

longer than the expected 2.236 Å calculated assuming 2.50 Å Na—O distances and ideal geometry. This longer Na—Na distance in tincalconite is believed to be due to the disordered and partially occupied nature of the Ow(2) site. The disorder requires a greater volume of space between the sodiums, and the incomplete occupancy provides less shielding between the repulsive sodium cations.

Sodium sites Na(1) and Na(2) have nearly regular octahedral environments. Na(1) sits on a twofold rotation axis and is coordinated to two adjacent OH(5) hydroxyl groups at a distance of 2.440 (3) Å, to two adjacent OH(4) hydroxyl groups at 2.493 (2) Å, and to two opposite Ow(1) waters at 2.436 (2) Å. Na(2) lies on the intersection of a threefold and three twofold axes and is coordinated to six separate tetraborate anions through OH(4) hydroxyl groups, 2.434 (2) Å. The edge of the Na(1) octahedron formed by OH(4) hydroxyl groups is shared with an Na(2) octahedron, giving an Na(1)⋯Na(2) distance of 3.663 (1) Å.

The tetraborate anion B₄O₅(OH)₄²⁻ consists of two BO₃(OH) tetrahedra and two BO₂(OH) triangles sharing corner oxygens. As with similar tetraborate anions (Levy & Lisensky, 1978; Wan & Ghose, 1977) the trigonal boron of tincalconite has markedly shorter B—O distances [average 1.367 (5) Å] than the tetrahedral boron [average 1.476 (4) Å]. In tincalconite as well as the other tetraborate structures mentioned the hydroxyl oxygens bonded to the trigonal borons have considerable anisotropic motion normal to the BO₃ planes. The B(2)—OH(5) bond distance corrected assuming a 2:1 riding model (Johnson, 1970) is 1.373 (5) Å.

Hydroxyl and water hydrogens are coordinated to borate-ring oxygens through hydrogen bonds (Table 3). E.s.d.'s for the distances and angles involving the

Table 3. *Hydrogen-bond contacts* (Å,^o)

O—H⋯O	O—H	H⋯O	O⋯O	O—H⋯O
OH(4)—H(4)⋯O(3 ⁱ)	0.79 (4)	2.06 (5)	2.831 (4)	169 (4)
OH(5)—H(5)⋯O(1 ⁱⁱ)	0.86 (6)	1.83 (6)	2.661 (4)	162 (4)
Ow(1)—Hw(1A)⋯O(2 ⁱⁱⁱ)	1.16 (4)	1.62 (5)	2.753 (4)	164 (4)
Ow(1)—Hw(1B)⋯O(2 ^{iv})	0.90 (5)	1.99 (5)	2.860 (4)	161 (4)
Ow(2)—Hw(2A)⋯Ow(1 ^v)	1.18	2.09	3.063 (8)	137 (9)
Ow(2)—Hw(2B)⋯OH(5 ^{vi})	1.01	2.28	2.937 (8)	122 (9)

Symmetry operations: (i) $\frac{2}{3} - x, \frac{4}{3} - x + y, \frac{4}{3} - z$; (ii) $1 - x + y, 1 - x, z$; (iii) $\frac{1}{3} - y, x - y - \frac{1}{3}, z - \frac{1}{3}$; (iv) $x - y - \frac{1}{3}, \frac{2}{3} - y, \frac{2}{3} - z$; (v) $-x, y - x, -z$; (vi) $\frac{4}{3} - x, \frac{2}{3} - x + y, \frac{2}{3} - z$.

hydrogens on Ow(2) are not included because these hydrogens were not refined. No other close contacts in the crystal structure are observed.

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References

- GIACOVAZZO, C., MENCHETTI, S. & SCORDARI, F. (1973). *Am. Mineral.* **58**, 523–530.
- JOHNSON, C. K. (1970). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 220–226. Copenhagen: Munksgaard.
- LARSEN, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 291–294. Copenhagen: Munksgaard.
- LEVY, H. A. & LISENSKY, G. C. (1978). *Acta Cryst.* **B34**, 3502–3510.
- MEITES, L. (1963). Editor. *Handbook of Analytical Chemistry*, 1st ed. New York: McGraw-Hill.
- MELLOR, J. W. (1980). *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, Part A, pp. 368–369. New York: Longman.
- SHELDRIK, G. M. (1990). *SHELXTL-Plus*. Version 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
- WAN, C. N. & GHOSE, S. (1977). *Am. Mineral.* **62**, 1135–1143.

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Redetermination of the Structure of Hexaaquaaluminium(III) Nitrate Trihydrate

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Abstract. [Al(H₂O)₆](NO₃)₃.3H₂O, *M*_r = 375.13, monoclinic, *P*2₁/*c*, *a* = 13.892 (2), *b* = 9.607 (1), *c* = 10.907 (2) Å, β = 95.51 (2)°, *V* = 1448.9 Å³, *Z* = 4,

*D*_x = 1.719 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 2.3 cm⁻¹, *F*(000) = 784, *T* = 293 K, final *R* = 0.041 for 2137 reflections with *I* > 3σ(*I*). The structure

Table 1. *Crystal data for the Al, Cr and Fe nitrate nonahydrates*

	Al(NO ₃) ₃ ·9H ₂ O ⁱ	Cr(NO ₃) ₃ ·9H ₂ O ⁱⁱ	Cr(NO ₃) ₃ ·9H ₂ O ⁱⁱⁱ	Al(NO ₃) ₃ ·9H ₂ O ^{iv}	Fe(NO ₃) ₃ ·9H ₂ O ^v
<i>a</i> (Å)	13·901 (15)	13·915 (15)	13·967 (1)	10·86	13·989 (1)
<i>b</i> (Å)	9·636 (15)	9·681 (15)	9·6528 (9)	9·59	9·701 (1)
<i>c</i> (Å)	10·903 (15)	10·981 (15)	10·981 (1)	13·83	11·029 (1)
β	84 48'	84 16'	95·41 (1)	96·10	95·52 (1)
<i>Z</i>	4	4	4	4	4
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>

References: (i) Kannan & Viswamitra (1965); (ii) Lazar *et al.* (1991); (iii) Herpin & Sudarsanan (1965); (iv) Hair & Beattie (1977).

differs from that previously reported [Herpin & Sudarsanan (1965). *Bull. Soc. Fr. Minéral. Cristallogr.* **88**, 595–601]. The unit cell comprises two crystallographically distinct Al(H₂O)₆³⁺ octahedra, with crystallographic $\bar{1}$ symmetry, connected by three-dimensional hydrogen bonding involving nitrate anions and water molecules.

Introduction. Groth (1906) found that the title compound is dimorphic, occurring as a monoclinic and an orthorhombic structure. To the best of our knowledge there are no other data for the orthorhombic form. The monoclinic form, together with that of Cr(NO₃)₃·9H₂O, was studied earlier by Kannan & Viswamitra (1965) by rotation and Weissenberg photographs (see Table 1). Similarities in the unit-cell dimensions of the Al and Cr nitrate nonahydrates and the existence of mixed crystals led these authors to conclude that the compounds are isomorphous.

Herpin & Sudarsanan (1965) carried out the crystal structure analysis of Al(NO₃)₃·9H₂O and found the heavy atom in a general position (0·2499, -0·0009, 0·2480) in contrast to Cr(NO₃)₃·9H₂O (Lazar, Ribár, Divjaković & Mészáros, 1991), where the heavy atoms occupy two independent sets of special positions in *P*2₁/*c*: [(*a*) 0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$ and (*d*) $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0], so that the isomorphism of the Al and Cr nitrate nonahydrates was questioned. However, the extremely high *R* value (0·23) reported by Herpin & Sudarsanan (1965) prompted a new structural analysis of the title compound.

Experimental. Single crystals of Merck's compound are white, transparent and highly hygroscopic. One of size 0·45 × 0·22 × 0·25 mm was sealed in a Lindemann-glass capillary for data collection. Approximate cell parameters were determined from oscillation and Weissenberg photographs. Accurate unit-cell parameters were obtained by least-squares refinement from 20 reflections measured on a diffractometer in the range 6 < 2θ < 17°. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo *K*α radiation. 3143 reflections were collected in the ω/2θ scan mode up to 2θ = 52°; *h* ≤ 17, *k* ≤ 11, -13 ≤ *l* ≤ 13; data corrected for Lorentz and polarization

effects, but not for absorption. The intensities of two standard reflections (642̄, 337̄) diminished by 23% during five days of data collection. A correction was made (Frenz, 1983). 2472 unique reflections, 2137 with *I* > 3σ(*I*) accepted for structure solution and refinement.

Reflections with either (*h* + *k*) or (*k* + *l*) or (*h* + *l*) even were on average stronger than those with *odd* values for these combinations. The pseudo-face-centered lattice, thus implied, was possible if the Al³⁺ ions occupied two independent sets of special positions in *P*2₁/*c*, like the Cr³⁺ ions in Cr(NO₃)₃·9H₂O (Lazar *et al.*, 1991).

The structure was solved assuming the isomorphism with Cr(NO₃)₃·9H₂O and refined by full-matrix least squares minimizing $\sum w(\Delta F)^2$ with *SHELX76* (Sheldrick, 1976), $w = 1·4843/[\sigma^2(F_o) + 0·000712 F_o^2]$. Positional atomic parameters were refined for all atoms; non-H atoms were refined with anisotropic displacement parameters and H atoms isotropically. *R* = 0·041, *wR* = 0·044, Δ/σ = 0·03, 0·37 > Δρ > -0·29 e Å⁻³. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final non-H atomic parameters with e.s.d.'s are listed in Table 2.*

Geometrical parameters were computed with the *CSU* program (Vicković, 1988). All calculations, including the structure analysis, were performed on a PC-AT computer.

Discussion. Selected interatomic distances and angles are listed in Table 3. The compound is isostructural with [Fe(H₂O)₆](NO₃)₃·3H₂O (Hair & Beattie, 1977) and [Cr(H₂O)₆](NO₃)₃·3H₂O (Lazar *et al.*, 1991). The volume of the unit cell is approximately 2% smaller than that of the Cr analog and 3% smaller than that of the Fe analog, reflecting the smaller ion radius of the Al atom.

The structure contains two crystallographically distinct Al(H₂O)₆³⁺ octahedra each possessing almost regular octahedral geometry. Fig. 1 shows the asym-

* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54270 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) for the non-H atoms

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Al1	0	0	0	170 (4)
Al2	$\frac{1}{2}$	0	$\frac{1}{2}$	192 (4)
N1	7150 (2)	-7130 (2)	2800 (2)	259 (4)
N2	7984 (2)	-3114 (2)	2076 (2)	238 (4)
N3	3064 (2)	-5094 (2)	3729 (2)	26 (4)
O11	7425 (1)	-6597 (2)	1855 (2)	382 (6)
O12	6278 (1)	-7381 (2)	2862 (2)	425 (6)
O13	7754 (1)	-7424 (2)	3696 (2)	328 (4)
O21	7449 (1)	-3136 (2)	1059 (2)	299 (4)
O22	8860 (1)	-2858 (2)	2059 (2)	344 (5)
O23	7627 (1)	-3346 (2)	3048 (2)	352 (5)
O31	2317 (1)	-4961 (2)	3003 (2)	362 (4)
O32	3023 (2)	-4863 (3)	4835 (2)	484 (6)
O33	3846 (1)	-5474 (2)	3354 (2)	381 (4)
Ow1	335 (2)	-1215 (2)	3697 (2)	290 (4)
Ow2	5489 (2)	-3857 (3)	3693 (2)	322 (4)
Ow3	8564 (2)	-254 (3)	4506 (2)	363 (6)
Ow11	-930 (1)	-1423 (2)	-48 (2)	225 (4)
Ow12	-715 (1)	1045 (2)	1054 (2)	240 (4)
Ow13	630 (1)	-851 (2)	1370 (2)	241 (4)
Ow21	5669 (2)	-1103 (3)	3922 (2)	283 (4)
Ow22	4031 (1)	-1369 (2)	4994 (2)	291 (4)
Ow23	4309 (1)	911 (2)	3689 (2)	268 (5)

Table 3. Selected bond lengths (\AA) and angles ($^\circ$)

Octahedron 1			
Al1—Ow11	1.878 (2)	Ow11—Al1—Ow12	90.2 (1)
Al1—Ow12	1.880 (2)	Ow11—Al1—Ow13	89.6 (1)
Al1—Ow13	1.870 (2)	Ow12—Al1—Ow13	89.8 (1)
Octahedron 2			
Al2—Ow21	1.892 (3)	Ow21—Al2—Ow22	90.0 (1)
Al2—Ow22	1.881 (2)	Ow21—Al2—Ow23	91.9 (1)
Al2—Ow23	1.862 (2)	Ow22—Al2—Ow23	90.5 (1)
Nitrate 1			
N1—O11	1.242 (3)	O11—N1—O12	120.3 (2)
N1—O12	1.244 (3)	O11—N1—O13	120.1 (2)
N1—O13	1.258 (3)	O12—N1—O13	119.6 (2)
Nitrate 2			
N2—O21	1.275 (3)	O21—N2—O22	118.7 (2)
N2—O22	1.243 (3)	O21—N2—O23	119.7 (2)
N2—O23	1.233 (3)	O22—N2—O23	121.6 (2)
Nitrate 3			
N3—O31	1.250 (3)	O31—N3—O32	119.2 (2)
N3—O32	1.233 (3)	O31—N3—O33	121.1 (2)
N3—O33	1.251 (3)	O32—N3—O33	119.7 (2)

metric unit and illustrates the overall similarities of the two independent octahedra. In fact, the asymmetric unit comprises two crystallographically independent half octahedra. The complete octahedra are generated by the $\bar{1}$ symmetry located at the central Al atoms. The independent $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ions are linked by hydrogen bonds to three nitrate groups and three water molecules. The hydrogen bonds involving interstitial water molecules are longer than those which involve coordinated water molecules (see Table 4). In the planar nitrate ions, each O atom acts as an acceptor for at least one hydrogen bond. Three O atoms (O21, O31 and O33) act as acceptor for one short hydrogen bond to a coordinated water mol-

Table 4. Bond distances (\AA) and angles ($^\circ$) pertinent to the H-bonded interactions $D\cdots H\cdots A$

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
Ow1—H11 \cdots Ow3 ⁱ	0.68	2.08	2.756	172
Ow1—H12 \cdots Ow3 ⁱⁱ	0.79	2.07	2.846	172
Ow2—H21 \cdots O33 ⁱⁱⁱ	0.74	2.06	2.756	158
Ow2—H22 \cdots O32 ^{iv}	0.72	2.07	2.780	176
Ow3—H31 \cdots O21 ^v	0.73	2.14	2.857	169
Ow3—H32 \cdots O31 ^{vi}	0.77	2.29	2.902	148
Ow11—H41 \cdots O22 ⁱⁱ	0.88	1.85	2.719	174
Ow11—H42 \cdots O23 ⁱⁱⁱ	0.80	1.96	2.753	173
Ow12—H51 \cdots Ow1 ^{viii}	0.81	1.89	2.693	174
Ow12—H52 \cdots O31 ^{viii}	0.84	1.89	2.717	170
Ow13—H61 \cdots O13 ^{vi}	0.76	1.92	2.667	167
Ow13—H62 \cdots Ow1 ^{viii}	0.85	1.84	2.648	159
Ow21—H71 \cdots Ow2 ⁱⁱⁱ	0.81	1.86	2.667	172
Ow21—H72 \cdots O33 ^{vi}	0.84	1.89	2.702	164
Ow22—H81 \cdots O11 ^{vi}	0.79	1.94	2.725	171
Ow22—H82 \cdots O12 ^{iv}	0.84	1.87	2.700	170
Ow23—H91 \cdots Ow2 ^{vi}	0.77	1.88	2.648	174
Ow23—H92 \cdots O21 ^{vi}	0.83	1.88	2.647	172

Average e.s.d.'s in the tabulated values: $D\cdots H$: 0.04; $H\cdots A$: 0.04; $D\cdots A$: 0.003 \AA ; $D\cdots H\cdots A$: 4° . Mean O—H: 0.791 (52) \AA .

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-1+x, y, z$; (iii) x, y, z ; (iv) $1-x, -1-y, 1-z$; (v) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (vi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $-1+x, -\frac{1}{2}-y, \frac{1}{2}+z$; (viii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

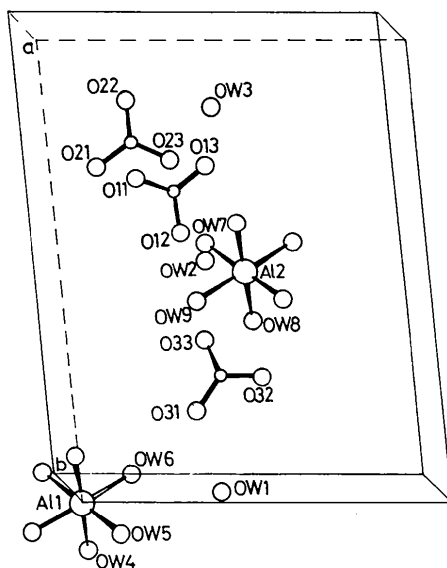


Fig. 1. Perspective view of the asymmetric unit and the atomic numbering scheme.

ecule and also for one longer bond to a lattice water molecule (Table 4). Within nitrate 2 the N2—O21 bond is significantly lengthened.

References

- FRENZ, B. A. (1983). *Enraf-Nonius Structure Determination Package; SDP Users Guide*. Version of 6 January 1983. Enraf-Nonius, Delft, The Netherlands.
- GROTH, P. (1906). *Chemische Kristallographie*, Vol. II, p. 133. Leipzig: Englemann.
- HAIR, N. J. & BEATTIE, J. K. (1977). *Inorg. Chem.* **16**, 245–250.
- HERPIN, P. & SUDARSANAN, K. (1965). *Bull. Soc. Fr. Minéral. Cristallogr.* **88**, 595–601.

KANNAN, K. K. & VISWAMITRA, M. A. (1965). *Acta Cryst.* **19**, 151–152.
 LAZAR, D., RIBÁR, B., DIVJAKOVIĆ & MÉSZÁROS, CS. (1991). *Acta Cryst.* **C47**, 1060–1062.

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 VICKOVIĆ, I. (1988). *CSU*. Faculty of Sciences, Univ. of Zagreb, Yugoslavia.

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Structure of Low-Ba₃P₄O₁₃

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Abstract. Ba₃P₄O₁₃, $M_r = 743.88$, triclinic, $P\bar{1}$, $a = 5.691$ (5), $b = 7.238$ (7), $c = 8.006$ (5) Å, $\alpha = 83.65$ (5), $\beta = 75.95$ (8), $\gamma = 70.49$ (7)°, $V = 301.4$ Å³, $Z = 1$, $D_x = 4.10$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 10.29$ mm⁻¹, $F(000) = 332$, $T = 293$ K, final $R = 0.039$ for 1222 counter-measured reflections. The structure comprises Ba²⁺ ions and non-centrosymmetric [P₄O₁₃]⁶⁻ polyanions consisting of four corner-shared phosphorus–oxygen tetrahedra with a P—P—P torsion angle of 180°. The mean P—O and Ba—O distances are 1.53 and 2.77 Å respectively.

Introduction. The structures of a number of compounds in the BaO–P₂O₅ system have been reported; however, only the unit-cell dimensions of the low- and high-temperature forms of Ba₃P₄O₁₃ were first given by Millet, Parker & Roth (1986). The structure of the low-temperature form (low-) of Ba₃P₄O₁₃ is reported here.

Experimental. A colourless crystal fragment with approximate faces $\bar{1}\bar{1}\bar{1}$, 111, 0 $\bar{1}$ 0, 010, 10 $\bar{2}$, and 1 $\bar{1}$ 3 and dimensions 0.035 × 0.035 × 0.065 mm, was selected from a preparation described elsewhere (Millet, Parker & Roth, 1986) and mounted on a silica capillary using 'Tyton 5 Minit' adhesive. Crystal data obtained using a Philips PW 1100 computer-controlled four-circle diffractometer equipped with a graphite monochromator. Cell parameters obtained as the means of 10 measurements made on the positions of 24 reflections $13 < 2\theta < 38^\circ$ as orientation checks during data collection. Data collected

out to $2\theta(\text{Mo } K\alpha) = 60^\circ$ using the ω -scan technique with a symmetric scan range of $\pm(0.65 + 0.3\tan\theta)^\circ$ in ω from the calculated Bragg angle, at a scan rate of $0.04^\circ \text{ s}^{-1}$. No reflection was sufficiently intense to require the insertion of an attenuation filter. 1751 unique reflections measured to $2\theta = 60^\circ$, 1222 unique reflections [$I > 3\sigma(I)$] used in analysis, $R_{\text{int}} = 0.042$; index range $h = 11/11$, $k = 10/7$, $l = 0/10$. Three standard reflections measured at 3 h intervals; no decomposition occurred. Data processed using the program written specifically for the Philips PW 1100 diffractometer (Hornstra & Stubbe, 1972). Absorption correction applied, max. and min. transmission factors 0.7727 and 0.6861, respectively. No extinction correction necessary. The Ba atom located by inspection on the origin, remaining atoms located in subsequent difference Fourier syntheses. Function minimized in full-matrix least-squares refinement on F , $\sum w(|F_o| - |F_c|)^2$, where w is the weight $[\sigma^2(F_o)]^{-1}$. During refinement O(7), on a centre of symmetry showed peaks in the difference synthesis consistent with disorder in such a way that the P—O—P angle about it departed from 180°. In addition O(5) and O(6) showed signs of disorder in the difference synthesis consistent with the O(7) disorder, indicating a small rotational disorder of the P(1) tetrahedron about the O(3)—P(1) bond. Each of the O(5) and O(6) atoms has been refined as two atoms with 50% occupancies and O(7) has been moved off the centre of symmetry. Ba and P atoms refined anisotropically, other atoms refined isotropically; 60 variable parameters, final $R = 0.039$ and $wR = 0.042$ (for observed reflections); max. Δ/σ in final cycle 0.005. Final difference synthesis had $\Delta\rho$ within 1.3 and $-1.3 \text{ e } \text{Å}^{-3}$, in vicinity of P(1) and O(6'). Scattering

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