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Structure of Tribarium Dichlorohexaoxoditellurate(IV), $Ba_3Te_2O_6Cl_2$

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Abstract. $M_r = 834{\cdot}1$, cubic, $Fd3m$, $a = 16{\cdot}6896\,(4)$ Å, $V = 4648{\cdot}8$ Å^3, $Z = 16$, $D_x = 4{\cdot}77$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 154{\cdot}7$ cm^{-1}, $F(000) = 5664$, $T = 293$ K. Final $R = 0{\cdot}044$ for 281 unique observed reflections. The structure contains Ba atoms roughly at the centre of polyhedra consisting of six O atoms and three Cl atoms. The base plane of the polyhedron is a boat-shaped hexagon with four coplanar O atoms at 2·89 (1) Å from the Ba atom, and two Cl atoms at 3·20 (1) Å. On the concave side the hexagons are capped by a Cl atom at 3·32 (1) Å, on the other side by two O atoms at 2·62 (1) Å. The polyhedra share faces with each other and edges with regular TeO_3 trigonal pyramids [Te—O = 1·86 (1) Å, O—Te—O = 95·9 (3)°] to form a three-dimensional network with holes, partially occupied by additional Cl atoms. The latter seem to exhibit a weak bonding interaction with the Te lone-pair electrons.

Introduction. In attempts to grow single crystals of Ba_3TeO_6 by the same method as was used for Ca_3TeO_6 (Hottentot & Loopstra, 1981) we isolated a product of which the Guinier powder pattern (Cu $K\alpha$, internal standard α-SiO_2) could be indexed on a cubic *F*-centred cell with $a = 16{\cdot}69$ Å. The compound was obtained by heating a mixture of TeO_2 and $BaCl_2.2H_2O$ (weight ratio 1:5) at 1073 K over 2 d followed by heating at 1273 K over 1 d. After removing excess $BaCl_2$ with water tiny crystals were found. X-ray fluorescence measurements indicated that the Ba/Te ratio was about 1·5 and hence we were faced with a new compound. A halogen analysis showed that the compound contained some 10% Cl, but it was not until the end of the structure refinement when it became clear that the proper composition is $Ba_3TeO_6Cl_2$.

Experimental. Crystal of irregular shape, 0·075 × 0·075 × 0·25 mm, selected for data collection. Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$, θ–2θ scan method. Accurate cell dimensions obtained by least-squares fitting of 20 reflections. Reference reflections for intensity and orientation remained constant during data collection. 363 reflections measured up to $2\theta = 60°$, range of $hkl = 0$–16, 0–13, 1–23, 82 reflections considered unobserved $[I < 3\sigma(I)]$ and remaining 281 reflections used in refinement based on *F*. No absorption or extinction corrections applied. Coordinates of Ba and Te found from Patterson maps while those of O revealed by Fourier difference maps. In this way we located Ba at $x, \frac{1}{8}, \frac{1}{8}$ [48(*f*)], Te at x, x, x [32(*e*)] and O at x, x, z [96(*g*)] (see Table 1). In difference maps three independent peaks were found at $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$ [8(*b*)] (35 e Å^{-3}), 0, 0, 0 [16(*c*)] (6 e Å^{-3}) and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ [16(*d*)] (30 e Å^{-3}). The 8(*b*) and 16(*d*) positions were assigned to Cl atoms. To achieve electroneutrality eight Cl had to be distributed over the 16(*c*) sites, but in doing so these atoms exhibited a very high temperature factor. Difference maps showed negative density at the site, surrounded by positive areas. This pointed to atomic positions slightly off the site, *i.e.* a 96(*h*) position with a population parameter of $\frac{1}{12}$. This model yielded a final *R* of 0·044 (unit weights); $S = 0{\cdot}59$. Temperature factors refined isotropically. $(\Delta/\sigma)_{\max} = 0{\cdot}1$ for Cl(3), 0·02 for Ba. $\Delta\rho = -3{\cdot}1$–$4{\cdot}4$ e Å^{-3} near Ba atom. Atomic scattering factors from Cromer & Mann (1968), dispersion factors for Te and Ba from *International Tables for X-ray Crystallography* (1974). All computations carried out with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Table 1 lists final coordinates and isotropic temperature factors.* Table 2 gives selected bond lengths and angles.

The barium coordination (see Fig. 1) consists of a boat-shaped hexagon of four coplanar O atoms in a rectangle and two Cl atoms which are 0·63 (1) Å out of this plane. At the concave side the hexagon is capped by a Cl atom [Cl(1)], at the convex side by two O atoms [O(*t*1) and O(*t*2)]. The Ba atom is at the convex side, 0·60 (1) Å away from the plane of the basal O atoms [O(*b*1)–O(*b*4)]. The symmetry of the polyhedron is C_{2v} with the twofold axis perpendicular to the base plane.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38789 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Due to its position on a threefold axis Te is at the apex of a regular trigonal TeO_3 pyramid with Te—O bonds of 1·86 (1) Å and O—Te—O angles of 95·9 (3)°. These values are in close agreement with the typical values of the *C* configuration (three coordination) given by Brown (1974) (1·88 Å, 96°) and Trömel (1980) (1·865 Å, av.; 98°, av.). The TeO_3 pyramids are not mutally connected, the smallest distance between a Te atom of one pyramid and an O atom of another is 4·63 (1) Å.

The structure can be considered as a packing of barium coordination polyhedra and TeO_3 pyramids. Each polyhedron shares planes with eight surrounding polyhedra (see Figs. 2 and 3). In Fig. 2 a stereoscopic view along the threefold axis is given. The Cl(1) atom at the centre of this figure is shared by six barium coordination polyhedra. The TeO_3 pyramids share edges with three polyhedra (Te—O bonds not drawn). In Fig. 3 the coordination of the 16(*c*) site is given. Six polyhedra form a cage by sharing O—Cl(2)—O faces. The apparent holes are blocked off by the Te free-electron pairs. On average each hole is occupied by half a Cl atom, situated off-centre to reduce two Te—Cl(3) [from 3·72 (1) to 3·43 (1) Å] and two Ba—Cl(3) distances [from 4·16 (1) to 3·73 (1) Å] at the expense of the remaining ones. The shortest Cl(3)—O distance is 3·37 (2) Å. While the Ba—Cl(3) distance is very close to the sum of the van der Waals radii (3·78 Å), the Te—Cl(3) distance is less than the sum of the van der Waals radii (4·00 Å), but considerably longer than the sum of the crystal radii (2·51 Å). Apparently this behaviour is indicative of a weak bonding interaction with the Te atom lone pair, analogous to the weak bonds which Te forms with O in the direction of the lone pair in most tellurites (Brown, 1974; Trömel, 1980). Like the Te—Cl(3) bonds, these Te—O bonds are shortened by 0·5 Å compared to the sum of their van der Waals radii. A possible mechanism for the stabilization of the Cl(3) atoms would seem a displacement of charge off the Te atoms towards an empty 16(*c*) site, giving rise to a net positive charge at Te and a lessening of the charge difference between empty and occupied sites.

In comparing the structure of $Ba_3Te_2O_6Cl_2$ with those of $Ni_3Te_2O_6(OH)_2$ and $Co_3Te_2O_6(OH)_2$ (Perez, Lasserre, Moret & Maurin, 1976) a remarkable fact is noticed. In these hydroxytellurites the exact position of the OH O atom O(5) is uncertain. This atom is placed on a position of high symmetry [2(*a*) in $P6_3mc$], exhibits a relatively high temperature factor, and has no cations within bonding distances. All this is reminiscent of the situation with Cl(3) in $Ba_3Te_2O_6Cl_2$. Apparently there is a class of tellurites $M_3Te_2O_6X_2$ in which a quarter of the *X* atoms are situated in (partially occupied) holes in the structure, centred around points of high symmetry.

Table 1. *Final atomic coordinates and isotropic temperature factors* ($Å^2 \times 10^2$)

	Position	*x*	*y*	*z*	*pp**	U_{iso}
Te	32(*e*)	0·21789 (7)	0·21789 (7)	0·21789 (7)	1·0000	2·14 (3)
Ba	48(*f*)	0·42599 (8)	$\frac{1}{8}$	$\frac{1}{8}$	1·0000	1·63 (2)
O	96(*g*)	0·2120 (6)	0·2120 (6)	0·3288 (8)	1·0000	3·4 (3)
Cl(1)	8(*b*)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	1·0000	2·0 (3)
Cl(2)	16(*d*)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1·0000	4·5 (3)
Cl(3)	96(*h*)	−0·022 (2)	0	0·022 (2)	0·0833	3·0 (9)

* Population parameter.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Te—O	1·86 (1)	(3×)	Ba—O	2·62 (1)	(2×)
				2·89 (1)	(4×)
O—Te—O	95·9 (3)	(3×)	Ba—Cl(1)	3·32 (1)	
			Ba—Cl(2)	3·20 (1)	(2×)

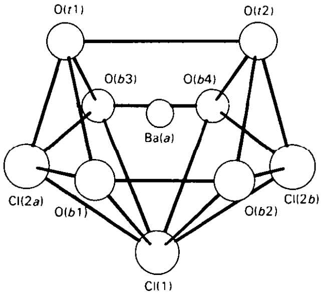

Fig. 1. The barium coordination polyhedron.

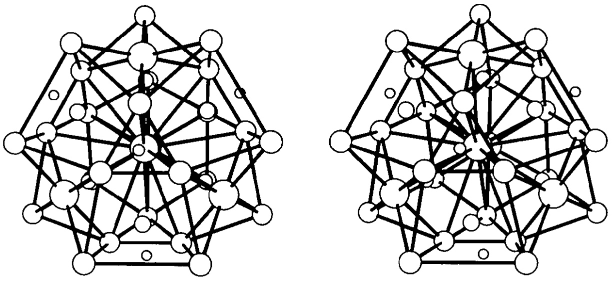

Fig. 2. Stereoscopic view of the packing around Cl(1). The ratio of the diameters of Te:Ba: O: Cl is 0·20: 0·30: 0·40: 0·55.

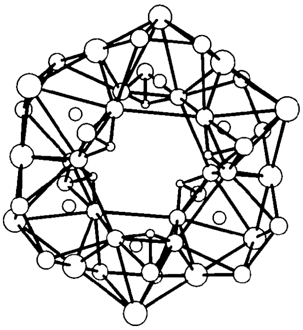

Fig. 3. The partially occupied hole at 16(*c*) [Cl(3) not drawn].

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References

BROWN, I. D. (1974). *J. Solid State Chem.* **11**, 214–233.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HOTTENTOT, D. & LOOPSTRA, B. O. (1981). *Acta Cryst.* B**37**, 220–222.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press.

PEREZ, G., LASSERRE, F., MORET, J. & MAURIN, M. (1976). *J. Solid State Chem.* **17**, 143–149.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TRÖMEL, M. (1980). *J. Solid State Chem.* **35**, 90–98.

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Caractéristiques Physiques et Structure du Molybdate Double $Co_3Na_4Mo_{22,33}O_{72}$

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Abstract. $M_r = 3563$, rhombohedral, $R\bar{3}c$, hexagonal-cell constants $a = 9{\cdot}118\,(6)$, $c = 22{\cdot}643\,(7)$ Å, $V = 1630{\cdot}29$ Å^3, $Z = 1$, $D_x = 3{\cdot}63$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo}\,K\alpha) = 50$ cm^{-1}, $F(000) = 1639$, $T = 294$ K. The structure was solved by conventional Patterson and Fourier techniques using 972 counter-measured reflections and refined to an R factor of 0·047. It may be described as units formed by two MO_6 octahedra (M = Co, Mo) and a trigonal antiprism NaO_6 sharing faces, connected through MoO_4 tetrahedra. Many sites are only partially occupied and the formula is $Na_4\square_2Co^{II}_{1+3x}Mo_{5-x}\square_{6-2x}Mo_{18}O_{72}$ with $0 < x < 1$. For the crystal studied $x = 0{\cdot}67$.

Introduction. Au cours de l'exploration du système ternaire Na_2O–ZnO–MoO_3, diverses phases ont été isolées par Gicquel-Mayer (1981). La substitution du zinc par des métaux(II) de transition a été réalisée en vue de l'étude de leur comportement magnétique par Gicquel-Mayer, Mayer & Perez (1979). Lors de ces synthèses devant conduire à des composés isotypes, deux nouvelles phases ont été identifiées ce présent travail est relatif à l'étude structurale de l'une d'elles: le molybdate mixte de formule $Co_3Na_4Mo_{22,33}O_{72}$.

Partie expérimentale. La synthèse est effectuée à partir d'un mélange de Na_2MoO_4 et de $CoCl_2$ dissous dans une solution normale d'acide chlorhydrique. Cette solution aqueuse est évaporée à 443 K. Les cristaux de NaCl formés et l'excès de $CoCl_2$ sont éliminés par plusieurs lavages à l'eau. Le résidu, séché, subit enfin un traitement à 873 K pendant quatre heures. Au refroidissement, on obtient un mélange de trois solides: le trioxyde MoO_3, le molybdate $Na_6Mo_{10}O_{33}$ dopé au cobalt isolé par Coquerel (1981) et le molybdate $Co_3Na_4Mo_{22,33}O_{72}$. Cette dernière phase rose-rouge est très minoritaire dans ce mélange.

Les conditions de mesure des intensités diffractéees* par un monocristal figurent au Tableau 1. Les tests statistiques de Wilson laissent supposer un caractère centrosymétrique de la structure. Aussi le groupe $R\bar{3}c$ a-t-il été retenu pour cette étude.

L'exploitation de la fonction de Patterson et des sections de Harker aux cotes $z = 0, \frac{1}{6}, \frac{1}{3}$ et $\frac{1}{2}$ a permis de localiser un atome de molybdène en position 18(e). Trois cycles d'affinement conduisent à un indice résiduel $R = 0{,}26$ (agitation thermique isotrope). La position [12(e)] d'un nouvel atome, assimilé tout d'abord au cobalt, est déterminée après une synthèse de Fourier.

Le facteur R converge alors vers 0,15. Après sélection de deux atomes d'oxygène en position générale [36(f)] et d'un atome de sodium [6(b)], la valeur $R = 0{,}088$ est atteinte après deux cycles d'affinement. Au vue de la valeur trop élevée de l'agitation thermique isotrope de l'ion sodium son taux d'occupation est affiné, sa valeur converge vers $\frac{2}{3}$ ($R = 0{,}082$). Par ailleurs l'étude du comportement magnétique de cette phase est réalisée entre 4,6 et 400 K. Ce molybdate

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