parameter, the $y$ coordinate of the $Mg_1$ atom. Calculations show (Table 2) that increase of the $y$ coordinate from 0·265 to 0·29 gives a significant worsening of the agreement between the observed and calculated structure factors. This change of the coordinate reduces the distance $Mg_1$–$O_3$ only from 2·5 to 2·3 Å, still leaving a value greater than the 2·1 Å value for all the other Mg–O distances. Thus it is taken that this distance is genuinely much longer than the other ones around the $Mg_1$ atom. The long distance goes to the $O_3$ atom, which is already bonded to two silicon atoms and which, on a strict interpretation of the valence bond rule, should already be satisfied by the bonding to the silicon atoms. Thus it is not surprising to find the $Mg_1$ atom further away from the $O_3$ atoms than from the $O_1$ and $O_2$ atoms. Nevertheless the coordination is very irregular, especially as the two long distances are adjacent in the $Mg_1$ polyhedron, and is regarded as the weak point of the structure.

Clino-enstatite, the monoclinic form of $MgSiO_3$, also shows pseudo-symmetry, the true lattice being primitive and the pseudo-lattice $C$ face-centered. Although a detailed analysis of the pseudo-symmetry of clino-enstatite must await the completion of the structure refinement by Dr N. Morimoto, it seems safe to say that the pseudo-symmetry arises from a slight collapse and twisting of the silicon–oxygen chains about the relatively small Mg ions. In diopside, the type structure of monoclinic pyroxenes, the Ca ions are sufficiently large to hold the structure in the more symmetrical arrangement. The irregular shape of the $Mg_1$ polyhedron of proto-enstatite in which the $Mg_1$–$O_3$ distances are greater than normal indicates that the pseudo-symmetries of both proto- and clino-enstatite arise from the relative smallness of the Mg ion.

At higher temperatures, where proto-enstatite may be the stable form of $MgSiO_3$, the $Mg_2$ atom along with other atoms will be vibrating considerably more and should fill the cavity more effectively. Furthermore, the known increase of solid solution with higher temperatures for many compounds shows that structural tolerance for valence mis-balance and size discrepancy is generally greater. For these two reasons, it is thought that the poor coordination of the $Mg_1$ atom will become of lesser importance at higher temperature, allowing proto-enstatite to become more stable.

The cooperation of Drs F. R. Boyd, N. Morimoto and J. F. Schairer of the Geophysical Laboratory was most valuable. This investigation forms part of a programme of fundamental research on the pyroxenes, supported by the National Science Foundation.

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*Acta Cryst.* (1959). **12**, 519

# The Crystal Structure of $Sr_4PtO_6$ and Two Related Compounds*

By John J. Randall, Jr. and Lewis Katz

*Department of Chemistry, The University of Connecticut, Storrs, Connecticut, U.S.A.*

(*Received* 30 *October* 1958 *and in revised form* 5 *January* 1959)

The crystal structure of $Sr_4PtO_6$ has been determined by a trial and error method. The crystals are trigonal with space group $R\bar{3}c$; the triply primitive hexagonal cell dimensions are $a = 9{\cdot}74$, $c = 11{\cdot}90$ Å. The platinum ions are octahedrally coordinated with oxygen and are linked in the $c$ direction through strontium ions surrounded by trigonal prisms of oxygens. These strings of coordination polyhedra are connected laterally by strontiums in eight fold coordination with oxygen. This structure is of the same type as that reported for $K_4CdCl_6$. The isolation of one $PtO_6$ group from the next is postulated as a reason for the ease of hydrolysis of the compound. $Sr_4IrO_6$ and $Sr_4RhO_6$ have the same structure.

## Introduction

In the course of an investigation of the interaction of the alkaline earth oxides with platinum metal oxides, we have prepared and studied compounds with the formulas $Sr_4PtO_6$, $Sr_4IrO_6$, and $Sr_4RhO_6$.† Powder photographs indicated that these compounds had essentially the same structure. In contrast to the behavior of most ternary oxides, these compounds

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* Part of this work was supported by a contract between the Office of Naval Research and The University of Connecticut. Reproduction in whole or in part is permitted for any purpose of the United States Government.

† The compound containing Rh was shown to be oxygen deficient.

hydrolyze readily on contact with water. This rapid hydrolysis suggested that the platinum metal coordination polyhedra did not share oxygens with each other. Since the X-ray powder patterns were simple in appearance, it seemed that a crystal structure determination would be feasible as well as informative.

## Experimental

Powder photographs of $Sr_4PtO_6$ and $Sr_4IrO_6$ could be indexed fairly well on the basis of a primitive cubic unit cell with $a = 6{\cdot}88$ Å. The measured density of the platinum containing compound (6·52 g.cm.$^{-3}$) corresponded to two formula weights for such a unit cell. Assuming a non-defect structure, only nine primitive cubic space groups could accommodate the numbers of atoms involved. In none of these space groups was it more than a one parameter problem to place all the cations. All the possibilities were examined and shown to be incorrect. It was, therefore, concluded that the compounds were not cubic and that single crystals studies would be necessary.

Attempts to prepare single crystals by starting with the $Sr_4PtO_6$ and $Sr_4IrO_6$ powders were not successful. However, by prolonged heating of a pelleted sample of $Sr_4RhO_6$ in a ceramic boat, a small, triangular, platy crystal was obtained. Zero and fourth level Weissenberg photographs were taken of this crystal with the rotation axis normal to the plate. The absences indicated a rhombohedral lattice. The hexagonal cell dimensions were determined as $a = 9{\cdot}74$, $c = 11{\cdot}84$ Å. Before further data could be accumulated, the crystal was lost and another of the same shape could not be found.

Rather large acicular crystals were obtained by again starting with the $Sr_4RhO_6$ powder but this time heating with $SrF_2$ as a flux in a platinum crucible. Some of these crystals were mounted with the needle axis as rotation axis, and Weissenberg photographs were taken of the zero through fourth levels using the equi-inclination method.

Intensity photographs were taken using the multiple film technique and were read by comparison with a calibrated intensity strip. Lorentz and polarization corrections were made using Lu's (1943) charts. No correction was made for extinction or absorption.

Approximately the same unit-cell size, $a = 9{\cdot}74$, $c = 11{\cdot}90$ Å, was found for the needle shaped crystals as for the triangular one. However, although the symmetry was still trigonal, more reflections were observed for the needles, and the rhombohedral lattice absence rule was not obeyed. In fact, the first of these crystals examined appeared to have $C_{6l}$ symmetry on upper levels, although for other crystals the upper level symmetry was clearly lower than $C_{6l}$. On further investigation it was found possible, for all of the acicular crystals photographed, to divide the reflections into two groups, one for which $h-k+l = 3n$, and the other for which $-h+k+l = 3n$. These two sets could be arranged in a one to one correspondence with the relative intensities within one set the same as those in the other. The intensity ratio between the two sets was not the same for different crystals. These observations could be explained by assuming the crystals to be rotation twins with, in general, one contribution larger than the other. Granting this assumption, the lattice would be rhombohedral. The probable space group is one of $R3c$ or $R\bar{3}c$.

By trial and error and the use of structure factor plots it was found that reasonable agreement between observed and calculated structure factors ($R < 0{\cdot}25$) could be obtained for all levels but the second using space group $R\bar{3}c$ by placing 6 Sr in '$a$', 6 Rh in '$b$', and 18 Sr in '$e$', with $x = 0{\cdot}370$.

For the second level, however, $R$ was about 0·5. Attempts to improve this poor fit for the second level by changing to space group $R3c$ were not successful.

At this point it was decided to substitute iridium for rhodium in the calculations in order to see how the structure factors so calculated would compare with the observed powder data for $Sr_4IrO_6$. The fit was acceptable. At the same time it was noted that $F(hk2)$ values calculated for $Sr_4IrO_6$ gave a more satisfactory fit with the observed $F(hk2)$ values for the single crystals (presumed to be $Sr_4RhO_6$) than did the structure factors calculated for $Sr_4RhO_6$. There was, however, no possibility of appreciable amounts of iridium in these crystals. The only explanation which seemed reasonable was that platinum from the platinum crucible had entered into the crystals. (Atomic numbers: Rh, 45; Ir, 77; Pt, 78). To test this hypothesis of platinum substitution, the formula for the single crystals examined was assumed to be $Sr_4Rh_{1-x}Pt_xO_6$ and $F(hk2)$ values were calculated (neglecting oxygen) for $x = 0{\cdot}00$; 0·25; 0·50; 0·75; 1·00, and compared with the observed values. In each case the scale factor was taken so as to make $\Sigma|F_o| = \Sigma|F_c|$ and $R$ was computed. The values for $R$ in the order of increasing $x$ are 0·46, 0·33, 0·23, 0·20, and 0·16. Thus, even though the single crystals were prepared from $Sr_4RhO_6$, the X-ray evidence indicates that the crystals examined were really $Sr_4PtO_6$. A chemical analysis of the whole batch of crystals prepared in the platinum crucible was made and showed that there actually was about a third as much Pt as Rh in the material, quite enough, certainly, to result in a formula of $Sr_4PtO_6$ for single crystals.

Since the platinum metals in the +4 oxidation state usually take on 6-fold coordination, it was assumed that along the 3-fold axis (Pt–Sr–Pt–Sr) there would be a triangle of oxygens located between each pair of cations. Assuming each of these oxygens to be 2·05 Å from Pt and 2·53 Å from Sr, the $z$ parameter for 36 '$f$' was fixed at 0·093. The orientation of this triangle was determined by calculating first level structure factors at various angles of rotation. Using this method, the $x$ and $y$ parameters for oxygen were chosen as $x = 0{\cdot}181$ and $y = 0{\cdot}011$. The overall $R$ factor was improved from 0·154 to 0·122 by including 36 oxygens at these positions. In summary, there are

Table 1. *Observed and calculated structure factors for* $Sr_4PtO_6$

| *hkl* | $F_{obs.}$ | $F_{calc.}$ |
|---|---|---|
| 110 | 410 | 340 |
| 300 | 887 | 976 |
| 220 | 295 | 266 |
| 410 | 392 | 307 |
| 330 | 811 | 703 |
| 600 | 685 | 746 |
| 520 | 408 | 409 |
| 440 | 228 | 250 |
| 710 | 308 | 188 |
| 630 | 441 | 430 |
| 550 | 385 | 429 |
| 900 | 308 | 350 |
| 820 | 328 | 397 |
| 660 | 223 | 320 |
| 211 | 99 | 97 |
| 131 | 346 | −276 |
| 321 | 111 | −113 |
| 241 | 261 | 245 |
| 511 | 207 | 177 |
| 431 | 125 | −144 |
| 161 | 329 | −313 |
| 541 | 201 | 198 |
| 271 | 238 | 253 |
| 461 | 173 | −213 |
| 731 | 128 | −152 |
| 191 | 255 | −292 |
| 012 | 324 | 358 |
| 202 | $< 70$ | 51 |
| 122 | 139 | 158 |
| 312 | 383 | 444 |
| 042 | 314 | 349 |
| 232 | $< 62$ | −34 |
| 502 | 174 | −102 |
| 422 | 294 | 218 |
| 152 | 229 | 202 |
| 342 | 314 | 280 |
| 612 | 279 | 329 |
| 452 | 254 | 240 |
| 372 | 199 | 170 |
| 182 | $< 149$ | 115 |
| 642 | 174 | 219 |
| 722 | 259 | 268 |
| 912 | 304 | 277 |
| 562 | $< 124$ | −20 |
| 832 | 174 | −199 |
| 113 | 386 | 395 |
| 223 | 482 | 490 |
| 413 | 256 | 225 |
| 333 | $< 137$ | 74 |
| 523 | 167 | 178 |
| 443 | $< 160$ | 128 |
| 553 | $< 148$ | −70 |
| 104 | 448 | 426 |
| 024 | 744 | 725 |
| 214 | 599 | 618 |
| 134 | 436 | 367 |
| 404 | 448 | 352 |
| 324 | 780 | 676 |
| 054 | 714 | 767 |
| 244 | 387 | 350 |
| 514 | 466 | 403 |
| 434 | 266 | 364 |
| 164 | 278 | 268 |
| 354 | 690 | 744 |
| 704 | 333 | 311 |
| 624 | 472 | 539 |
| 544 | 303 | 389 |
| 084 | 726 | 707 |
| 464 | 248 | 266 |
| 184 | 417 | 482 |
| 734 | 315 | 248 |
| 654 | 484 | 426 |
| 384 | 472 | 597 |

6 Sr in 6 '*a*', 0, 0, $\frac{1}{4}$; 6 Pt in 6 '*b*', 0, 0, 0; 18 Sr in 18 '*e*', *x*, 0, $\frac{1}{4}$, with $x = 0{\cdot}370$; 36 O in 36 '*f*', *x*, *y*, *z*, with $x = 0{\cdot}181$, $y = 0{\cdot}011$, $z = 0{\cdot}093$. The structure factors are listed in Table 1.

The resulting structure has platinum atoms in octahedral coordination with oxygen, while strontium has two different coordinations. The strontiums in the 6-fold position are surrounded by six oxygens in an approximately trigonal prism arrangement, while those in the 18-fold position are surrounded by eight oxygens. This latter coordination polyhedron has an irregular shape. Figs. 1(*a*) and (*b*) indicate the atomic arrangement.

At the time this structure determination was in progress, it was found that Bellanca (1947) had determined the structure of $K_4MnCl_6$ using space group $R\bar{3}c$, and different space group positions from those used in this investigation. A check showed that these positions were impossible for $Sr_4PtO_6$.

Bellanca (1948) stated that $K_4CdCl_6$ is isotypic with $K_4MnCl_6$. While our manuscript was in preparation, our attention was called to the work of Bergerhoff & Schmitz-Dumont (1956) who reported that $K_4CdCl_6$ does not have the structure reported by Bellanca. The structure we have found for $Sr_4PtO_6$ and the related $Sr_4IrO_6$ and $Sr_4RhO_6$ compounds is of the same type as that reported for $K_4CdCl_6$ by Bergerhoff & Schmitz-Dumont. To the best of our knowledge, these are the first ternary oxides reported to have this structure.

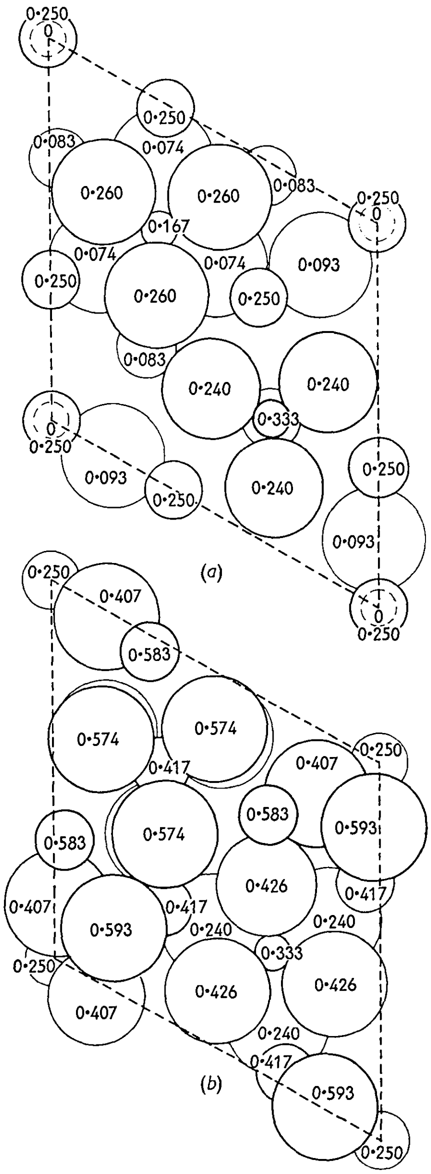

Fig. 1. (*a*) Projection of $Sr_4MO_6$ down the *c* axis between $z = 0$ and $z = 0{\cdot}260$. (*b*) Projection of $Sr_4MO_6$ down the *c* axis between $z = 0{\cdot}240$ and $z = 0{\cdot}600$. Large atoms are oxygens. Middle sized atoms are strontiums. Small atoms are platinums or rhodiums.

Financial support (to J. J. R.) provided by an Eastman Kodak Fellowship is gratefully acknowledged.

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