

Table 12. *Symmetry operations used to generate neighbouring molecules from coordinates of atoms in the asymmetric unit (Table 6)*

(i)	($-x, -y, -z$)
(ii)	($2-x, 1-y, -z$)
(iii)	($x, y, 1+z$)
(iv)	($1-x, 1-y, -z$)
(v)	($1-x, 2-y, -1-z$)
(vi)	($1+x, y, z$)
(vii)	($x, 1+y, z$)

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Crystallography of $\text{Pr}(\text{ReO}_4)_3 \cdot 3\text{H}_2\text{O}$, Praseodymium Perrhenate Trihydrate

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The monoclinic crystals of praseodymium perrhenate trihydrate have a well developed {100} pinacoid form, and poorly developed remaining crystallographic forms: {001}, {011}, {012}, {102}, {102}, {110} and {112}. The crystallographic constants could be computed from the observed interfacial angles: $a:b:c = 1.539:1:2.141$ and $\beta = 86^\circ 03'$. The crystals are light green, with no appreciable pleochroism, presenting the following optical constants: $X = \alpha = 1.678$; $b = Y = \beta = 1.688$; $Z = \gamma = 1.690$; $Z \wedge c = 35^\circ - 40^\circ$ and $2V_{\text{calc}}^{(+)} = 53^\circ$. The unit-cell parameters, determined by precession photographs and refined by powder diagrams, resulted in the values: $a_0 = 11.68$, $b_0 = 7.47$, $c_0 = 16.06 \text{ \AA}$ and $\beta = 86^\circ 04'$, space group $P2_1/c$. With four molecules per unit cell the calculated specific gravity of 4.49 g.cm^{-3} agrees very well with the observed one of 4.51 g.cm^{-3} .

Crystals of praseodymium perrhenate trihydrate, $\text{Pr}(\text{ReO}_4)_3 \cdot 3\text{H}_2\text{O}$, synthesized for the first time by Giesbrecht, Perrier & Vicentini (1966) (in the Chem-

istry Department of the University of São Paulo, Brazil) have been the object of the crystallographic investigation reported in this paper.

The crystals are monoclinic, of well developed tabular shape (Fig. 1), sometimes reaching as much as 1.0 cm in width. The main crystallographic form, the orthopinacoid {100}, is often associated with the forms {011}, {012}, {102} and {102}. Nearly ideal crystals show a poor development of the {001}, {110} and {112} forms. Goniometric measurements (Table 1), yielded the following crystallographic constants:

$$a:b:c = 1.539:1:2.141; \beta = 86^\circ 03'.$$

Table 1. Goniometric measurements

Faces	$\varphi_{\text{meas.}}$	ϱ	$\varphi_{\text{calc.}}$	ϱ
(001)	90° 00'	3° 57'	—	—
(100)	90 00	90 00	—	—
(110)	32 31	90 00	33 08	—
(011)	1 51	64 54	1 54	64 59
(012)	3 41	47 07	3 43	46 11
(102)	90 00	37 15	—	37 27
(102)	-90 00	32 25	—	32 08
(112)	~ 37 15	~ 51 49	-33 08	48 58

Table 2. Powder data for praseodymium perrhenate trihydrate

Cu K α radiation, $r = 57.3$ mm and quartz internal standard.

<i>hkl</i>	d_{calc} (Å)	d_{obs} (Å)	I/I_0^*	<i>hkl</i>	d_{calc} (Å)	d_{obs} (Å)	I/I_0		
100	11.65	11.72	6	411	2.65	2.66	2		
002	8.01	8.02	1	106	2.64				
011	6.77	6.76	3	314	2.54	2.53	0.5		
102	6.78			412	2.52				
102	6.36	6.35	7	224	2.52				
110	6.29			322	2.52				
200	5.83	5.81	2	404	2.44	2.43	1		
112	5.02	5.04	5	130	2.44				
211	4.48	4.50	2 <i>d</i>	224	2.43	2.37	0.5		
202	4.55			025	2.43				
013	4.34	4.34	0.5	032	2.38	2.33	0.5		
211	4.35			206	2.37				
212	4.07	4.09	4	132	2.34	2.29	2		
004	4.01	4.01	1	500	2.33				
113	4.00			132	2.32				
300	3.88	3.89	5	421	2.29	2.29	2		
212	3.89			230	2.29				
104	3.87	3.64	3	225	2.29	2.21	2 <i>d</i>		
021	3.64			324	2.29				
121	3.49	3.49 to 3.38	10 <i>d</i>	—	—	2.16	1		
121	3.46			—	—	2.09	3		
310	3.45			—	—	2.05	2		
114	3.44			—	—	2.01	3		
311	3.41			—	—	1.975 to 1.959	2 <i>d</i>		
204	3.41			—	—	1.932	0.5		
302	3.40			—	—	1.899	3		
213	3.39			—	—	1.854	1		
022	3.38			—	—	1.821	1		
114	3.32			3.32	2	—	—	1.806	1
311	3.33					—	—	1.735	3
204	3.20			3.20	2	—	—	1.690	1
312	3.10	—	—			1.662	1		
214	3.10	3.10	2	—	—	1.544	2 <i>b</i>		
221	3.11			—	—	1.531	2 <i>b</i>		
123	2.99	2.99	3	—	—	1.447	2		
313	2.98			—	—	1.345	1 <i>b</i>		
222	2.96	2.91	2 <i>d</i>	—	—	1.248	1 <i>b</i>		
123	2.93			—	—	1.188	1 <i>b</i>		
400	2.91	2.91	2 <i>d</i>	—	—	1.160	1 <i>b</i>		
115	2.90			—	—	0.845 α_1	1		
304	2.89	2.82	1	—	—	0.842 α_1	1		
313	2.82			—	—	0.809 α_2	1 <i>b</i>		
115	2.81	2.81	1	—	—	0.806 α_1	1 <i>b</i>		
204	2.80			—	—	—	—		
024	2.73	2.71	2	—	—	—	—		
410	2.72			—	—	—	—		
411	2.71	2.71	2	—	—	—	—		
314	2.70			—	—	—	—		
402	2.68	2.67	2 <i>d</i>	—	—	—	—		
321	2.68			—	—	—	—		
006	2.67	2.67	2 <i>d</i>	—	—	—	—		
223	2.67			—	—	—	—		
124	2.67	—	—	—	—	—			

* Intensities visually estimated. *b* = broad, *d* = doublet. Very weak and diffuse reflections are not recorded.

The symmetry $2/m$ has been determined by the microscopic observation of centrosymmetrical etch pits, which were successfully obtained on the (100) and $(\bar{1}00)$ crystal faces after immersion in ethyl alcohol for about 10 seconds. The small percentage of water, usually contained in alcohol, was enough to permit the partial dissolution of the crystals.

Under the polarizing microscope the crystals are apple-green in colour, with no appreciable pleochroism, the extinction angle $Z \wedge c$ ranging between 35° and 40° , and with positive optical character. The angle $2V$ has been computed from the refraction indices as measured by the immersion method. The following optical constants were obtained:

$$\begin{aligned} X = \alpha &= 1.678 \\ b = Y = \beta &= 1.688 \\ Z = \gamma &= 1.690 \\ \text{Birr.} &= 0.012 \\ Z \wedge c &= 35^\circ - 40^\circ \\ 2V_{\text{calc}} &= 53^\circ. \end{aligned}$$

Both unit cell and space group were determined by the precession method, with a single crystal of about $1.0 \times 0.5 \times 0.2$ mm. Film measurements, made on the reciprocal level ($h0l$), ($0kl$) and ($hk0$) photographs, yielded the following unit-cell dimensions:

$$\begin{aligned} a_0 &= 11.69 \text{ \AA} \\ b_0 &= 7.49 \text{ \AA} \\ c_0 &= 15.93 \text{ \AA} \\ \beta &= 86^\circ \\ V_0 &= 1391.45 \text{ \AA}^3. \end{aligned}$$

The systematic absences of $h0l$ and $0k0$ reflexions for l and k odd indicated a 2_1 screw axis and a c glide plane, and consequently the space group $P2_1/c$. The observed specific gravity 4.51 g.cm^{-3} , measured by the pycnometer method (immersion in benzol), suggests 4.02 molecules per unit cell. Assuming these four molecules, the calculated density was 4.49 g.cm^{-3} , which is in very good agreement with the experimental data.

The unit-cell parameters determined by the precession method were refined by powder photographs taken with a 114.6 mm camera and Cu $K\alpha$ radiation (Table 2). A quartz internal standard was used to minimize random errors in the measurements. The following cell parameters were obtained by the powder method:

$$\begin{aligned} a_0 &= 11.68 \text{ \AA} \\ b_0 &= 7.47 \text{ \AA} \\ c_0 &= 16.06 \text{ \AA} \\ \beta &= 86^\circ 04' \\ V_0 &= 1397.93 \text{ \AA}^3. \end{aligned}$$

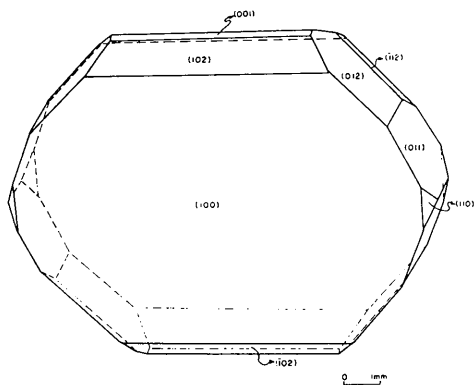


Fig. 1. Crystal of praesodymium perhenate trihydrate showing the forms: $\{001\}$, $\{100\}$, $\{110\}$, $\{011\}$, $\{012\}$, $\{102\}$, $\{\bar{1}02\}$ and $\{\bar{1}12\}$.

According to the 'Bravais rule', the best developed crystal faces are related to the lattice planes with the greatest interplanar spacing (d_{hkl}), or, in other words, lattice planes with the lowest unit reticular area (S_{hkl}), since V_0 , the unit volume ($V_0 = S_{hkl} \cdot d_{hkl}$), is a reticular constant.

This law, further modified by Donnay & Harker (1937), and extended to the effect produced by both lattice type and space group, may, with some restrictions, be applied to the present case.

In the space group $P2_1/c$, the screw axis 2_1 will reduce the d_{010} spacing by a factor $\frac{1}{2}$ and the corresponding form will recede in morphological significance. The effect of the c glide plane, applied to the $[010]$ zone, will reduce to a half the d_{h0l} spacings, when $l = \text{odd}$. The corresponding planes ($h0l$) are thus also decreased in morphological significance. The observed

Table 3.

Observed morphological sequence	Ideal morphological sequence	Lattice planes	d_{hkl} \AA	Unit-lattice areas S_{hkl} \AA ²
(100)	(100)	100	11.72	119.28
(011)	(001)	002	8.02	174.31
(102)	(011)	011	6.76	206.79
($\bar{1}02$)	(102)	102	6.76	206.79
(012)	($\bar{1}02$)	$\bar{1}02$	6.35	220.15
(001)	(110)	110	6.35	220.15
(110)	(012)	012	5.46	256.03
($\bar{1}12$)	($\bar{1}12$)	$\bar{1}12$	5.04	277.37

crystal forms follow, in general, the conditions imposed by the space group $P2_1/c$. From structural data, the ideal morphological sequence does not agree fully with the observed sequence of morphological importance (Table 3); only the {001} and {110} crystal forms do not follow the 'Donnay-Harker law'. These anomalies may be ascribed to other physical factors, not considered by this rule (bond energy, *etc.*).

The authors do not propose to carry out further work on this compound.

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Determination of the Light-Atom Positions in Mo₂BC*

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A previous investigation of the crystal structure of Mo₂BC by Jeitschko, Nowotny & Benesovsky (*Mh. Chem.* (1963) **94**, 565) resulted in the direct location of the Mo atoms; the light atoms were assigned probable positions on the basis of geometrical arguments. The authors reinvestigated the crystal structure using diffractometrically recorded intensities. The crystals are orthorhombic, $a=3.086$, $b=17.35$, $c=3.047$ Å; space group, $Cmcm$. For four units of Mo₂BC per unit cell, the calculated density is 8.74 g.cm⁻³. Full-matrix, least-squares refinement resulted in an R index of 3.5%, and a confirmation of the structure model of Jeitschko *et al.*, *viz.* C atoms in octahedral sites (six Mo neighbors) and B atoms forming zigzag chains passing through the centers of trigonal prisms of Mo atoms. Bond distances are: Mo-C, 2.08–2.17; Mo-B, 2.31 and 2.77; B-B, 1.79; Mo-Mo, 2.93–3.10 Å. A number of other metal-B, C systems were examined in a search for additional examples of the Mo₂BC-type structure, but without success. The metals studied were: Ti, V, Cr, Nb, Ta and W; the authors were also unable to prepare Mo₂BSi.

Introduction

In their investigation of the crystal structure of Mo₂BC, Jeitschko, Nowotny & Benesovsky (1963) (hereafter referred to as JNB) were able to determine only the metal-atom positions from their diffraction data. Using geometrical arguments, JNB placed the light atoms so that the boron atoms formed zigzag chains, as found frequently in monoborides and the carbon atoms occupied octahedral holes (six Mo neighbors) as found, for example, in NaCl-type monocarbides. The structure resulted in very reasonable interatomic distances. On the other hand, several metallic borocarbides of composition MB₂C₂, with M = a lanthanide element (Smith, 1964) or scandium (Smith, Johnson & Nordine, 1965), have exhibited novel connected B, C networks. It therefore seemed of interest to establish directly the light-atom positions in Mo₂BC. Further interest is attached to this problem with the discovery (Johnston, 1964) that Mo₂BC becomes superconductive below 5.4°K.

Experimental

The compound was prepared by arc-melting appropriate amounts of Mo metal filings, boron and carbon (as graphite) in a gettered argon atmosphere. The fused button was turned over and remelted several times to improve the homogeneity. Parallelepiped-shaped single crystals were obtained by crushing the button.

An X-ray powder pattern was readily indexed on the basis of the C -centered orthorhombic cell ($a=3.086$, $b=17.35$, $c=3.047$ Å) given by JNB. These lattice constants were used in subsequent calculations, our own values based on $\lambda_{Cu K\alpha}=1.5418$ Å being insignificantly different. Probable errors in the lattice constants are estimated to be about 0.2%. No impurity lines were observed.

A chemical analysis of a portion of the button gave these percentages: Mo, 89.0 ± 0.1; B, 4.97 ± 0.02; C, 5.43 ± 0.12 (average of two analyses). Corresponding theoretical percentages for Mo₂BC are 89.37, 5.04 and 5.59, respectively. The analysis corresponds to a Mo:B:C atomic ratio of 2.000 ± 0.002:0.991 ± 0.004:0:0.971 ± 0.022. JNB reported that the phase was possibly carbon-poor, but no quantitative figures were given.

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