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THE CRYSTAL STRUCTURE OF BERGENITE, A NEW GEOMETRICAL ISOMER OF THE PHOSPHURANYLITE GROUP

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ABSTRACT

The crystal structure of bergenite, ideally $Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$, monoclinic, space group $P2_1/c$, a 10.092(1), b 17.245(2), c 17.355(2) Å, β 113.678(2)°, V 2766.2(3) Å^3, $Z = 2$, D_{calc} 4.82 g/cm^3, was solved by direct methods and refined by full-matrix least-squares techniques on the basis of F^2 to agreement indices $R1$ of 5.0% calculated for 4118 unique observed reflections ($|F_o| \geq 4\sigma_F$), and wR_2 of 11.9% for all data. Intensity data were collected at room temperature using Mo$K\alpha$ radiation and a CCD-based area detector. The structure of bergenite contains five symmetrically independent uranium atoms, each of which is part of a $(UO_2)^{2+}$ uranyl ion. The uranyl ions of U(1), U(2) and U(3) are coordinated by five additional ligands giving pentagonal bipyramids, and the uranyl ions of U(4) and U(5) are coordinated by six additional ligands yielding hexagonal bipyramids. The uranyl pentagonal bipyramids share edges, forming dimers, which are linked to uranyl hexagonal bipyramids on either side, resulting in chains of bipyramids. Each uranyl hexagonal bipyramid shares two equatorial edges with phosphate tetrahedra, and the resulting uranyl phosphate chains are linked into sheets by the sharing of vertices of phosphate tetrahedra with uranyl pentagonal bipyramids of adjacent chains. The uranyl phosphate sheet in bergenite is a new geometrical isomer of the phosphuranylite group; the phosphate tetrahedra between the uranyl chains vary orientations in an up-up-down up-up-down (uuduud) pattern, and the pairs of tetrahedra attached to uranyl hexagonal bipyramids change orientations in a complementary same-same-opposite (SSO) manner (symbol uuduudSSO). In bergenite, the uranyl phosphate sheets are oriented parallel to ($\bar{1}02$), and the interlayer contains one calcium atom, two barium atoms and eight symmetrically distinct H_2O groups.

Keywords: bergenite, phosphuranylite, uranyl phosphate, geometrical isomer, crystal structure.

SOMMAIRE

Nous avons résolu la structure cristalline de la bergenite, de formule idéale $Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$, monoclinique, groupe spatial $P2_1/c$, a 10.092(1), b 17.245(2), c 17.355(2) Å, β 113.678(2)°, V 2766.2(3) Å^3, $Z = 2$, D_{calc} 4.82 g/cm^3, par méthodes directes, et nous l'avons affinée par moindres carrés sur matrice entière en utilisant les facteurs F^2 jusqu'à un résidu $R1$ de 5.0% calculé avec 4118 réflexions uniques observées ($|F_o| \geq 4\sigma_F$), et wR_2 de 11.9% pour toutes les données. L'intensité des réflexions a été mesurée à température ambiante avec un rayonnement Mo$K\alpha$ et un détecteur à aire de type CCD. La structure de la bergenite contient cinq atomes d'uranium symétriquement indépendants, chacun faisant partie d'un ion uranyle, $(UO_2)^{2+}$. Les ions uranyles U(1), U(2) et U(3) ont des liaisons à cinq ligands additionnels, ce qui donne des bipyramides pentagonales, et les ions uranyles U(4) et U(5) ont des liaisons à six ligands additionnels, ce qui donne des bipyramides hexagonales. Les bipyramides pentagonales partagent des arêtes et forment ainsi des dimères, qui sont liés aux bipyramides uranylées hexagonales de chaque côté, pour donner des chaînes de bipyramides. Chaque bipyramide uranylée hexagonale partage deux arêtes équatoriales avec les tétraèdres de phosphate, et les chaînes de phosphate à uranyle qui en résultent sont agencées en feuillets par partage de vertex des tétraèdres de phosphate avec des dipyramides uranylées pentagonales des chaînes adjacentes. Le feuillet de phosphate uranylé dans la bergenite est un isomère géométrique nouveau du groupe de la phosphuranylite; les tétraèdres de phosphate entre les chaînes d'uranyle changent d'orientation selon la séquence haut-haut-bas haut-haut-bas (uuduud), et les paires de tétraèdres rattachés aux bipyramides uranylées hexagonales changent d'orientation de façon complémentaire: même-même-opposée (SSO) (symbole uuduudSSO). Dans la bergenite, les feuillets de phosphate à uranyle sont orientés parallèles à ($\bar{1}02$), et l'interfeuillet contient un atome de calcium, deux atomes de barium, et huit groupes H_2O symétriquement distincts.

(Traduit par la Rédaction)

Mots-clés: bergenite, phosphuranylite, phosphate uranylé, isomère géométrique, structure cristalline.

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INTRODUCTION

The phosphuranylite group is one of the two major groups of uranyl phosphate and uranyl arsenate minerals (autunite – meta-autunite is the other); it consists of at least sixteen minerals, of which nine have had their structures determined (Finch & Murakami 1999, Burns 1999). The structures, chemical compositions and stabilities of uranyl phosphate minerals are of interest because of their significance to the environment. They exert an impact on the mobility of uranium in phosphate-rich systems (Sowder *et al.* 1996), such as in the Koongarra uranium deposit in Australia (Murakami *et al.* 1997), the soils of the Fernald site in Ohio (Buck *et al.* 1996), and the K1300 locality of the DOE–K 25 site at Oak Ridge, Tennessee (Roh *et al.* 2000). As part of our ongoing research into the structures of uranyl phosphates (Locock & Burns 2002a, b, 2003), we have determined the crystal structure of bergenite, the calcium–barium member of the phosphuranylite group.

PREVIOUS STUDIES

Bergenite was originally described by Bültemann & Moh (1959) as a member of the phosphuranylite group; it was discovered in material from a now-vanished mine dump of the SDAG Wismut 254 shaft in the area of Streuberg, near Bergen on the Trieb, Vogtland, Sachsen, Federal Republic of Germany. Bergenite was reported to have orthorhombic symmetry, a density greater than 4.1 g/cm^3, and was interpreted to be the natural analogue of the synthetic "barium-phosphuranylite" of Ross (1956), $Ba(UO_2)_4(PO_4)_2(OH)_4 \bullet 8H_2O$, on the basis of the similarities between the optical properties and the X-ray diffraction patterns of the two compounds (Bültemann & Moh 1959). No quantitative chemical data were presented.

Piret & Deliens (1981) re-investigated bergenite, using material from the holotype specimen, and concluded that although bergenite is a member of the phosphuranylite group, the equivalence of bergenite and synthetic "barium-phosphuranylite" is far from complete. They reported new optical data for bergenite, a chemical formula of $Ba_{4/3}Ca_{2/3}(UO_2)_3(PO_4)_2(OH)_4 \bullet{\sim}5.5(H_2O)$ based on electron-microprobe analyses, and the following crystallographic data: monoclinic, space group $P2_1/c$, a 23.32, b 17.19, c 20.63 Å, β 93.0°, V 8259 Å^3, $Z = 18$, D_{calc} 4.98 g/cm^3, $D_{\text{meas}} > 4.05$ g/cm^3.

In addition to the Vogtland locality, bergenite has been found in the uranium deposits of the Black Forest, Federal Republic of Germany (Walenta 1985), and in the graphitic uranium ore of the Black Slate Formation of the Ogcheon Group in the Republic of [South] Korea (Lee *et al.* 1982).

EXPERIMENTAL

The bergenite sample studied is from the collection of L'Institut Royal des Sciences Naturelles de Belgique in Brussels, sample RV9/535. It was donated to the Institute by George Vanacker, who had originally obtained the specimen from William Pinch. The sample investigated is not part of the holotype, but is from the type locality.

Electron-microprobe examination

In light of the lack of agreement concerning the presence of K in phosphuranylite (Demartin *et al.* 1991, Piret & Piret-Meunier 1991), the chemical composition of bergenite was confirmed by qualitative electron-microprobe examination. Crystals of bergenite were mounted on an adhesive carbon tab and carbon-coated. An energy-dispersion X-ray emission spectrum was acquired for 140 s with an ultra-thin-window Si(Li) detector on a JEOL JXA–8600 Superprobe at an excitation voltage of 15 kV and a probe current of 0.9 nA. Following EDS examination, a wavelength-dispersion X-ray emission spectrum was acquired in the energy range 3.05–3.45 kV (PET crystal, excitation voltage 15 kV, probe current 20 nA) to check for the presence of K and resolve the potential overlap of the $KK\alpha$ peak with that of $UM\beta$. The only elements present (Fig. 1a) were U, Ba, Ca, P, O and C; K was not detected (Fig. 1b).

Single-crystal X-ray diffraction

An optically homogeneous fragment of bergenite was mounted on a Bruker PLATFORM three-circle X-ray diffractometer operated at 50 keV and 40 mA and equipped with a 4K APEX CCD detector with a crystal-to-detector distance of 4.7 cm. A sphere of three-dimensional data was collected using graphite-monochromatized Mo$K\alpha$ X-radiation and frame widths of 0.6° in ω, with count-times per frame of 240 seconds. Data were collected in 84 hours for $4° \leq 2\theta \leq 69°$; comparison of the intensities of equivalent reflections measured at different times during data acquisition showed no significant decay. The unit cell (Table 1) was refined with 3472 reflections using least-squares techniques; its volume is three times smaller than that reported by Piret & Deliens (1981). The intensity data were examined carefully for indications of a larger cell, but no reflections with $I \geq 2\sigma_I$ were found to support this possibility, despite the high sensitivity of the CCD detector (Burns 1998) and the long count-time per frame (240 s). The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical correction for

TABLE 1. CRYSTALLOGRAPHIC DATA AND DETAILS OF THE STRUCTURE REFINEMENT FOR BERGENITE

a (Å)	10.092(1)	Crystal size	0.08 mm × 0.06 mm × 0.02 mm
b (Å)	17.245(2)	R_{int} (%)	16.3
c (Å)	17.355(2)	Total reflections	54,037
β (°)	113.678(2)	Unique reflections	11,359
V (Å^3)	2766.2(3)	Unique $F_o \geq 4\sigma_F$	4118
Temperature (K)	293(2)	Refinement method	Full-matrix least-squares on F^2
Space group	$P2_1/c$	Parameters varied	227
F(000)*	3452.0	$R1$† (%) for $F_o \geq 4\sigma_F$	5.0
μ (mm^{-1})*	29.53	wR_2‡ (%) all data	11.9
D_{calc} (g/cm^3)*	4.82(1)	Goodness of fit all data	0.777
Wavelength	Mo$K\alpha$	Max. min. peaks (e/Å^3)	4.9, -2.9
Data range (θ)	2.20 to 34.56°	Data collected	$-16 \leq h \leq 15$, $-27 \leq k \leq 27$, $-27 \leq l \leq 27$
Formula weight*	4013.78	Formula (Z = 2)	$Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$

* Calculated with ideal occupancy of all atomic positions

† $R1 = [\Sigma F_o - F_c] / \Sigma F_o \times 100$

‡ $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5} \times 100$, $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2$, $P = ⅓ \max(0, F_o^2) + ⅔F_c^2$, $a = 0.0372$

absorption was applied by modeling the crystal as an ellipsoid; this lowered R_{INT} of 1916 intense reflections from 8.3% to 6.2%.

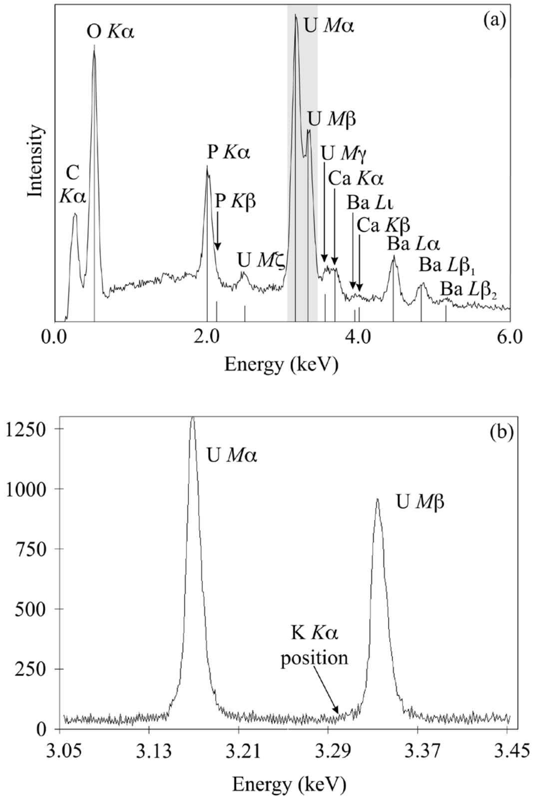


FIG. 1. (a) Energy-dispersion X-ray emission spectrum of bergenite; the shaded area corresponds to the energy range investigated by WDS. (b) Wavelength-dispersion X-ray emission spectrum of bergenite; the U$M\alpha$ and U$M\beta$ lines are well resolved, and K$K\alpha$ is not detected.

Systematic absences of reflections for bergenite were found to be consistent with space group $P2_1/c$. A total of 54,917 intensities was collected, of which 880 were discarded as being inconsistent with the space group; none of these latter intensities were classified as observed. Of the 54,037 remaining intensities, 11,359 are unique (R_{INT} = 16.3%), of which 4118 are classified as observed reflections ($|F_o| \geq 4\sigma_F$).

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography, Volume IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 series of programs was used for the solution and refinement of the crystal structure.

Structure solution and refinement

The structure of bergenite was solved by direct methods and was refined successfully on the basis of F^2 for all unique data in space group $P2_1/c$. A structure model including anisotropic displacement parameters for all non-O atoms converged, and gave an agreement index ($R1$) of 5.0%, calculated for the 4118 observed unique reflections ($|F_o| \geq 4\sigma_F$). The final value of wR_2 was 11.9% for all data using the structure-factor weights assigned during least-squares refinement. In the final cycle of refinement, the mean parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 4.8 and –2.9 e/Å^3. The locations of the H atoms in the unit cell were not determined. The positional parameters and anisotropic displacement parameters of atoms in bergenite are given in Tables 2 and 3 respectively, and selected interatomic distances are in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. Bond-valence sums at the cation and anion sites are presented in Table 5, and were calculated assuming ideal occupancy of all cation sites and using the parameters of Burns *et al.* (1997) for U, and those of Brown & Altermatt (1985) for P, Ba and Ca. Delineation of the H_2O groups was accomplished using the results of the bond-valence analysis.

The site occupancies (Hawthorne *et al.* 1995) of the Ba(1) and Ba(2) sites were refined, assuming no vacancies and only Ca ö Ba substitution, consistent with the qualitative elemental data presented herein (Fig. 1) and the quantitative electron-microprobe results of Piret &

TABLE 2. ATOM COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR BERGENITE

	x	*y*	*z*	U_{eq}
U(1)	0.3119(1)	0.3921(1)	0.6823(1)	0.012(1)
U(2)	0.3234(1)	0.6086(1)	0.6779(1)	0.013(1)
U(3)	1.0002(1)	0.3929(1)	0.9942(1)	0.012(1)
U(4)	0	½	½	0.016(1)
U(5)	0.6382(1)	0.5023(1)	0.8603(1)	0.014(1)
Ba(1)*	0.2494(1)	0.4880(1)	0.8786(1)	0.026(1)
Ba(2)†	0.3888(1)	0.6584(1)	0.4582(1)	0.024(1)
Ca(1)	0.0538(4)	0.6942(2)	0.7974(2)	0.025(1)
P(1)	0.6278(4)	0.3099(2)	0.8703(3)	0.013(1)
P(2)	0.6239(5)	0.6927(2)	0.8719(3)	0.014(1)
P(3)	0.0352(4)	0.6885(2)	0.4729(3)	0.016(1)
O(1)	0.2043(10)	0.5019(6)	0.6131(6)	0.019(2)
O(2)	0.4480(12)	0.5990(6)	0.6280(7)	0.025(3)
O(3)	0.4360(13)	0.3967(7)	0.6314(8)	0.033(3)
O(4)	0.0908(13)	0.4872(7)	0.4289(7)	0.034(3)
O(5)	0.1964(11)	0.3862(6)	0.7381(7)	0.021(2)
O(6)	0.7167(12)	0.5076(7)	0.7846(7)	0.034(3)
O(7)	0.5653(10)	0.5001(6)	0.9394(6)	0.022(2)
O(8)	0.6646(11)	0.2457(5)	0.8206(6)	0.013(2)
O(9)	0.1997(12)	0.6232(6)	0.7284(7)	0.025(3)
O(10)	0.6792(11)	0.7554(6)	0.8307(6)	0.016(3)
O(11)	0.5270(11)	0.6351(6)	0.8051(7)	0.020(3)
O(12)	0.8576(10)	0.4999(6)	0.9664(6)	0.021(2)
O(13)	-0.0998(11)	0.6350(6)	0.4430(6)	0.019(2)
O(14)	0.4101(9)	0.5018(6)	0.7635(6)	0.017(2)
O(15)	0.9747(12)	0.3862(6)	1.0906(7)	0.029(3)
O(16)	0.0050(11)	0.7569(5)	0.5179(6)	0.016(2)
O(17)	0.5064(12)	0.3623(6)	0.8113(7)	0.027(3)
O(18)	1.0265(11)	0.3996(6)	0.8984(6)	0.020(2)
OW(19)	0.3159(12)	0.3322(6)	0.9160(7)	0.024(3)
O(20)	0.7534(12)	0.3692(6)	0.9070(7)	0.026(3)
O(21)	0.7463(10)	0.6389(5)	0.9280(6)	0.015(2)
O(22)	0.5912(13)	0.2769(7)	0.9389(8)	0.036(3)
OW(23)	0.3016(12)	0.6498(6)	0.9093(7)	0.024(3)
O(24)	0.5425(13)	0.7262(6)	0.9207(7)	0.030(3)
O(25)	0.0821(13)	0.7139(6)	0.4042(7)	0.029(3)
O(26)	0.1529(12)	0.6373(6)	0.5384(7)	0.029(3)
OW(27)	-0.2083(15)	0.6712(8)	0.7411(9)	0.054(4)
OW(28)	-0.0199(13)	0.5349(7)	0.7490(8)	0.035(3)
OW(29)	-0.0588(15)	0.7430(8)	0.6558(8)	0.047(4)
OW(30)	0.2215(14)	0.8029(7)	0.7858(8)	0.041(3)
OW(31)	0.6613(17)	0.4891(9)	0.6064(10)	0.071(5)
OW(32)	-0.2998(16)	0.6375(8)	0.5629(9)	0.059(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
* Ba(1) refined occupancy: Ba 0.968(6), Ca 0.032(6).
† Ba(2) refined occupancy: Ba 0.879(5), Ca 0.121(5).

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR BERGENITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	0.011(1)	0.006(1)	0.014(1)	-0.001(1)	-0.002(1)	0.001(1)
U(2)	0.011(1)	0.007(1)	0.015(1)	0.000(1)	-0.001(1)	0.000(1)
U(3)	0.008(1)	0.007(1)	0.017(1)	0.000(1)	0.001(1)	-0.001(1)
U(4)	0.015(1)	0.011(1)	0.015(1)	0.001(1)	-0.002(1)	0.001(1)
U(5)	0.010(1)	0.012(1)	0.016(1)	0.001(1)	0.001(1)	0.001(1)
Ba(1)	0.022(1)	0.019(1)	0.031(1)	-0.004(1)	0.006(1)	-0.006(1)
Ba(2)	0.030(1)	0.015(1)	0.025(1)	-0.002(1)	0.009(1)	0.001(1)
Ca(1)	0.030(2)	0.019(2)	0.029(2)	-0.005(1)	0.016(2)	-0.008(1)
P(1)	0.007(2)	0.003(2)	0.019(2)	0.000(2)	-0.004(2)	0.001(2)
P(2)	0.016(2)	0.002(2)	0.018(2)	0.003(2)	0.001(2)	-0.001(2)
P(3)	0.014(2)	0.002(2)	0.021(2)	-0.001(1)	-0.003(2)	-0.002(1)

The anisotropic displacement parameter exponent takes the form: $-2\pi^2[h^2\mathbf{a}^{*2}U_{11} + \ldots + 2hk\,\mathbf{a}^*\,\mathbf{b}^*\,U_{12}]$.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) FOR BERGENITE

U(1)-O(5)	1.792(11)	P(1)-O(22)	1.493(13)
U(1)-O(3)	1.802(12)	P(1)-O(17)	1.536(11)
U(1)-O(1)	2.271(10)	P(1)-O(8)	1.539(10)
U(1)-O(14)	2.328(10)	P(1)-O(20)	1.554(11)
U(1)-O(17)	2.366(11)	<P(1)-O>	1.53
U(1)-O(10)a	2.374(10)		
U(1)-O(13)b	2.407(10)	P(2)-O(24)	1.510(12)
<U(1)-O_{ur}>	1.80	P(2)-O(10)	1.520(11)
<U(1)-O_{eq}>	2.35	P(2)-O(21)	1.539(10)
		P(2)-O(11)	1.541(11)
U(2)-O(2)	1.797(11)	<P(2)-O>	1.53
U(2)-O(9)	1.809(11)		
U(2)-O(1)	2.238(10)	P(3)-O(16)	1.512(10)
U(2)-O(14)	2.307(10)	P(3)-O(25)	1.514(12)
U(2)-O(8)c	2.366(10)	P(3)-O(26)	1.548(12)
U(2)-O(11)	2.380(10)	P(3)-O(13)	1.552(11)
U(2)-O(26)	2.392(11)	<P(3)-O>	1.53
<U(2)-O_{ur}>	1.79		
<U(2)-O_{eq}>	2.34	Ba(1)-OW(19)	2.783(11)
		Ba(1)-OW(23)	2.850(11)
U(3)-O(18)	1.789(10)	Ba(1)-O(18)e	2.851(10)
U(3)-O(15)	1.796(11)	Ba(1)-OW(28)	2.862(12)
U(3)-O(12)	2.270(11)	Ba(1)-O(5)	2.876(11)
U(3)-O(12)d	2.270(11)	Ba(1)-O(7)	2.935(9)
U(3)-O(16)a	2.354(9)	Ba(1)-O(7)f	2.962(9)
U(3)-O(20)	2.373(11)	Ba(1)-O(14)	3.046(9)
U(3)-O(21)d	2.428(10)	Ba(1)-O(12)f	3.284(9)
<U(3)-O_{ur}>	1.79	Ba(1)-O(15)f	3.329(11)
<U(3)-O_{eq}>	2.27	Ba(1)-O(9)	3.381(11)
		<Ba(1)-φ>	3.01
U(4)-O(4)	1.821(11)		
U(4)-O(4)b	1.821(11)	Ba(2)-O(22)c	2.668(12)
U(4)-O(1)b	2.204(9)	Ba(2)-OW(31)g	2.743(16)
U(4)-O(1)	2.204(9)	Ba(2)-O(24)h	2.756(12)
U(4)-O(13)	2.572(10)	Ba(2)-OW(30)h	2.862(13)
U(4)-O(13)b	2.572(10)	Ba(2)-O(3)g	2.942(12)
U(4)-O(26)	2.757(11)	Ba(2)-O(2)	2.947(11)
U(4)-O(26)b	2.757(11)	Ba(2)-OW(32)i	2.954(15)
<U(4)-O_{ur}>	1.82	Ba(2)-O(25)	3.007(12)
<U(4)-O_{eq}>	2.51	Ba(2)-O(26)	3.225(11)
		Ba(2)-OW(23)h	3.440(11)
U(5)-O(6)	1.789(11)	<Ba(2)-φ>	2.95
U(5)-O(7)	1.799(9)		
U(5)-O(14)	2.240(9)	Ca(1)-O(25)j	2.367(12)
U(5)-O(12)	2.240(9)	Ca(1)-OW(29)	2.408(14)
U(5)-O(20)	2.554(11)	Ca(1)-OW(27)	2.456(15)
U(5)-O(11)	2.561(10)	Ca(1)-O(15)f	2.496(12)
U(5)-O(21)	2.662(10)	Ca(1)-O(9)	2.553(11)
U(5)-O(17)	2.723(11)	Ca(1)-OW(30)	2.587(13)
<U(5)-O_{ur}>	1.79	Ca(1)-OW(23)	2.590(11)
<U(5)-O_{eq}>	2.50	Ca(1)-OW(28)	2.882(12)
		<Ca(1)-φ>	2.54

a = -x + 1, y - 1/2, -z + 3/2
b = -x, -y + 1, -z + 1
c = -x + 1, y + 1/2, -z + 3/2
d = -x + 2, -y + 1, -z + 2
e = x - 1, y, z
f = -x + 1, -y + 1, -z + 2
g = -x + 1, -y + 1, -z + 1
h = x, -y + 3/2, z - 1/2
i = x + 1, y, z
j = x, -y + 3/2, z + 1/2

φ: (O, H_2O)

Deliens (1981). The refined atomic contents of the Ba(1) site are 96.8(6)% Ba and 3.2(6)% Ca, whereas the Ba(2) site contains 87.9(5)% Ba and 12.1(5)% Ca. These results yield the empirical formula $Ca_2(Ba_{3.69}Ca_{0.31})[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$, which may be idealized as $Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$, in excellent agreement with that reported by Piret & Deliens (1981).

DESCRIPTION OF THE STRUCTURE

The structure of bergenite is shown projected along [010] in Figure 2. As with other structures of the phosphuranylite group (see Burns 1999), bergenite contains uranyl phosphate sheets of the phosphuranylite sheet anion-topology, with H_2O groups and cations (Ca and Ba in this case) in the interlayer.

There are five symmetrically independent U atoms in bergenite, each of which is part of an approximately linear $(UO_2)^{2+}$ cation. The uranyl ions of U(1), U(2) and U(3) are coordinated by five additional O atoms arranged at the equatorial positions of pentagonal bipyramids, with the uranyl ion O atoms at the apices of the bipyramids, whereas the uranyl ions of U(4) and U(5) are coordinated in a similar fashion with six additional O atoms arranged at the equatorial positions of hexagonal bipyramids (Table 4).

The uranyl pentagonal bipyramids share equatorial edges with each other and with the hexagonal bipyramids to form chains that have a ratio of pentagonal bipyramids to hexagonal bipyramids of 2:1. Each of the three symmetrically distinct phosphate tetrahedra shares an edge with a hexagonal bipyramid, and its opposite corner with a pentagonal bipyramid, thus serving to link the offset chains of uranyl polyhedra into sheets (Fig. 3).

The interlayer of bergenite contains two symmetrically independent barium positions, one calcium position and eight distinct H_2O groups. Ba(1) is in eleven-fold coordination with a mean Ba(1)–φ (φ: O, H_2O) distance of 3.01 Å, and Ba(2) is in ten-fold coordination with a mean Ba(2)–φ distance of 2.95 Å. Ba(1)

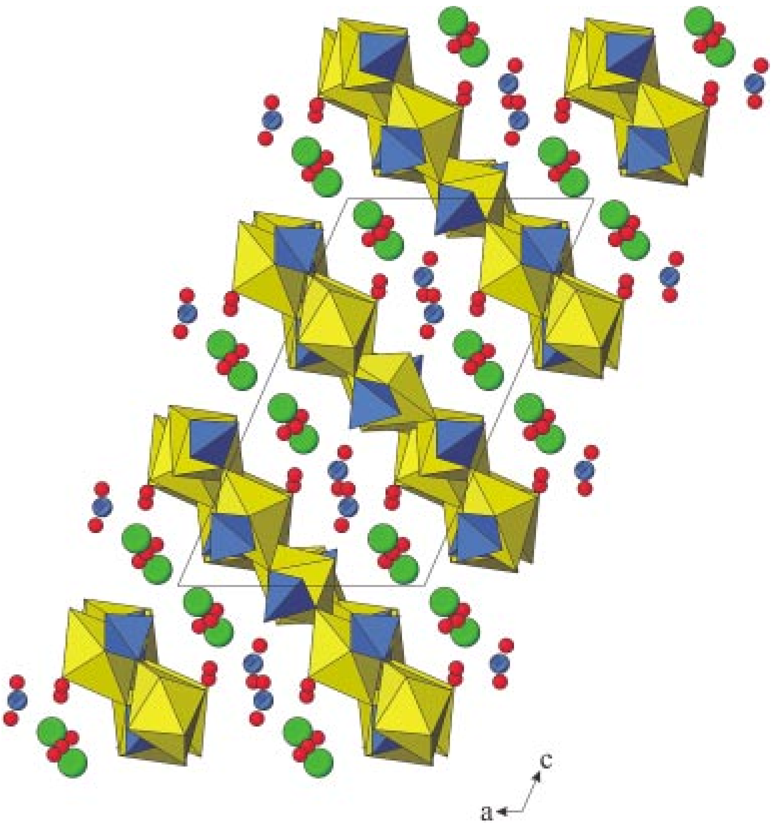


FIG. 2. Polyhedron representation of the crystal structure of bergenite projected along [010]. The uranyl polyhedra are shown in yellow, and the phosphate tetrahedra, in blue. The Ba atoms are shown as large green spheres, the Ca atoms as striped blue spheres, and the H_2O groups as small red spheres.

TABLE 5. BOND-VALENCE ANALYSIS FOR BERGENITE (*vu*)*

	U(1)	U(2)	U(3)	U(4)	U(5)	P(1)	P(2)	P(3)	Ba(1)	Ba(2)	Ca(1)	Total
O(1)	0.64	0.68		$0.73^{\times2\downarrow}$								2.05
O(2)		1.72								0.17		1.88
O(3)	1.61									0.17		1.78
O(4)				$1.55^{\times2\downarrow}$								1.55
O(5)	1.64								0.20			1.84
O(6)					1.65							1.65
O(7)					1.61				$0.17^{\times2\downarrow}$			1.79
O(8)		0.53				1.24						1.77
O(9)		1.59							0.05		0.21	1.85
O(10)	0.52						1.30					1.82
O(11)		0.52			0.36		1.23					2.10
O(12)			$0.64^{\times2\downarrow\rightarrow}$		0.68				0.07			2.03
O(13)	0.49			$0.35^{\times2\downarrow}$				1.19				2.03
O(14)	0.57	0.60			0.68				0.13			1.98
O(15)			1.63						0.06		0.24	1.93
O(16)			0.55					1.33				1.88
O(17)	0.53				0.26	1.24						2.04
O(18)			1.65						0.22			1.87
OW(19)									0.26			0.26
O(20)			0.53		0.36	1.19						2.08
O(21)			0.47		0.29		1.23					2.00
O(22)						1.40				0.36		1.75
OW(23)									0.22	0.04	0.19	0.45
O(24)							1.33			0.28		1.61
O(25)								1.32		0.14	0.34	1.80
O(26)		0.51		$0.24^{\times2\downarrow}$				1.20		0.08		2.03
OW(27)											0.27	0.27
OW(28)									0.21		0.08	0.29
OW(29)											0.30	0.30
OW(30)										0.21	0.19	0.40
OW(31)										0.29		0.29
OW(32)										0.16		0.16
Total	6.02	6.15	6.11	5.74	5.89	5.07	5.09	5.04	1.75	1.90	1.81	

* Calculated with ideal occupancy of all atomic positions.

is coordinated mostly by the apical O atoms of uranyl ions (Table 4) and also by equatorial O atoms of uranyl polyhedra and interlayer H_2O groups, whereas Ba(2) is coordinated by apical O atoms of phosphate tetrahedra, interlayer H_2O groups and apical O atoms of uranyl ions. The eight-fold-coordinated Ca(1) is coordinated mostly by interlayer H_2O groups and has a mean Ca(1)–φ distance of 2.54 Å (Table 4).

DISCUSSION

The uranyl phosphate sheets in the minerals of the phosphuranylite group differ mainly in the orientations of their phosphate tetrahedra (Burns 1999), and may be divided on this basis (Fig. 4, Table 6) into four different geometrical isomers (Hawthorne 1983). In the vanmeersscheite-type sheet, found in vanmeersscheite and dumontite, the phosphate tetrahedra between the uranyl chains alternate orientations in an up-down up-down up-down (ududud) pattern, and each pair of tetrahedra attached to a given uranyl hexagonal bipyramid has the same (S) orientation. This geometrical isomer may thus be referred to by the symbol ududud S. In the phosphuranylite-type sheet, found in upalite, phosphuranylite, françoisite-(Nd) and dewindtite, the tetrahedra change orientation in an up-up down-down up-up (uudduu) sequence, and the tetrahedra attached to the same uranyl hexagonal bipyramid have the same (S) orientation, yielding the geometrical isomer uudduuS. The phurcalite-type sheet, found in phurcalite, phuralumite and althupite, has tetrahedra that also change orientations in an up-up down-down up-up (uudduu) pattern, but the tetrahedra attached to the same uranyl hexagonal bipyramid have opposite (O) orientations, giving the geometrical isomer uudduuO. The uranyl phosphate sheet in bergenite is a novel geometrical isomer; the tetrahedra vary orientations in an up-up-down up-up-down (uuduud) pattern, and the pairs of tetrahedra attached to uranyl hexagonal bipyramids change orientations in a complementary same-same-opposite (SSO) sequence, yielding the symbol uuduudSSO (Table 6).

Comparison with previous work

The unit cell presented in this work is one-third the volume of that reported by Piret & Deliens (1981) on the basis of precession and Weissenberg photographs,

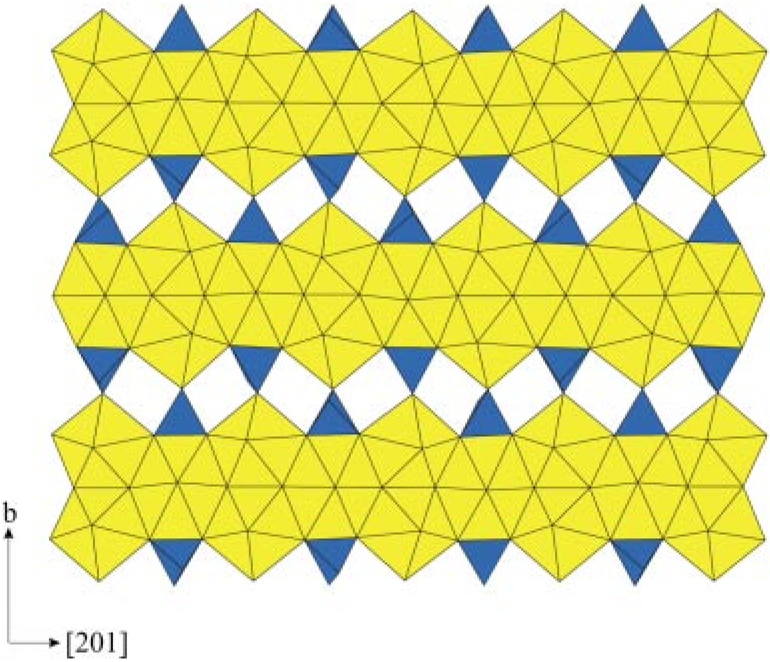


FIG. 3. The uranyl phosphate sheet of bergenite, projected normal to ($\bar{1}02$). The uranyl polyhedra are shown in yellow, and the phosphate tetrahedra, in blue.

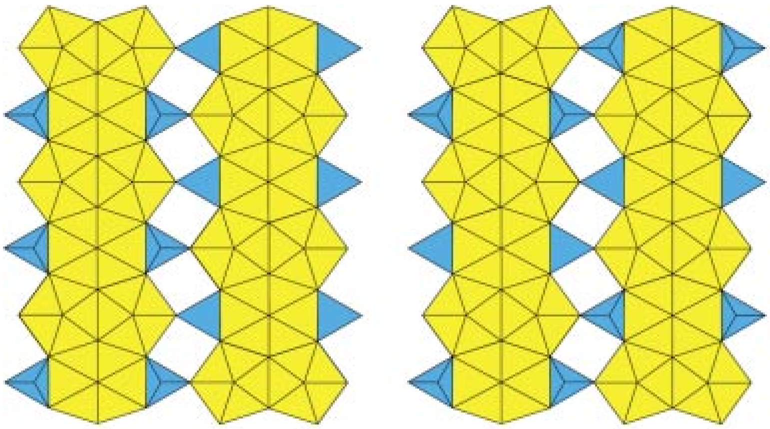
TABLE 6. CELL PARAMETERS AND ORIENTATIONS OF PHOSPHURANYLITE-GROUP STRUCTURES

Mineral	Space Group	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*R*1 (%)	OS	CD	Geometrical Isomer	Formula	Ref.
vanmeersscheite	$P2_1mn$	17.06	16.76	7.02		12.6	(010)	[001]	ududud$S$	$U^{6+}[(UO_2)_3(OH)_2(PO_4)_2](OH)_4(H_2O)_4$	1
dumontite	$P2_1/m$	8.12	16.82	6.98	109.0	5.0	(100)	[001]	ududud$S$	$Pb_2[(UO_2)_3O_2(PO_4)_2](H_2O)_5$	2
upalite	$P2_1/a$	13.70	16.82	9.33	111.5	4.9	(010)	[100]	uudduu$S$	$Al[(UO_2)_3O(OH)(PO_4)_2](H_2O)_7$	3
phosphuranylite	*Cmcm*	15.78	13.70	17.25		3.6	(100)	[010]	uudduu$S$	$(H_3O)_3KCa(UO_2)[(UO_2)_3O_2(PO_4)_2]_2(H_2O)_8$	4
phosphuranylite	*Bmmb*	15.83	17.32	13.72		8.9	(100)	[001]	uudduu$S$	$Ca(UO_2)[(UO_2)_3(OH)_2(PO_4)_2]_2(H_2O)_{12}$	5
françoisite-(Nd)	$P2_1/c$	9.30	15.61	13.67	112.8	6.1	(010)	[001]	uudduu$S$	$(Nd,REE)[(UO_2)_3O(OH)(PO_4)_2](H_2O)_6$	6
dewindtite	*Bmmb*	16.03	17.26	13.61		6.3	(100)	[001]	uudduu$S$	$Pb_3[(UO_2)_3(OH)O(PO_4)_2]_2(H_2O)_{12}$	7
phurcalite	*Pbca*	17.42	16.04	13.60		3.8	(010)	[001]	uudduu$O$	$Ca_2[(UO_2)_3O_2(PO_4)_2](H_2O)_7$	8
phuralumite	$P\underline{2}_1/a$	13.84	20.92	9.43	112.4	7.0	(010)	$[1\underline{0}0]$	uudduu$O$	$Al_2[(UO_2)_3(OH)_2(PO_4)_2](OH)_4(H_2O)_{10}$	9
althupite*	$P\bar{1}$	10.95	18.57	13.50	68.2	8.2	(100)	$[0\bar{1}2]$	uudduu$O$	$AlTh(UO_2)[(UO_2)_3O(OH)(PO_4)_2]_2(OH)_3(H_2O)_{15}$	10
bergenite	$P2_1/c$	10.09	17.24	17.35	113.7	5.0	($\bar{1}02$)	[201]	uuduudSSO	$Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$	11

* althupite: α 72.6°, γ 84.2°. References: (1) Piret & Deliens (1982), (2) Piret & Piret-Meunier (1988), (3) Piret & Declercq (1983), (4) Demartin *et al.* (1991), (5) Piret & Piret-Meunier (1991), (6) Piret *et al.* (1988), (7) Piret *et al.* (1990), (8) Atencio *et al.* (1991), (9) Piret *et al.* (1979), (10) Piret & Deliens (1987), (11) this work. OS: orientation of sheet, CD: chain direction.

and can be transformed to the larger cell with the matrix [$10\bar{1}$/010/201]. The relationship between the two unit cells is shown in Figure 5, along with the corresponding changes in the optical orientation of bergenite.

The powder X-ray-diffraction pattern of bergenite was calculated using the program ATOMS version 5.1 (Dowty 2000) and the structural parameters were derived from the results of the single-crystal structure re-

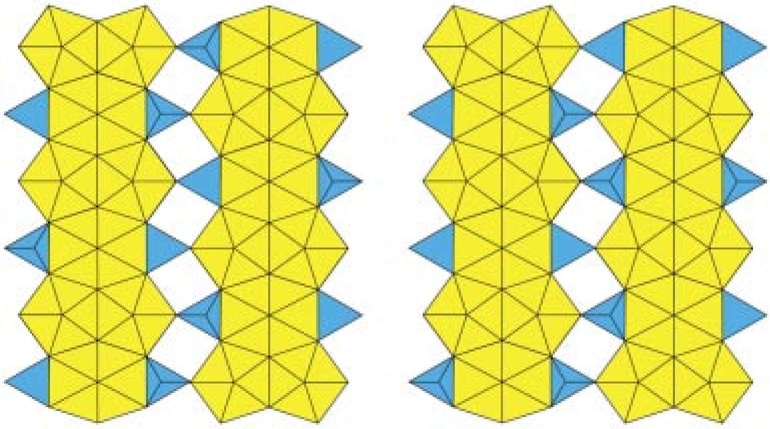


udududS

(a)

uudduuS

(b)



uudduuO

(c)

uuduudSSO

(d)

FIG. 4. Geometrical isomers of the uranyl phosphate sheet in members of the phosphuranylite group: (a) the vanmeersscheite-type sheet, in which tetrahedra between uranyl chains alternate orientations in an up-down up-down up-down (ududud) pattern, and each pair of tetrahedra attached to a given uranyl hexagonal bipyramid has the same (S) orientation; (b) the phosphuranylite-type sheet, in which tetrahedra change orientations in an up-up down-down up-up (uudduu) pattern, and the pair of tetrahedra attached to the same uranyl hexagonal bipyramid have the same (S) orientation; (c) the phurcalite-type sheet, in which tetrahedra change orientations in an up-up down-down up-up (uudduu) pattern, and the tetrahedra attached to the same uranyl hexagonal bipyramid have opposite (O) orientations; (d) the sheet that occurs in bergenite, in which tetrahedra change orientations in an up-up-down up-up-down (uuduud) pattern, and the pairs of tetrahedra attached to uranyl hexagonal bipyramids vary orientations in a complementary same-same-opposite (SSO) sequence.

finement (Table 7). The simulated pattern yielded *d* values whose positions are in agreement with the powder X-ray-diffraction data for bergenite of Piret & Deliens (1981) [PDF 43–0668] and Bültemann & Moh (1956) [PDF 20–0154], but differ in the low-angle reflections from the "barium-phosphuranylite" of Ross (1956).

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TABLE 7. COMPARISON OF POWDER X-RAY-DIFFRACTION DATA FOR BERGENITE AND "BARIUM-PHOSPHURANYLITE"

this work (calculated)			Piret & Deliens (1981)		Bültemann & Moh (1959)		Ross (1956)		
bergenite			bergenite		bergenite		"barium-phosphuranylite"		
d_{calc} (Å)	I/I_o	*h k l*	d_{obs} (Å)	I/I_o	d_{obs} (Å)	intensity	d_{obs} (Å)	I/I_o	remarks
11.687	7	$01\bar{1}$							
8.622	**34**	**020**							
8.588	11	$11\bar{1}$	**8.54**	**40**					
7.760	**100**	**$10\bar{2}$**	**7.73**	**100**	**7.79**	**strong**	8.0	50	broad
							6.9*	30	broad
6.389	14	111	6.31	10	6.41	weak	6.46	20	
5.768	19	$12\bar{2}$	5.74	20	5.80	weak			
5.400	6	$11\bar{3}$	5.35	8	5.43	weak			
4.411	**23**	**131**	4.38	20	4.41	weak	4.412	40	doublet
4.343	9	$21\bar{3}$	4.31	15					
3.896	12	$03\bar{3}$							
3.880	**39**	**$20\bar{4}$**	**3.837**	**80**	**3.883**	**strong**	3.83	70	
3.777	16	$23\bar{1}$	**3.742**	**40**	3.762	weak			
3.769	6	$14\bar{2}$							
3.538	7	$22\bar{4}$							
3.440	**27**	**202**	**3.415**	**40**	**3.437**	**middle**	3.47	50	
3.364	1	$30\bar{2}$			3.361	weak			
3.223	3	$31\bar{1}$	**3.220**	**40**					
3.212	**23**	**104**	**3.184**	**40**	**3.203**	**middle**	3.18	40	doublet
3.083	**39**	**151**	**3.054**	**60**	**3.076**	**strong**	3.08	100	
3.081	**20**	**300**							
2.967	7	$13\bar{5}$	2.940	5					
2.891	**32**	**$05\bar{3}$**	**2.874**	**50**	**2.882***	**mid-strong**	2.88	70	
2.841	**29**	**$25\bar{1}$**							
2.821	6	$31\bar{5}$	**2.826**	**50**					
2.695	2	$16\bar{2}$	2.680	3					
2.649	5	$00\bar{6}$	2.632	5					
2.444	5	$15\bar{5}$	2.422	5	2.436	weak			
2.385	4	$35\bar{3}$	2.368	5	2.384	weak			
2.292	1	$42\bar{5}$	2.285	5	2.307	very weak			
2.185	2	$36\bar{2}$	2.179	3					
2.130	4	333	2.139	5	2.149	very weak	2.13	5	
2.126	3	$10\bar{8}$	2.116	3					
2.082	6	235	2.064	25	**2.074**	**middle**			
2.014	3	$50\bar{4}$	2.014	10	2.021	weak			
1.991	1	$44\bar{6}$	1.991	10	1.999	very weak			
1.940	2	$40\bar{8}$	1.943	3					
1.930	1	$35\bar{7}$	1.928	5					
1.910	14	353	1.898	20	**1.904**	**middle**			
1.884	3	$28\bar{4}$			1.883	weak			
1.875	6	255	1.874	25	1.872	weak			
1.824	1	$54\bar{4}$	1.817	15	1.823	weak			
1.790	3	184	1.788	8					
1.746	5	157	1.736	10	1.742	weak			
1.720	2	404	1.711	5	1.721	weak			
1.682	4	$55\bar{1}$	1.672	10	1.677	weak			
1.659	3	502	1.646	8	1.653	very weak			

* corrected from the original reference.

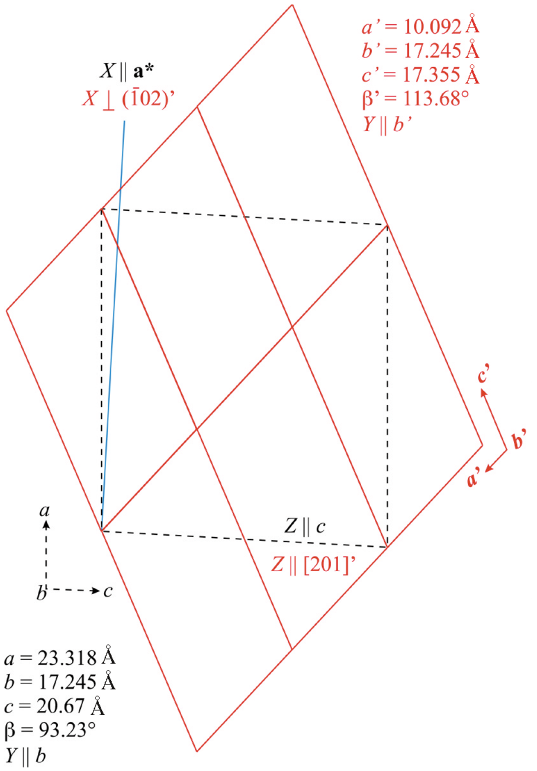

FIG. 5. Projection along [010] of the relationship between the large unit-cell of Piret & Deliens (1981), *a b c* β (shown in black stipple), and the smaller unit cell, *a' b' c'* β' (shown in red and denoted by ') presented in this work. The *X* direction is shown in blue. The optical orientation for the previous large cell is: *Z* parallel to *c*, *Y* parallel to *b*, and *X* parallel to **a***. The optical orientation for the new small cell is: *Z* parallel to [201]', *Y* parallel to *b'*, and *X* perpendicular to $(\bar{1}02)'$.

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