CRYSTAL STRUCTURE OF $\mathrm{Pr_3WO_6Cl_3}$

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Abstract

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CRYSTAL STRUCTURE OF $Pr_3WO_6Cl_3$

The compound $Pr_3WO_6Cl_3$ is formed during hydrothermal crystallization in systems containing Pr_2O_3, WO_3 and HCl solutions of Li, K, Na, and NH_4, as well as solutions of mixed chlorides. The crystals studied by us were obtained by crystallization from a solution in a LiCl melt ([1]). From their growth forms and from X-ray diffraction data, $Pr_3WO_6Cl_3$ belongs to the diffraction class $C_{6h} = P6/m$, with possible Fedorov groups $C_{6h}^2 = P6_3/m$ and $C_6^6 = P6_3$, at the parameters of the hexagonal cell $a = 9.31_4$, $c = 5.36_9$ Å ($Z = 2$).

For the X-ray structural study a single crystal was used—a faceted hexagonal prism measuring $0.12 \times 0.14 \times 0.7$ mm^3. In a KFOR camera with Mo radiation, layer-line photographs $hk0 \div hk5$ and $h0l$ were taken. Intensities were estimated visually on a $^4\sqrt{2}$ blackening scale, and after exclusion of the LP factor (no absorption correction was introduced) we had 1000 nonzero values of F_{hkl}^2 ($\max \sin\vartheta/\lambda = 1.1$).

The coordinates of the heavy atoms W and Pr were established from analysis of projections of the Patterson function $P(uw)$ and $P(uv)$. From the first it immediately followed that, at least, the heavy atoms are located on two levels with a height difference $c/2$, and then, for the group $P6_3/m$ taken as the basis, the possible variants of the arrangement of these atoms become two special complexes: a twofold one at the intersection of threefold axes and symmetry planes (W atoms without parameters), and a sixfold one around these axes on mirror planes (Pr atoms). The horizontal coordinates of W and Pr were determined from $P(uv)$ by the known theorem ([2]). The "mean" Cl atoms by weight appeared on the electron-density projection $\sigma(xy)$, constructed from $F_{hk0}^{\exp}$ with signs calculated from W and Pr. In order to reduce the influence of termination ripples on the localization of oxygen atoms, an xy projection of electron density was calculated with coefficients

$$F'_{hk0} = F_{hk0} \exp[-B(\sin\vartheta/\lambda)^2] \quad (B \approx 1),$$

and also a difference projection without both heavy atoms (Fig. 1). The only basal O atom in the structure is fixed in a general position with $x = 0.358$, $y = 0.525$ and coordinate $z = 0$, calculated from the probable W–O distance.

The constructed structural model was refined by the least-squares method, first by projections ($R_{hk0} = 11.3$, $R_{h0l} = 11.2\%$), then by the three-dimensional set of intensities ([3]). Since, because of the nonisometric form of the specimen, the accuracy of estimating intensities in the $h0l$ zone is considerably worse, the F_{h0l} were used only to bring to a common scale the intensities of reflections on the layers $hk0 \div hk5$.

In addition to refinement within the centrosymmetric Fedorov group, an attempt was made at refinement in the lower group $P6_3$. The centrosymmetric variant corresponded to a lower value of the R factor (13.4% against 14%), and there was no point in abandoning it. At the last stages of refinement, 52 strong reflections, which could have been noticeably distorted by extinction, were excluded from the array F_{hkl}, and for the remaining 923 nonzero experimental F_{hkl} the factor $R = 12.1\%$.

The final coordinates of the atoms and their isotropic thermal parameters B are presented in Table 1. We give the principal interatomic distances in Å, calculated from these coordinates (the multiplicity is indicated in parentheses—

···ness):

Pr decahedron

Pr—O: 2.40 (2)
2.50 (2)
2.66 (2)
Cl—Cl: 3.38 (4)
3.56 (1)

Pr—Cl: 2.93 (1)
3.01 (2)
3.03 (1)

O—O: 2.45 (1)
2.58 (2)
2.92 (2)

W prism
W—O: 1.93 (6)
O—O: 2.45 (3)
2.58 (6)

Cl—O: 3.07 (4)
3.08 (4)
3.50 (2)

Intercation distances: W—W = 6.03 Å; W—Pr = 3.57 (3); 3.66 (3); Pr—Pr = 4.03; 4.08; 4.09; 4.35 Å.

A very large W—W distance, as was to be expected, corresponds to isolated W polyhedra. It must be considered unexpected that these isolated polyhedra

Fig. 1. Difference xy synthesis (with the contributions of heavy W and Pr removed) of electron density. a –Pr positions, b –W. Doubled oxygen atoms are clearly fixed

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proved to be six-vertex polyhedra, and moreover not octahedra

Fig. 1. Difference xy-synthesis (the contributions of the heavy atoms W and Pr have been removed) of the electron density. a –positions of Pr, b –W. Doubled oxygen atoms are clearly fixed

but, within the accuracy of the experiment, regular trigonal prisms. Such a form of oxygen coordination polyhedron apparently is still unknown for W^{6+}; its occurrence in the present case may be attributed to the ordering action of symmetry. Usually, for sixfold coordination, W(Mo) is characterized by a wide spread and even a clear differentiation

Table 1

Atom	x/a	σ_x	y/b	σ_y	z/c	σ_z	B
W	1/3	–	2/3	–	0.250	–	–0.46
Pr	0.664	0.0002	0.0904	0.0002	0.250	–	–0.29
Cl	0.0433	0.0003	0.2408	0.0003	0.250	–	–0.0226
O	0.365	0.002	0.525	0.002	0.022	0.004	–0.0615

of the W(Mo)–O distances. Thus, in WO_3 they are 1.72-2.16 Å with an average of 1.93 ([4]), in $NiWO_4$ 1.79-2.19, average 1.92 ([5]), in $K_{0.26}MoO_3$ 1.67-2.56, the averages for two groups 2.08 and 1.87-2.35, with an overall average of 1.99 ([6]), in $K_{0.28}MoO_3$ 1.68-2.34, average 1.96 ([7]), in $K_2Mo_3O_{10}$ 1.71-2.14, average 1.95 ([8]). But for the average W(Mo)–O distances over all these compounds one obtains a fairly narrow interval of values, 1.92-2.08 Å, into which our W–O = 1.95 Å also falls.

With distances between neighboring W and Pr of 3.57 and 3.66 Å, the corresponding polyhedra must have common edges, similarly to what occurred in the structure of $NdWO_6OH$ ([9]). There, another fact was also noted, manifested in $Pr_3WO_6Cl_3$ to an even greater degree: shortening of the common

edge of a W-polyhedron with a neighboring polyhedron, even if this polyhedron is occupied by a rare-earth cation rather than by tungsten, in which case the fact of shortening may be regarded as trivial. In our case the common oxygen edges of the W- and Pr-polyhedra have decreased to 2.45 and 2.58 Å.

Fig. 2. Projection of the structure of Pr3WO6Cl3 onto the (001) plane. The upper triplets of Pr-polyhedra are left light, the lower ones (at c/2) are hatched. The occupied prism is shown black with white circles; the alternating empty one is white with black circles.

Figure 2: Fig. 2. Projection of the structure of Pr3WO6Cl3 onto the (001) plane. The upper triplets of Pr-polyhedra are left light, the lower ones (at c/2) are hatched. The occupied prism is shown black with white circles; the alternating empty one is white with black circles.

The highest coordination number noted for Pr, namely 9—a trigonal prism "centered" on all faces—was

Fig. 2. Projection of the structure of $Pr_3WO_6Cl_3$ onto the (001) plane. The upper triplets of Pr-polyhedra are left light, the lower ones (at $c/2$) are hatched. The occupied prism is shown black with white circles; the alternating empty one is white with black circles.

found in $PrCl_3$ ([10]). In yttrium hydroxychlorides related to praseodymium ([11–14]), the coordination of the latter varies from 7 to 9 depending on whether one, two, or three lateral faces are "centered." In tungstates of rare-earth elements, including yttrium, the coordination number is usually 8—an eight-vertex polyhedron in the form of a twisted cube ([15–17]). In our compound the coordination ten-vertex polyhedron of Pr is composed of 4 Cl atoms and 6 O atoms. A certain similarity can be found between the arrangement of the Cl atoms in this ten-vertex polyhedron and in the polyhedron characteristic of the structure of $PrCl_3$, if one compares the internal diagonal connecting the Cl atoms, i.e., the translation c (5.37 Å), in the first case with the distance between the Cl atom centering the face of the prism and one of the opposite vertices of the prism (5.45 Å) in the second. In this case the remaining Cl—Cl distances also come into satisfactory agreement, which gives grounds for considering the "chlorine" part of our ten-vertex polyhedron as a fragment of the Pr-polyhedron from the structure of $PrCl_3$. On the other hand, the configuration of four Cl atoms may be regarded as a strongly bent square face of an eight-vertex polyhedron, while the nearest quartet of O atoms to Pr may be taken as the second square face. The remaining pair of oxygen atoms "centers" the elongated Cl—O edges of the eight-vertex polyhedron. Thus, the Pr-polyhedron in $Pr_3WO_6Cl_3$ represents, as it were, a combination of these two types. The Pr—O distances fall within the limits characteristic of vectors in an eight-vertex polyhedron, while the Pr—Cl distances correspond to the vectors of the nine-vertex polyhedron of $PrCl_3$. The Pr-polyhedron has common edges with neighboring polyhedra, the cations of which are located at distances of 4.03 and 4.08 Å from the central—

fact, to which attention has already been drawn in (9), and common faces with polyhedra whose cations are 4.35 Å from the central one.

The projection of the structure onto the plane (001) is shown in Fig. 2. A

Fig. 3. Pr3WO6Cl3. Fragment of the structure in projection onto the plane (001). Common faces of Pr ten-vertex polyhedra are emphasized. W atoms are shown by black circles.

Figure 3: Fig. 3. Pr3WO6Cl3. Fragment of the structure in projection onto the plane (001). Common faces of Pr ten-vertex polyhedra are emphasized. W atoms are shown by black circles.

characteristic detail is a hollow column (shaft) of Pr ten-vertex polyhedra, the faces

Fig. 3. $Pr_3WO_6Cl_3$. Fragment of the structure in projection onto the plane (001). Common faces of Pr ten-vertex polyhedra are emphasized. W atoms are shown by black circles.

of which are at the same time faces of empty Cl octahedra strung on the axis of the shaft 6_3 according to the hexagonal law (with common bases). The connection between Pr polyhedra in the column occurs through common edges and faces; the connection between columns is through common edges and with the aid of W prisms. The relation of the above-mentioned polyhedra to one another can be seen from Fig. 3. The W prisms along the 3-fold axes alternate with empty ones.

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