

A Structural Model for Barium Platinum Oxide, $\text{Ba}_3\text{Pt}_2\text{O}_7$

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Received January 14, 1977

A single crystal study of $\text{Ba}_3\text{Pt}_2\text{O}_7$ shows that the structure tolerates a variable composition which can be written $\text{Ba}_3\text{Pt}_{2-x}\text{O}_{7+2x}$. The crystal studied has a hexagonal cell of dimensions $a = 10.108 \pm 0.006 \text{ \AA}$ and $c = 8.638 \pm 0.009 \text{ \AA}$, and a probable space group $P6_2c$, $Z = 4$. The density determined by water displacement is 7.99 g/cm^3 ; the theoretical density for $\text{Ba}_3\text{Pt}_2\text{O}_7$ is 7.94 g/cm^3 . The structure was determined from the set of 401 observed independent reflections obtained from 5189 reflections measured by automated counter methods. Refinement on F was carried to a conventional R of 8.0%. The structure has barium-oxygen layers with an essentially four-layer stacking sequence of the double hexagonal (ABAB) type. Platinum is found mainly in face-sharing octahedra, but is also distributed over some sites in which the coordination is nearly square planar and other sites in which the coordination is trigonal prismatic with three Pt-O bond lengths of 2.00 \AA and three long Pt-O distances of 2.65 \AA . The platinum with planar coordination is 0.08 \AA from the plane of the four oxygen atoms.

Introduction

Rousseau (1) first isolated and analyzed $\text{Ba}_3\text{Pt}_2\text{O}_7$ in 1889. He prepared this phase by the reaction of BaO and PtCl_4 at 1100°C in an open platinum crucible, although he could also obtain it by reaction of BaCl_2 or BaBr_2 and Ba(OH)_2 with no other source of platinum than the crucible itself. Later, while investigating the BaO-TiO₂ system, Statton (2) isolated and analyzed crystals of $\text{Ba}_3\text{Pt}_2\text{O}_7$ which had formed in preparations of low titanium content through reactions with the platinum container. The $\text{Ba}_3\text{Pt}_2\text{O}_7$ phase was also formed in a study of the BaO-Pt system

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carried out by Schneider and McDaniel (3). An incompletely characterized analog, $\text{Sr}_3\text{Pt}_2\text{O}_7$, was prepared by Randall and Ward (4). Despite its relatively long history, the structure of $\text{Ba}_3\text{Pt}_2\text{O}_7$ was not known. We undertook this problem, which proved to be much more difficult than anticipated, as part of our program on complex metal oxides.

Experimental

The reaction of BaCO_3 and PtO_2 in a 3:2 ratio at 1000°C for 12 hr yielded a pure product. Single crystals of this phase were grown from a BaCl_2 flux containing a trace of Ba(OH)_2 , which kept the growth medium basic and prevented the decomposition of the desired product. The platinum crucible con-

taining the melt was cooled slowly from 1000 to 800°C over a period of 24 hr. The hexagonal prisms obtained were brownish red and gave an X-ray powder pattern identical to that of the starting powder.

Intensities were measured using Zr filtered Mo radiation with a Picker FACS-1 single crystal diffractometer equipped with a scintillation counter and pulse height analyzer. The Laue group, $6/mmm$, with hhl reflections present only for $l=2n$, indicated that the probable space group was one of $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$. Cell dimensions, determined from least-squares refinement of the setting angles of 12 reflections, are $a=10.108(6)$, $c=8.638(9)$. The density determined by water displacement is 7.99 g/cm^3 ; the calculated density for $Z=4$ is 7.94 g/cm^3 . An absorption correction was made based on $\mu=525.2 \text{ cm}^{-1}$, the corresponding transmission factors ranged from 0.031 to 0.088. Data were processed as previously described (5). All reflections with 2θ less than 40° and all reflections with $+h$, $+k$, $+l$, with 2θ between 40 and 70° were measured. A total of 5189 reflections were processed of which 2595 had $F_o^2 > 3\sigma(F_o^2)$ and were considered observed. Those related by symmetry were averaged, so that the final structure determination was based on 401 independent reflections.

The Structure Model and Refinement

The initial examination of the data revealed that all the intense $hk0$ reflections could be assigned to a subcell with a $a_{\text{subcell}} = a/3^{1/2}$. A vector map showed that all of the heavy scatterers lay on the $00z$; $\frac{1}{3}, \frac{2}{3}, z$; and $\frac{2}{3}, \frac{1}{3}, z$ lines. An electron density projection down the c axis showed no other heavy atom locations. By working with the subcell it was determined that the true cell x, y coordinates are at least close to $0, 0; \frac{1}{3}, \frac{2}{3}$; and $\frac{2}{3}, \frac{1}{3}$ for Pt and $\frac{1}{3}, 0; \frac{2}{3}, 0; \frac{1}{3}, \frac{1}{3}; \frac{2}{3}, \frac{2}{3}; 0, \frac{1}{3}; 0, \frac{2}{3}$ for Ba. Since it was not possible to place 12 Ba in the other two space groups so that they would be sufficiently far apart, $P\bar{6}2c$ was chosen. With the 12 Ba in $6h$ at $\frac{2}{3}, 0, \frac{1}{3}$, and in $6g$ at $\frac{1}{3}, 0, 0$ an electron density map showed large peaks for Pt sites at $\frac{1}{3}, \frac{2}{3}, 0.10$ and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$. Subsequent work showed additional diffracting matter along the $0, 0, z$ line,

which, however, was not well resolved into individual peaks. A maximum at $0, 0, 0.15$ was used as a Pt site. Difference electron density maps were used to locate sites sufficient to accommodate 30 oxygen atoms.

Least-squares refinement with anisotropic thermal parameters for the heavy atoms resulted in very large thermal anisotropy for the Pt atom at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ with a particularly large amplitude of vibration in the c axis direction. At this stage the R factor was about 15%. Splitting the $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ site into five parts, one above, one below, and three in an equilateral triangle centered on the $\frac{1}{3}, \frac{2}{3}, z$ line created a trigonal bipyramid of sites. These sites were tested for partial occupancy by allowing the population parameters to vary. The sum of these partial occupancies indicated very nearly one Pt atom in the vicinity of $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$, and, with isotropic temperature factors for these atoms, resulted in a reduction in R to about 10%. Placing a total of 2 Pt atoms along the $0, 0, z$ line by partial occupation of two four-fold positions reduced R to about 9%, and correcting for anomalous dispersion reduced R to 8.5%. (If only the 228 most intense reflections were considered, R could be reduced to about 5%.) Efforts to relax parameter restrictions by using less symmetric space groups (for example, $P31c$) did not help, nor did efforts to develop an ordered model with fully occupied sites by tripling the c -axis effect any improvement. Varying the population parameters for the oxygen atoms did suggest a way to reduce the total number of oxygens to 28 per cell, so that the formula for the model became close to $\text{Ba}_3\text{Pt}_2\text{O}_7$. However, there was still indication on difference maps for some additional scattering matter along the $0, 0, z$ line, including the origin. By introducing such additional fractional contributions, R was reduced to 8% and probably could be reduced further. The chief conclusion is that the formula should be written $\text{Ba}_3\text{Pt}_{2+x}\text{O}_{7+2x}$ rather than writing it in a way which suggests a fixed composition.

Atomic scattering factors for neutral atoms and the real and imaginary parts of the anomalous dispersion corrections were taken from the International Tables (6). Atomic scattering factors from the tabulation of Cromer and Waber (7) were also tried but made no

TABLE I
 ATOMIC PARAMETERS FOR $\text{Ba}_3\text{Pt}_2\text{O}_7$,^a SPACE GROUP $F\bar{6}2c$ (No. 190)

Atom	Position	x	y	z	Population	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	6h	0.3337(8)	0.0192(7)	$\frac{1}{3}$	1.0	72(17)	142(20)	221(25)	46(18)	0	0
Ba(2)	6g	0.6646(9)	0	0	1.0	223(25)	284	569(54)	142(21)	49(14)	98
Pt(1)	4f	$\frac{1}{3}$	$\frac{1}{3}$	0.0907(6)	1.0	52	52	386(25)	26(4)	0	0
Pt(2)	4f	$\frac{1}{3}$	$\frac{1}{3}$	0.6984(18)	0.25 ^c	114(19)					
Pt(3)	6h	0.4025(15)	0.7378(16)	$\frac{1}{3}$	0.17 ^c	35(19)					
Pt(4)	4e	0	0	0.1554(12)	0.33(1)	80	80	107(31)	40(11)	0	0
Pt(5)	4e	0	0	0.0877(15)	0.18(1)	381(96)					
Pt(6)	2a	0	0	0	0.12(2)	133(72)					
O(1)	12i	0.824(4)	0.336(5)	0.055(4)	1.0	95(54)					
O(2)	6h	0.168(5)	0.643(5)	$\frac{1}{3}$	1.0	38 ^b					
O(3)	6h	0.140(11)	0.170(10)	$\frac{1}{3}$	1.0	348(186)					
O(4)	6g	0.156(12)	0	0	0.74(19)	298(211)					

^a Thermal parameters multiplied by 10^4 .

^b Variable held at a fixed value.

^c After initial refinement indicated a total of 1.0 Pt spread over five sites, the population parameter was held at a fixed value.

difference in the refinement. However, the two possible anomalous dispersion corrections differed in their effect on R by about 0.01 ($R \approx 0.09$ and $R \approx 0.08$). All calculations were carried out with the program package "The X-Ray System" (8). Unit weights were used in the final refinements (on F). Except for the temperature factor for O(2), which tended to go negative, all positional and thermal parameters were refined simultaneously, although only isotropic temperature factors were considered justified for oxygen and low population parameter platinum atoms. Atomic parameters are given in Table I, bond lengths and angles in Table II, and observed and calculated structure factors in Table III.

The stereo illustration of the unit cell contents, plus a few atoms outside the cell (Fig. 1), a drawing of the interior Pt environment (Fig. 2), and a drawing of the Pt coordination polyhedra (Fig. 3) were prepared using ORTEP (9).

Discussion

The essentially four-layer stacking sequence is of the double hexagonal ($ABAB$) type. As shown in Fig. 1, one oxygen is missing from each Ba_3O_9 "A" layer, and three oxygens are missing from each "B" layer. Since there is a full complement of 12 Ba in the unit cell, the actual O content depends on the number of Pt atoms and their charge. The oxygen content shown corresponds to the composition $\text{Ba}_3\text{Pt}_2\text{O}_7$. Positions are available to make the composition of all layers Ba_3O_9 ; however, the omission of O atoms in the structure is consistent with the short average interlayer spacing of 2.15 Å (vs the 2.3 or 2.4 Å values usually found for close-packed structures with oxygen or BaO_3 layers).

The face-sharing pairs of octahedra (Pt_2O_9 groups) in the interior of the cell are connected in the c direction by platinum distributed on a trigonal bipyramid of sites, a total of one platinum over the five sites. These sites are too close to allow more than one to be occupied at a time. They do allow, however, two kinds of platinum environment, one of which is planar with bond lengths of 2.15 Å ($2x$) and 2.19 Å ($2x$), and the other trigonal prismatic

TABLE II
INTERATOMIC DISTANCES AND ANGLES OF Ba₃Pt₂O₇

Distances		
Ba(1)–O(1)	2.61(4) Å	2x
	3.14(3)	2x
–O(2)	2.71(4)	
	2.97(4)	
–O(3)	2.50(13)	
	3.18(1)	
–O(4)	2.75(7)	2x
Ba(2)–O(1)	2.92(4)	2x
	2.98(4)	2x
–O(2)	2.82(2)	2x
–O(3)	2.84(7)	2x
–O(4)	2.94(1)	2x
Pt(1)–O(1)	2.02(3)	3x
–O(2)	2.08(2)	3x
–Pt(1)	2.75(1)	
–Pt(2)	2.50(2)	
Pt(2)–O(1)	2.00(3)	3x
	2.65(3)	3x
–Pt(2)	0.89(2) ^a	
–Pt(3)	0.84(1) ^a	3x
Pt(3)–O(1)	2.15(4)	2x
	2.19(4)	2x
–Pt(3)	1.23(2) ^a	
Pt(4)–O(3) Å	1.79(7)	3x
–O(4)	2.07(7)	3x
–Pt(4)	1.64(2) ^a	
	0.58(1) ^a	
	2.68(2)	
–Pt(5)	2.10(1) ^a	
	2.22(1) ^a	
–Pt(6)	1.34(1) ^a	
	2.98(1)	
Pt(5)–O(3)	2.12(6)	3x
–O(4)	1.75(8)	3x
–Pt(5)	1.52(1) ^a	
	2.80(1)	
–Pt(6)	0.58(1) ^a	
Pt(6)–O(3)	2.68(5)	6x
–O(4)	1.57(9)	3x
O(1)–O(1)	2.73(4)	2x
–O(2)	2.97(4)	
	3.17(4)	
–O(4)	3.16(12)	
O(2)–O(2)	2.71(4)	2x
–O(3)	3.13(12)	
O(3)–O(3)	2.76(12)	2x
–O(4)	2.55(7)	2x
	2.81(9)	2x
O(4)–O(4)	2.73(15)	2x
Angles		
O(1)–Pt(1)–O(1)	85(1) ^b	
O(1)–Pt(1)–O(2)	93(1)	
O(1)′–Pt(1)–O(2)	101(1)	
O(1)–Pt(1)–O(2)	173(2)	
O(2)–Pt(1)–O(2)	81(1)	
O(1)–Pt(2)–O(1)	86(1)	
O(1)–Pt(3)–O(1)	103(2)	
O(1)′–Pt(3)–O(1)′	101(2)	
O(1)–Pt(3)–O(1)′	78(2)	
O(1)–Pt(3)–O(1)′	176(1)	
O(3)–Pt(4)–O(3)	101(2)	
O(4)–Pt(4)–O(4)	82(2)	
O(3)–Pt(4)–O(4)	82(2)	
O(3)–Pt(4)–O(4)′	93(2)	
O(3)–Pt(4)–O(4)	165(2)	

^a For short interatomic distances, both atoms cannot be present simultaneously.

with bond lengths 2.00 Å (3x) and 2.65 Å (3x). That these sites result in plausible planar arrangements in the one case and reasonable

bond lengths for the close approaches in the other lend credibility to the result.

Along the 0, 0 line there are several partially

TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTORS^a

H _{0,0}	H _{0,1}	7 616 -638 10 425 -343 14 431 109	H _{0,3}	1 2050 -2110 6 2029 2971	H _{0,5}	8 712 -694	H _{0,7}	11 437 -451 12 800 714	H _{0,9}	14 790 799 15 990 -913 17 506 419	H _{1,1}	1 1158 1091 2 563 -612 3 798 -379 4 975 973 5 601 -620 6 742 -684 7 628 673 8 844 -553 9 747 -730	H _{1,3}	1 4394 4316 3 4349 -437 4 1123 2977 5 345 -383 6 668 -689 7 1943 2017 8 577 -613	H _{1,5}	1 316 180 4 1787 -1698 5 237 2391 7 866 -702 8 2127 2126 9 1393 1510 10 1135 -1530 11 2018 1994 12 585 -921	H _{1,7}	2 339 -209 3 692 745 5 573 -642 6 741 767 8 815 827 9 1029 845 10 1204 845 11 1308 -1218 12 1308 874	H _{1,9}	2 2352 -2407 3 1178 1218 4 815 827 5 2023 -1064 6 1022 991 7 818 688 8 657 553 9 841 874 10 657 553	H _{2,1}	3 543 888 4 1222 -1189 5 914 -901 6 662 621 7 1204 -1224 8 625 -692 9 1338 1210 10 857 553	H _{2,3}	4 584 449 5 601 -620 6 742 -684 7 628 673 8 844 -553 9 747 -730 10 657 553 11 580 -604 12 704 739	H _{2,5}	6 685 595 5 1165 1127 6 357 -594 7 543 494 8 606 -804 9 804 -367 10 523 545 11 433 -346	H _{2,7}	6 685 595 5 1165 1127 6 357 -594 7 543 494 8 606 -804 9 804 -367 10 523 545 11 433 -346	H _{2,9}	6 685 595 5 1165 1127 6 357 -594 7 543 494 8 606 -804 9 804 -367 10 523 545 11 433 -346	H _{3,1}	1 498 520 2 563 -604 3 606 -520 4 596 -530 5 528 -528 6 455 -557	H _{3,3}	1 498 520 2 563 -604 3 606 -520 4 596 -530 5 528 -528 6 455 -557	H _{3,5}	1 498 520 2 563 -604 3 606 -520 4 596 -530 5 528 -528 6 455 -557	H _{3,7}	1 498 520 2 563 -604 3 606 -520 4 596 -530 5 528 -528 6 455 -557	H _{3,9}	1 498 520 2 563 -604 3 606 -520 4 596 -530 5 528 -528 6 455 -557	H _{4,1}	2 564 554 5 560 377 7 512 51 8 395 350 9 511 -395 10 626 -48	H _{4,3}	2 564 554 5 560 377 7 512 51 8 395 350 9 511 -395 10 626 -48	H _{4,5}	2 564 554 5 560 377 7 512 51 8 395 350 9 511 -395 10 626 -48	H _{4,7}	2 564 554 5 560 377 7 512 51 8 395 350 9 511 -395 10 626 -48	H _{4,9}	2 564 554 5 560 377 7 512 51 8 395 350 9 511 -395 10 626 -48	H _{5,1}	3 580 559 4 651 -489 5 578 77 6 504 308 7 500 -513 8 635 21 9 534 189	H _{5,3}	3 580 559 4 651 -489 5 578 77 6 504 308 7 500 -513 8 635 21 9 534 189	H _{5,5}	3 580 559 4 651 -489 5 578 77 6 504 308 7 500 -513 8 635 21 9 534 189	H _{5,7}	3 580 559 4 651 -489 5 578 77 6 504 308 7 500 -513 8 635 21 9 534 189	H _{5,9}	3 580 559 4 651 -489 5 578 77 6 504 308 7 500 -513 8 635 21 9 534 189	H _{6,1}	4 207 -1394 4 509 481 5 1151 -1136 6 557 404 7 504 -451 8 429 -516 9 609 693 9 521 404	H _{6,3}	4 207 -1394 4 509 481 5 1151 -1136 6 557 404 7 504 -451 8 429 -516 9 609 693 9 521 404	H _{6,5}	4 207 -1394 4 509 481 5 1151 -1136 6 557 404 7 504 -451 8 429 -516 9 609 693 9 521 404	H _{6,7}	4 207 -1394 4 509 481 5 1151 -1136 6 557 404 7 504 -451 8 429 -516 9 609 693 9 521 404	H _{6,9}	4 207 -1394 4 509 481 5 1151 -1136 6 557 404 7 504 -451 8 429 -516 9 609 693 9 521 404	H _{7,1}	4 460 -611 7 540 -630 10 410 -591	H _{7,3}	4 460 -611 7 540 -630 10 410 -591	H _{7,5}	4 460 -611 7 540 -630 10 410 -591	H _{7,7}	4 460 -611 7 540 -630 10 410 -591	H _{7,9}	4 460 -611 7 540 -630 10 410 -591	H _{8,1}	4 460 -611 7 540 -630 10 410 -591	H _{8,3}	4 460 -611 7 540 -630 10 410 -591	H _{8,5}	4 460 -611 7 540 -630 10 410 -591	H _{8,7}	4 460 -611 7 540 -630 10 410 -591	H _{8,9}	4 460 -611 7 540 -630 10 410 -591	H _{9,1}	4 460 -611 7 540 -630 10 410 -591	H _{9,3}	4 460 -611 7 540 -630 10 410 -591	H _{9,5}	4 460 -611 7 540 -630 10 410 -591	H _{9,7}	4 460 -611 7 540 -630 10 410 -591	H _{9,9}	4 460 -611 7 540 -630 10 410 -591
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^a The columns are h , $10F_o$, $10F_c$. The signs on F_c are the signs of A .

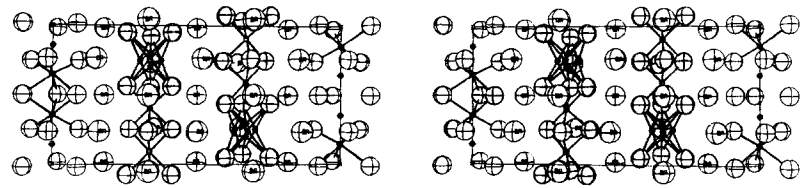


FIG. 1. Stereoview of extended unit cell contents: Ba atoms are labeled, O atoms shown as large circles, Pt atoms as small circles.

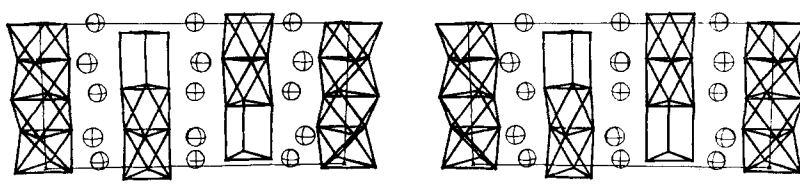


FIG. 2. Portion of structure showing Pt coordination in interior of cell.

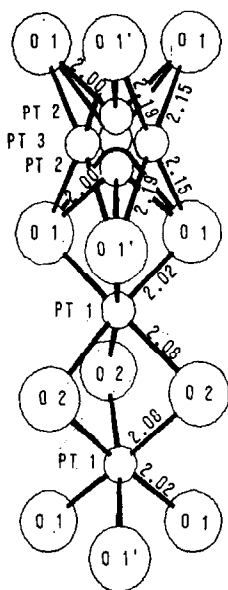


FIG. 3. Stereo view of Pt coordination polyhedra.

occupied sites indicated for platinum; the less compatible the site is with the oxygen positions, the lower the population parameter turns out to be. The effect is that of a column of scattering matter with several relative maxima. The same effect could be obtained with fewer sites and strongly anisotropic thermal motion with large amplitudes of vibration along z . In this respect it resembles the chain of Cu atoms in $\text{Cu}_4\text{Mo}_3\text{O}_{12}$ (10) or of Co atoms in $\text{NaCo}_{2.31}\text{Mo}_3\text{O}_{12}$ (11).

The cell contents of the model are $\text{Ba}_{12}\text{Pt}_{8.31}\text{O}_{28.44}$, which lacks 0.2 of an oxygen for charge balance with Pt(IV) (or has about 0.1 of a platinum too much). In any case, the charge balance is reasonably good and suggests that an acceptable formula might be written $\text{Ba}_3\text{Pt}_{2+x}\text{O}_{7+2x}$. By filling the available oxygen sites with oxygen atoms and the octahedra thereby created with platinum atoms the cell contents become $\text{Ba}_{12}\text{Pt}_{12}\text{O}_{36}$, which corresponds to $\text{Ba}_3\text{Pt}_{2+x}\text{O}_{7+2x}$ with $x = 1$. This is the key to the matter. As pointed out by Schneider and McDaniel (3), $\text{Ba}_3\text{Pt}_2\text{O}_7$ is a solid solution. The composition range indicated by these authors is $2\text{BaO}\cdot\text{PtO}_2$ to $\text{BaO}\cdot\text{PtO}_2$; thus $\text{Ba}_3\text{Pt}_2\text{O}_7$ is in the middle of the range. A point of discrepancy between our results and

those reported by Schneider and McDaniel is in the relationship between cell size and composition. These authors indexed their powder patterns on the basis of an orthorhombic cell with $a_{\text{orth}} \approx 3^{1/2} a_{\text{hex}}$, $b_{\text{orth}} \approx a_{\text{hex}}$, and $c_{\text{orth}} \approx c_{\text{hex}}$, which, of course, could be essentially the orthohexagonal choice of cell in the hexagonal system. The orthohexagonal cell dimensions which we would report are $a = 17.51$, $b = 10.11$, $c = 8.64$ Å, which are closer to the dimensions $a = 17.53$, $b = 10.09$, $c = 8.59$ Å reported by Schneider and McDaniel for the 1:1 composition, $\text{BaO}\cdot\text{PtO}_2$, than to the values $a = 17.62$, $b = 10.17$, $c = 8.85$ for the 2:1 composition, $2\text{BaO}\cdot\text{PtO}_2$, and so are not quite what would be expected for the 1.5:1 composition, $\text{Ba}_3\text{Pt}_2\text{O}_7$. However, the dimension most sensitive to composition, c , does lie within the range reported for the solid solution. In summary, then, what we have called $\text{Ba}_3\text{Pt}_2\text{O}_7$ does appear to be a phase of variable composition, and the structure model allows for such variability.

Acknowledgments

The authors are grateful to the National Science Foundation for support under Grants DMR 74-11818 and DMR 73-02616. We are also grateful to Professor James A. Ibers for his interest and for providing laboratory facilities for one of us (A.G.). Discussions with Dr. M. Mueller of Argonne National Laboratories are also acknowledged. Computations were carried out in the Computer Center of the University of Connecticut. Photographs of the figures were prepared by the University of Connecticut Photographic Laboratory.

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