References

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.
BURZLAFF, H. (1967). *Neues Jahrb. Mineral. Monatsh.* pp. 157–169.
CHRIST, C. L. & CLARK, J. R. (1977). *Phys. Chem. Mineral.* **2**, 59–87.
CLARK, J. R. & APPLEMAN, D. E. (1964). *Science*, **145**, 1295–1296.
CORAZZA, E., MENCHETTI, S., SABELLI, C. & STOPPIONI, A. (1977). *Neues Jahrb. Mineral. Abh.* **131**, 208–233.
GHOSE, S. & WAN, C. (1979). *Am. Mineral.* **64**, 187–195.
GHOSE, S., WAN, C. & CLARK, J. R. (1978). *Am. Mineral.* **63**, 160–171.
GHOSE, S., WAN, C. & ULBRICH, H. H. (1976). *Acta Cryst.* B**32**, 824–832.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.
MENCHETTI, S. & SABELLI, C. (1977). *Acta Cryst.* B**33**, 3730–3733.
MENCHETTI, S. & SABELLI, C. (1979). *Acta Cryst.* B**35**, 2488–2493.
MENCHETTI, S., SABELLI, C. & TROSTI-FERRONI, R. (1982). Submitted.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
RUMANOVA, I. M., KURBANOV, KH. M. & BELOV, N. V. (1966). *Sov. Phys. Crystallogr.* **10**, 513–522.
TENNYSON, C. (1963). *Fortschr. Mineral.* **41**, 64–91.

Acta Cryst. (1982). B**38**, 2991–2997

Structure Determination of the Fluorite-Related Superstructure Phases $Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$

BY D. J. M. BEVAN AND J. DRENNAN

School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia, Australia 5042

AND H. J. ROSSELL

CSIRO Division of Materials Science, Advanced Materials Laboratory, PO Box 4331, *Melbourne, Victoria, Australia* 3001

(*Received* 24 *March* 1982; *accepted* 23 *June* 1982)

Abstract

$Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$ are orthorhombic, space group *Pbcn*, $Z = 4$: for the former, $a = 15{\cdot}8221\,(11)$, $b = 10{\cdot}4814\,(9)$, $c = 10{\cdot}5407\,(8)$ Å, $D_x = 9{\cdot}029$ Mg m^{-3}, and for the latter, $a = 15{\cdot}8761\,(13)$, $b = 10{\cdot}5232\,(8)$, $c = 10{\cdot}5778\,(10)$ Å, $D_x = 5{\cdot}986$ Mg m^{-3}; $T = 298$ K. The structures were determined and refined from integrated powder X-ray diffraction data supplemented by single-crystal electron diffraction results. [$R = 0{\cdot}037$ ($0{\cdot}051$) for 159 (158) observations for the Y(Er) compounds.] The phases are isostructural, and have unit cells derived from a 3 × 2 × 2 array of fluorite-type subcells: cations and formal anion vacancies are ordered so that the W cations are all in sixfold coordination by O, whilst four-fifths of the Er or Y cations are sevenfold and the remainder sixfold coordinated. Corner-linked pairs of WO_6 octahedra form isolated groups in the structure.

Introduction

Some success has already been achieved in identifying the structural principles relating certain homologous series of *anion-excess*, fluorite-related superstructures. Vernier structures (Hyde, Bagshaw, Andersson & O'Keeffe, 1974) of the series M_nX_{2n+1} have been studied in various systems (Galy & Roth, 1973; Jung & Juza, 1973; Bevan & Mann, 1975; Bärnighausen, 1976; Lüke & Eick, 1976; Bärnighausen & Haschke, 1978; Papiernik, Mercurio & Frit, 1980), and quite recently the principle underlying the series M_nX_{2n+5} of the CaF_2–LnF_3 (Ln = rare earth, Y) systems has been discovered (Bevan, Greis & Strähle, 1980). However, there has been little success with *anion-deficient*, fluorite-related superstructures because, despite the existence of many such phases, detailed structural information is sparse. Some structures, determined from single-crystal X-ray studies, have been reported

0567-7408/82/122991-07$01.00

(Byström, 1944*a*,*b*; Bartram, 1966; Ray & Cox, 1975; Moore & Araki, 1976; Gatehouse, Grey, Hill & Rossell, 1981), but, in general, single crystals are not readily available since the cation ordering usually responsible for the phases' existence occurs only at relatively low temperatures, and is often very slow. Most preparations therefore consist only of microcrystalline powders. Nevertheless, at the magnification provided by the electron microscope, single-crystal fragments may be selected in crushed samples, and the corresponding electron diffraction patterns yield unambiguously the relationship of the supercell to the subcell, as well as considerable symmetry information. Thus, knowing the parent substructure, models of the superstructure consistent with the electron diffraction data can be constructed. However, since electron diffraction intensities are inappropriate, in general, for structure determination, selection of the most probable model, and its refinement, must be based on powder X-ray diffraction intensities.

The limited nature of powder X-ray data precludes refinement of the model parameters to the precision normally achieved in single-crystal work; nevertheless, the important features of cation and anion ordering, and the general pattern of atomic shifts from the ideal fluorite positions, can be established readily. This technique has proved useful in the determination of other fluorite-related superstructures (Thornber, Bevan & Graham, 1968; Rossell & Scott, 1975; Allpress, Rossell & Scott, 1976; Von Dreele, Eyring, Bowman & Yarnell, 1975; Rossell, 1976, 1979, 1980), and has been applied here to the compounds $Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$, as single crystals suitable for conventional X-ray study were unavailable.

The phase $Ln_{10}W_2O_{21}$ appears in the systems Ln_2O_3–WO_3 for Ln = Nd – Er, and Y (Summerville, Drennan & Bevan, 1977; Drennan, 1978). It is stable only at elevated temperatures, the temperature at which it forms from the component oxides increasing from 1173 K for Ln = Nd, to ~1623 K for Ln = Er. At lower temperatures the evidence suggests that it is metastable with respect to Ln_6WO_{12} and a more tungsten-rich oxide with $O/M \simeq 1{\cdot}82$. In the studies quoted above it was established as being a superstructure phase with an orthorhombic unit cell composed of 12 fluorite-type subcells in a 3 × 2 × 2 array: the axial relationships are: $a_o = 3[100]_F$, $b_o = 2[010]_F$, $c_o = 2[001]_F$.

Experimental

Data relating to the materials used and the methods of sample preparation are contained in a previous publication (Summerville *et al.*, 1977). Samples of $Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$ were crushed and then dispersed on carbon-coated grids for electron microscope studies, for which either an AEI EM802 (100 kV) or a JEM 200 (200 kV) microscope was used: both instruments were fitted with a tilting stage. Electron diffraction patterns obtained from a single-crystal fragment in different orientations then allowed an unambiguous determination of the unit-cell geometry, and gave information on the space-group symmetry.

Powder X-ray diffraction photographs were taken with a Guinier focusing camera (Cu $K\alpha_1$ radiation: internal standard, thoria; $a_o = 5{\cdot}5972$ Å). Lines were indexed on the basis of the electron diffraction data, and the unit-cell parameters (see *Abstract*) were determined by a least-squares technique.

Powder X-ray diffraction intensity data for Ni-filtered Cu $K\alpha$ radiation were obtained with a powder diffractometer that was fitted with a scintillation counter, and operated in a continuous-scan mode at 0·5° (2θ) min^{-1}. Peaks were recorded on chart, and their areas were measured with a planimeter. The separation of partially resolved peaks involved some subjective judgement. However, numerous groups of peaks that were partially resolved on the diffractometer chart were clearly resolved on the Guinier photographs, and in these instances the total area of the group was divided between the constituent peaks in proportion to their heights on a microdensitometer trace of the Guinier photograph. This technique was particularly valuable in the higher-θ region, where the Guinier photographs gave much better resolution because of the strictly monochromatic radiation used. Unobserved reflections were given an area value one half that of the smallest observed peak and were included in subsequent refinements.

The region of reciprocal space scanned for $Y_{10}W_2O_{21}$ contained 766 unique reflections: overlap reduced these to 194 intensity observations, of which 159 were above background and 95 consisted of a single reflection. Similarly, the data for $Er_{10}W_2O_{21}$ consisted of 575 reflections and 196 observations (158 above background, 97 with one reflection).

Refinement was carried out with *POWDER*, a full-matrix least-squares computer program based on *ORFLS* (Busing, Martin & Levy, 1962), for the treatment of powder data (Rossell & Scott, 1975). The quantity minimized is $\sum w(I_o - I_c)^2$, where I is the intensity of an observation; $w = k/(I_o + I_{\min})$, $I_{\min}$ being approximately equal to the smallest observable intensity, and k being a multiplier, usually unity, which may reflect a reduced confidence in any particular observation. It was also found useful to include an additional factor, $(\sin\theta/\lambda)^{-n}$, in the expression for w (Agarwal, 1978). In the early stages of refinement a value of $n \simeq 2$ was used to dampen oscillations in shifts of atomic parameters with each cycle, and to ensure that the light atoms in particular did not move dramatically from their trial positions. As refinement proceeded n was reduced in stages to zero.

The residual R used here is $\frac{1}{2}[\sum w(I_o - I_c)^2/\sum wI_o^2]^{1/2}$: it is numerically comparable to the weighted residual commonly quoted for structure refinements based on F (Rossell & Scott, 1975). In a well refined structure, the above choice of $I_{\min}$ corresponds to a general minimum in the e.s.d.'s of the refined parameters, rather than the lowest obtainable value of R.

Scattering factors for neutral atoms, with corrections for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). The refinement included an overall isotropic temperature factor (B = 0·0 Å^2). Diffraction effects due to preferred orientation occurred when the materials were simply pressed into the sample holder: specimens free from this effect were made by evaporation of a slurry of the specimen in acetone on a glass slide. The surface of such specimens was not as smooth as required normally, and since the effects of this on the data would be accounted for largely by the temperature factor during refinement, the final value could not be regarded as structurally significant.

Structure determination

Electron diffraction patterns from both substances (Fig. 1) showed that reflections $h0l$ with l odd and $hk0$ with $h + k$ odd were absent, whilst reflections $0kl$ with k odd were extremely weak or absent, depending on the particular crystal and the exposure of the plate. Reflections $0kl$, $k \neq 2n$ were not observed in the X-ray powder patterns.

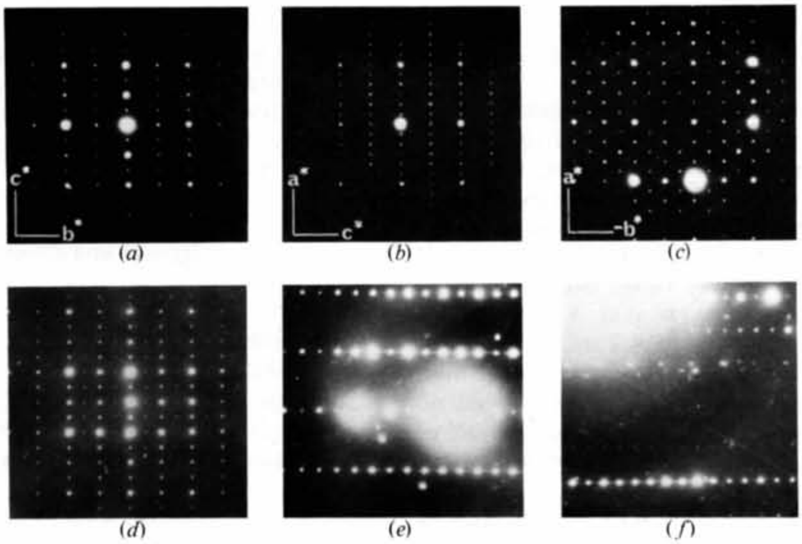
When crystals of either material were so oriented in the electron microscope that the a^* axis appeared in the diffraction patterns, streaks of intensity, parallel to **a*** and often nearly continuous, occurred along some rows of reflections (Fig. 1*e*,*f*) indicating that a type of faulting was occurring on planes normal to **a**, with consequent destruction of the periodicity in certain directions. Sections of reciprocal space normal to **a*** would include the cross sections of these streaks.

The rows of reflections containing the streaks could be mapped in part by suitable tilting experiments, and several contained reflections of the type hkl, k odd. Thus, even if the reflections $0kl$, with k odd, were systematically absent, weak spots from streak cross sections would occur in their place, and would be observed at all such positions since multiple processes always occur in electron diffraction.

These diffraction results show that the probable space group of both compounds is *Pbcn* (No. 60). The space groups *Pmcn* (a setting of *Pnma*: No. 62) and $P2_1cn$ (a setting of $Pna2_1$: No. 33) were also considered since the presence of the b glide was not absolutely confirmed. A test for the absence of a centre of symmetry, based on non-linear optical properties (Kurtz & Perry, 1968), was applied, but without positive result.

The unit cell of each compound formally contains 12 fluorite M_4O_8 subunits: the assumed contents are then $Ln_{40}W_8O_{84}V_{12}$ (V = oxygen vacancy), in accord with the well established property of a fully occupied cation sublattice for fluorite-related structures.

The structures were determined by a trial-and-error procedure: trial structures with atoms in ideal fluorite positions were refined by the least-squares method, and were retained or rejected according to the value of the



(*a*) (*b*) (*c*)
(*d*) (*e*) (*f*)

Fig. 1. Electron diffraction patterns from single crystals of $Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$. (*a*)–(*c*) Typical basal sections. In (*b*), reflections $h00$ with h odd appear because of multiple scattering. (*d*) $0kl$ section from $Y_{10}W_2O_{21}$, corresponding to (*a*), but with weak reflections for k odd present. (*e*) Enlarged portion of a pattern in the [100] zone of a crystal of $Y_{10}W_2O_{21}$, showing some streaked rows of reflections parallel to **a*** (horizontal). (*f*) As for (*e*), but from $Er_{10}W_2O_{21}$.

residual R. Structures in all of the possible space groups were investigated, although those in the noncentrosymmetric space groups could be examined in detail since the number of possible parameters to be varied was too large compared to the number of observations. Although the two compounds seemed isostructural they were treated independently, and different strategies were employed in each determination.

(1) $Y_{10}W_2O_{21}$

For this compound it seemed that the supercell intensities would be dominated by contributions arising from the ordering of cations with markedly different scattering factors. The residual was calculated (after refinement of the scale factor) for trial structures comprising all possible ordered arrangements of cations in all possible space groups, with atoms placed on ideal fluorite sites, and all anion sites occupied. One trial structure in *Pbcn* (and the identical one in the noncentrosymmetric space group $P2_1cn$) gave R = 0·22, and could be preferred, since the alternative in *Pbcn* and the four possible structures in *Pmcn* gave values of R in excess of 0·3.

The coordinates of the cations of this selected model were refined first in *Pbcn*. Since trial structures with atoms in ideal fluorite positions are degenerate in the sense that all structure factors are extreme, refinement cannot proceed unless some perturbation is introduced. In the present case, ordering of the cations was not a sufficient perturbation. Two procedures were adopted.

(*a*) The y coordinate of the W atom (on a general eightfold site) was first perturbed and refined; the sense of the perturbation is irrelevant. The y coordinates of the other cations could then be refined together without further perturbation, followed by refinement of all the cation coordinates.

(*b*) Degeneracy in the cation coordinates could be removed if four of them were perturbed by a small amount. The residual was calculated for the 16 models representing all permutations of the senses of these perturbations, and the cation coordinates of the most favourable models were refined. This procedure yielded one result which was notably better than the others, and which was identical with that arrived at by procedure (*a*) above. The value of R was 0·13.

Refinement of the cation coordinates for the noncentrosymmetric version of this model produced no significant improvement, despite the greater number of variable parameters, and so this was not considered further.

Those anion sites formally vacant were then located through refinement of anion site occupancies, which fell nearly to zero for one eightfold and one fourfold site. This result was confirmed by examination of the tetrahedron of cations around each of these sites: in common with all known fluorite-related structures both these tetrahedra were dilated by 0·2 Å or more in average cation–cation distance compared to the tetrahedra about occupied anion sites. Refinement of scale, temperature factor, and all atomic coordinates together (50 parameters) produced a value for R of 0·037, with mean parameter shift $\sim 10^{-2}\,\sigma$ in the final cycle.*

(2) $Er_{10}W_2O_{21}$

Since the scattering factors for Er and W were similar, a single effective cation type, with mean scattering factor, was considered initially. The cation coordinates of the trial structures were first refined in all of the possible space groups, the effects of degeneracy being avoided by a procedure similar to (*b*) above. For the only trial structure in *Pbcn* the resultant value of R was 0·14, whereas for the trial structures in the other space groups R was 0·18 or higher. Further refinement in the noncentrosymmetric space group $P2_1cn$ was then discontinued. Refinement of anion occupancies indicated an ordered array of vacancies only in the case of the structure in *Pbcn*.

Refinement of anion positions was attempted in both possible centrosymmetric space groups: certain anion coordinates were degenerate, but this effect disappeared if the non-affected coordinates were refined first. The cation order was then assessed through refinement of the cation occupancies, and again an ordered array was indicated only for the structure in *Pbcn*. At this stage, the structure in *Pbcn* gave R = 0·08, whereas that in *Pmcn* had R = 0·13. Since there was, in addition, no clear indication of ordering of either cations or anion vacancies in the *Pmcn* model, it was rejected.

Finally, all 50 parameters for the structures in *Pbcn* were refined together, with correct scattering factors and dispersion corrections for the now-ordered cations: the final R was 0·051, and the structure the same as that determined for $Y_{10}W_2O_{21}$.

Results and discussion

Table 1 contains the refined atomic coordinates for the two compounds, and some interatomic distances are shown in Fig. 2.

Although the basic features of the structure have been determined quite well, anion positions and, consequently, cation–anion distances are imprecise.

---

* Lists of calculated and observed powder intensities for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38039 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates*

Formal anion vacancies are at ($\frac{1}{3}$,$\frac{5}{8}$,0) and (0,$\frac{5}{8}$,$\frac{1}{4}$).

	x	y	z
$Er_{10}W_2O_{21}$			
W	0·5860 (6)	0·2510 (15)	0·1203 (11)
Er(1)	0·0806 (10)	−0·0080 (17)	0·1364 (13)
Er(2)	0·2736 (7)	0·2498 (20)	0·1284 (13)
Er(3)	0·0871 (10)	0·4852 (15)	0·1119 (16)
Er(4)	0·6006 (8)	0·7474 (17)	0·1558 (11)
Er(5)	0·7449 (13)	0·0088 (18)	0·1412 (13)
O(1)	0·328 (9)	0·419 (12)	0·013 (14)
O(2)	0·549 (8)	0·400 (12)	0·043 (14)
O(3)	0·361 (10)	0·382 (14)	0·286 (13)
O(4)	0·305 (9)	0·593 (13)	0·225 (12)
O(5)	0·509 (8)	0·154 (11)	0·042 (13)
O(6)	0·324 (7)	0·216 (13)	0·498 (10)
O(7)	0·645 (8)	0·879 (12)	−0·005 (14)
O(8)	0·152 (10)	0·612 (15)	0·262 (13)
O(9)	0·159 (9)	0·350 (12)	0·228 (12)
O(10)	0·5	0·288 (19)	0·25
O(11)	0·5	0·620 (23)	0·25
O(12)	0·0	0·379 (22)	0·25
$Y_{10}W_2O_{21}$			
W	0·5854 (4)	0·2504 (8)	0·1209 (7)
Y(1)	0·0806 (9)	−0·0110 (14)	0·1383 (15)
Y(2)	0·2711 (7)	0·2505 (14)	0·1296 (14)
Y(3)	0·0878 (9)	0·4839 (14)	0·1152 (15)
Y(4)	0·5984 (7)	0·7471 (15)	0·1518 (11)
Y(5)	0·7441 (13)	0·0083 (13)	0·1406 (14)
O(1)	0·331 (6)	0·399 (7)	0·009 (9)
O(2)	0·545 (5)	0·385 (7)	0·018 (8)
O(3)	0·352 (6)	0·380 (8)	0·296 (8)
O(4)	0·320 (6)	0·604 (8)	0·225 (8)
O(5)	0·514 (5)	0·144 (7)	0·054 (7)
O(6)	0·328 (5)	0·185 (8)	0·478 (7)
O(7)	0·662 (6)	0·895 (8)	−0·004 (9)
O(8)	0·142 (6)	0·626 (10)	0·260 (8)
O(9)	0·172 (6)	0·353 (8)	0·229 (9)
O(10)	0·5	0·311 (10)	0·25
O(11)	0·5	0·595 (13)	0·25
O(12)	0·0	0·394 (12)	0·25

This is particularly so in the case of $Er_{10}W_2O_{21}$. The main cause of this lay in the dominance of the cation scattering contributions to the supercell intensities. Also, the data contained a great many observations composed of multiple reflections, and only a few observations effected a separation of reflection types *hkl* and *hlk*. The form of the diffraction profiles was such that the extraction of a reasonably large number of observations was difficult, so that the data were subject to more errors than is usual. With hindsight, it is possible that the profile-matching procedures developed by Werner, Salomé, Malmros & Thomas (1979) would have been more appropriate.

The structure possesses features found in other anion-deficient fluorite-related superstructures. The six anions which surround a formally vacant anion site have relaxed towards it by approximately 0·4 Å, as compared to their ideal fluorite positions. The cations are ordered, and the smaller cation type (W^{6+}) has assumed an octahedral coordination by O, which may

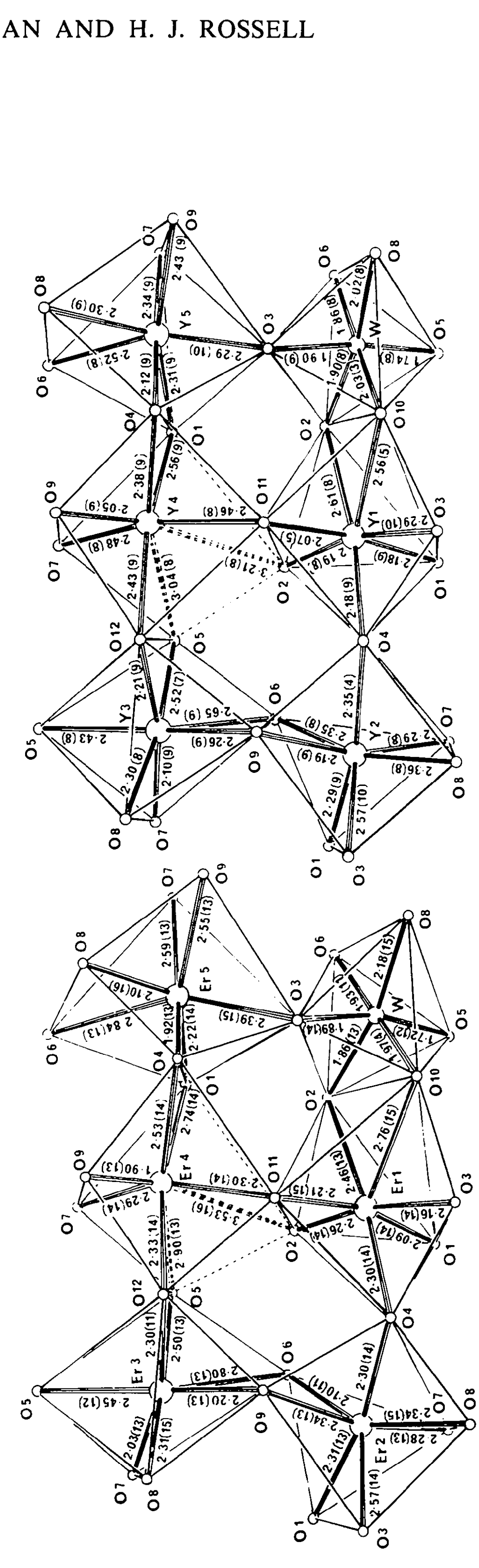
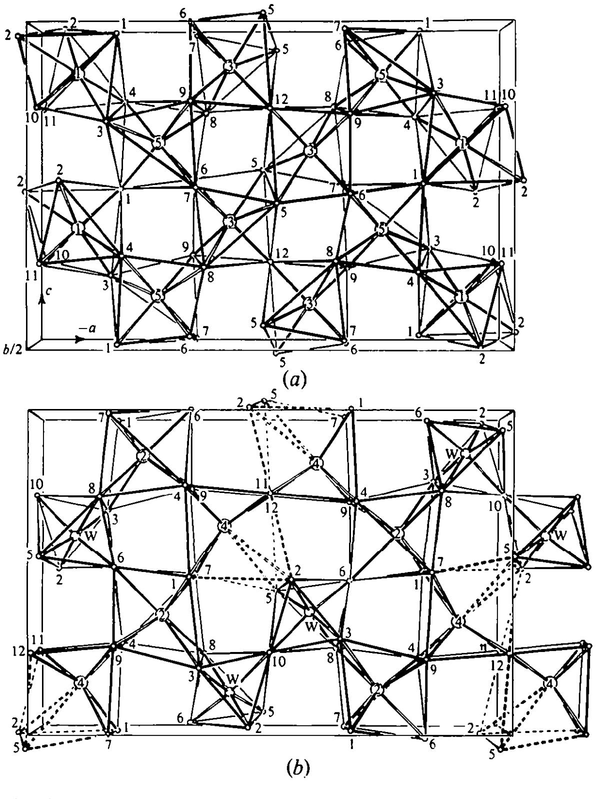


Fig. 2. Part of the structure viewed approximately down **c**, showing the coordination of the six non-equivalent cations. (Distances in Å).

be viewed as derived from the parent fluorite arrangement by an association of a pair of O vacancies separated by a $\frac{1}{2}[111]$ (fluorite) lattice vector with the W^{6+} cation in between. In the present cases, the requirement of three O vacancies for every two W^{6+} cations has been satisfied by a grouping of two adjacent W^{6+} cations, separated by a $\frac{1}{2}[110]$ (fluorite) lattice vector, each sharing one vacancy of its pair, *i.e.* a grouping of two corner-linked WO_6 octahedra. These groups form isolated units throughout the structure (Fig. 3*b*).

The coordination of Ln(1), Ln(2), Ln(3) and Ln(5) by O is sevenfold, and alternate planes of cations normal to **b** contain only such seven-coordinated Ln (Fig. 3*a*). The $Ln(1)O_7$ polyhedron may be described as a pentagonal bipyramid: The vectors from Ln(1) to O(2), O(2), O(10), O(3) and O(4) lie within 10° of their mean plane, while the vectors Ln(1)–O(1) and Ln(1)–O(11) are essentially normal to it. The remaining seven-coordinated figures are distorted cubes with one vertex removed (a vacant O site).

The cation Ln(4) is shown in the figures as having eightfold coordination by O. However, the atoms O(2) and O(5) in the $Ln(4)O_8$ grouping are sufficiently remote from Ln(4) to contribute only about 0·06 valence units each to a bond-strength sum, and thus a sixfold triangular-prismatic coordination could be considered reasonable for this cation. The Ln(4) site, unlike the other Ln sites, produces the same cation pattern in the structure as does the site occupied by W, and it may be speculated that chance occupancy of this alternative site by W could occur during the ordering process. If this were the case, it would appear as a form of faulting on planes normal to **a**, and could give rise to such non-periodic effects as observed in electron diffraction.



(*a*)

(*b*)

Fig. 3. $Y_{10}W_2O_{21}$ viewed down **b**, showing two successive layers of cations (*a*) at $y \sim 0$ and (*b*) at $y \sim \frac{1}{4}$. The upper net of anions in (*a*) coincides with the lower net in (*b*).

The authors are indebted to Mr R. Tobin of the Physics Department, Monash University, Victoria, Australia, who carried out the optical tests for noncentrosymmetry, and to Drs O. Greis and H. G. Scott for helpful discussion.

References

Agarwal, R. C. (1978). *Acta Cryst.* A**34**, 791–809.

Allpress, J. G., Rossell, H. J. & Scott, H. G. (1976). *J. Solid State Chem.* **14**, 264–273.

Bärnighausen, H. (1976). *Proc. 12th Rare Earth Res. Conf.* Denver, Colorado, edited by C. E. Lundin, Vol. 1, pp. 404–413.

Bärnighausen, H. & Haschke, J. M. (1978). *Inorg. Chem.* **17**, 18–21.

Bartram, S. F. (1966). *Inorg. Chem.* **5**, 749–754.

Bevan, D. J. M., Greis, O. & Strähle, J. (1980). *Acta Cryst.* A**36**, 889–890.

Bevan, D. J. M. & Mann, A. W. (1975). *Acta Cryst.* B**31**, 1406–1411.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Byström, A. (1944*a*). *Ark. Kemi. Mineral. Geol.* **18A**(21), 1–8.

Byström, A. (1944*b*). *Ark. Kemi. Mineral. Geol.* **18B**(10), 1–7.

Drennan, J. (1978). PhD Thesis, Flinders Univ. of South Australia.

Galy, J. & Roth, R. S. (1973). *J. Solid State Chem.* **7**, 277–285.

Gatehouse, B. M., Grey, I. E., Hill, R. J. & Rossell, H. J. (1981). *Acta Cryst.* B**37**, 306–312.

Hyde, B. G., Bagshaw, A. N., Andersson, S. & O'Keeffe, M. (1974). *Ann. Rev. Mater. Sci.* **4**, 43–92.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jung, W. & Juza, R. (1973). *Z. Anorg. Allg. Chem.* **399**, 129–147.

Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **49**, 3798–3813.

Lüke, H. & Eick, H. A. (1976). *Proc. 12th Rare Earth Res. Conf.*, Denver, Colorado, edited by C. E. Lundin, Vol. 1, pp. 424–432.

Moore, P. B. & Araki, T. (1976). *Am. Mineral.* **61**, 1226–1240.

Papiernik, R., Mercurio, D. & Frit, B. (1980). *Acta Cryst.* B**36**, 1769–1774.

Ray, S. P. & Cox, D. E. (1975). *J. Solid State Chem.* **15**, 333–343.

ROSSELL, H. J. (1976). *Solid State Chem.* **19**, 103–111.
ROSSELL, H. J. (1979). *Solid State Chem.* **27**, 115–122.
ROSSELL, H. J. (1980). *Nature* (*London*), **283**, 282–283.
ROSSELL, H. J. & SCOTT, H. G. (1975). *Solid State Chem.* **13**, 345–350.
SUMMERVILLE, E., DRENNAN, J. & BEVAN, D. J. M. (1977). *J. Phys.* (*Paris*) *Colloq.* **7**, 73–79.
THORNBER, M. R., BEVAN, D. J. M. & GRAHAM, J. (1968). *Acta Cryst.* B**24**, 1183–1190.
VON DREELE, R. B., EYRING, L., BOWMAN, A. L. & YARNELL, J. L. (1975). *Acta Cryst.* B**31**, 971–974.
WERNER, P.-E., SALOMÉ, S., MALMROS, G. & THOMAS, J. O. (1979). *J. Appl. Cryst.* **12**, 107–109.

Acta Cryst. (1982). B**38**, 2997–3000

Tripotassium *cis*-Dibromo(hydrogenbissulfito)platinate(II) Monohydrate

BY DIETRICH K. BREITINGER,* GÜNTER PETRIKOWSKI AND GERD BAUER

Institut für Anorganische Chemie, Universität Erlangen–Nürnberg, Egerlandstrasse 1, *D*-8520 *Erlangen, Federal Republic of Germany*

(*Received* 1 *October* 1981; *accepted* 24 *June* 1982)

Abstract

$K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1), M_r = 651·35, monoclinic, $P2_1/c$, a_1 = 8·764 (4), b_1 = 6·934 (2), c_1 = 21·544 (9) Å, β_1 = 99·32 (4)°, Z = 4, V = 1292·0 (1·7) Å^3, D_m = 3·47, D_c = 3·35 Mg m^{-3}, $F(000)$ = 1179·71, μ(Ag $K\alpha$) = 9·87 mm^{-1}. The structure was solved by Patterson and Fourier methods and refined to R = 0·0248 and R_w = 0·0288 (1801 unique reflections). In the distorted square-planar anion, Pt is surrounded by two S and two Br atoms in *cis* positions. Short Pt—S and long Pt—Br bonds (averages 2·244 and 2·488 Å, respectively) suggest a strong *trans* influence of the sulfite ligand. An extremely short asymmetric intramolecular hydrogen bond [O···H···O distance 2·380 (8) Å] links the sulfite ligands to form a six-membered ring. The anions are arranged in layers, held together by three sets of K^+ ions to different extents and by hydrogen-bonded H_2O molecules. In the anions of (1) and of $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2) the Pt—S and hydrogen bonds are very similar. The structural arrangements in (1) and (2) show common features, leading to close relations of the cell dimensions of both compounds.

Introduction

As part of our structural studies of sulfito complexes of Pd and Pt, with increasing emphasis on the *trans* influence of sulfite in these four-coordinate species (Messer, Breitinger & Haegler, 1979, 1981; Kehr, Breitinger & Bauer, 1980), a series of *cis*-dihalo(hydrogenbissulfito)platinates(II), $M_3[Pt\{(SO_3)_2H\}X_2]$ (M = K, Rb, Cs; X = Cl and Br), was prepared and studied by vibrational spectrometry (Bauer, 1979). The structure of $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1) and its relations to that of $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2) (Kehr *et al.*, 1980) will be discussed here.

Experimental

Preparation

Through a suspension of 1·5 g (2·0 mmol) K_2PtBr_6 and 0·14 g (1·0 mmol) K_2CO_3 in 10 ml of H_2O, SO_2 was passed with slight heating (328–333 K). The amounts given in the procedure for (2) (Kehr *et al.*, 1980) should be corrected correspondingly. After dissolution and nearly complete decolorization, the reaction mixture was cooled to room temperature and mixed with 50 ml acetone for precipitation of (1) (analytical data have been deposited). Recrystallization from water yielded single crystals.

Crystal data

Cell parameters were determined by a least-squares refinement of 30 powder reflections, with $Pb(NO_3)_2$ as external standard. Systematic absences $h0l$: $l = 2n$, and

---

* Author to whom correpondence should be addressed.

0567-7408/82/122997-04$01.00