amendments and show only deviations due to errors in the measurements. Elimination of the thermal smearing from the models allows the calculation of the static difference density $(M - A)$ between the molecular charge distribution and isolated atoms, which can be compared directly with quantum-chemical calculations. The comparison shows good agreement in some respects, disagreement in others.

Introduction

It is well known that localized bonds and lone pairs of electrons cause broad diffuse peaks in $X - N$ syntheses, very similar to peaks in $F_o - F_c$ syntheses, from which the positions of hydrogen atoms are derived in a structure determination. This may justify the attempt to approximate these peaks by smeared point charges and treating them in a similar way to light atoms. On the

other hand, the corresponding charge must come from the atoms within the molecule, and therefore it would no longer be correct to treat the atoms as electrically neutral.

Based on these considerations, Brill, Dietrich & Dierks (1971) – hereinafter referred to as BDD – proposed a purely empirical model, which approximates the total molecular electron density by a superposition of spherical atomic cores and smeared point charges. BDD's model (model 1 in this paper) was refined with trial-and-error and Fourier methods and was subject to a number of restrictions. It contained only 15 density parameters.

---
* New address: Fachbereich Geowissenschaften der Universität Marburg, Lahnberge, 3550 Marburg, Federal Republic of Germany.