Hill, R. J. & Jones, J. B. (1976). *Am. Miner.* **61**, 987–995.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kumbasar, I. & Finney, J. J. (1968). *Miner. Mag. J. Miner. Soc.* **36**, 621–624.
Mori, H. & Ito, T. (1950). *Acta Cryst.* **3**, 1–6.
Riffel, H., Keller, P. & Hess, H. (1980). *Tschermaks Miner. Petrogr. Mitt.* **27**, 187–199.
Riou, A., Cudennec, Y. & Gerault, Y. (1986). *Rev. Chim. Miner.* **23**, 810–818.
Riou, A., Cudennec, Y. & Gerault, Y. (1989). *Acta Cryst.* **45**, 1412–1413.
Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS User Guide*. University of Göttingen, Germany.
Siemens (1995). *SMART and SAINT Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stephens, J. S. & Calvo, C. (1967). *Can. J. Chem.* **45**, 2303–2312.
Takagi, S., Mathew, M. & Brown, W. E. (1986). *Am. Miner.* **71**, 1229–1233.

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Mercury(II) Diphosphate, $Hg_2P_2O_7$

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Abstract

Mercury(II) diphosphate, $Hg_2P_2O_7$, belongs to the $M_2X_2O_7$ family of compounds with dichromate-type crystal structures and is isotypic with $Cd_2P_2O_7$. The structure consists of alternating layers built from P_2O_7 groups and highly distorted HgO_6 polyhedra with bond distances in the ranges $2.120\,(6) \leq d(\mathrm{Hg1O_6}) \leq 2.793\,(7)$ Å and $2.208\,(6) \leq d(\mathrm{Hg2O_6}) \leq 2.509\,(6)$ Å. The diphosphate anion has a P—O—P bridging angle of 133.4 (4)°. The average P—O bond length is 1.604 Å for bridging and 1.524 Å for terminal bonds. $[\mathrm{Hg1_2O_{10}}]$ and $[\mathrm{Hg2_2O_{10}}]$ form chains running along [110] through edge-sharing dimers. These chains link to form layers parallel to $(\bar{1}10)$ *via* common vertices.

Comment

Until now, in the system Hg–P–O only the structure of the mercury(II) orthophosphate, $Hg_3(PO_4)_2$, has been refined from single-crystal data (Aurivillius & Nilsson, 1975). For $Hg(PO_3)_2$, isotypism with the corresponding cadmium phosphate was proved (Beucher & Tordjman, 1968) by comparison of the X-ray powder diffraction patterns. Although the diphosphate $Hg_2P_2O_7$ has been known for a long time (Schwarzenberg, 1848), no crystallographic information for it has been published so far. Preliminary investigation of the X-ray powder pattern of $Hg_2P_2O_7$ showed it to be isotypic with $Cd_2P_2O_7$ (Weil, 1997), the structure of which has been refined previously (Calvo & Au, 1969). During our studies on the thermal behaviour of mercury(II) phosphates, we obtained crystals of $Hg_2P_2O_7$ suitable for X-ray investigations. Because of the particular crystal chemistry of Hg^{2+} with its d^{10} electronic configuration, refinement of the structure seemed appropriate. Additional interest in a detailed structural study arises from the relationship of dichromate-type $Hg_2P_2O_7$ (Brown & Calvo, 1970; Clark & Morley, 1976; Nord & Kierkegaard, 1980) with diphosphates of divalent 3*d* metals with thortveitite-type structures.

The crystal structure comprises alternating layers of HgO_6 polyhedra and diphosphate groups parallel to $(\bar{1}10)$ (Fig. 1). The two independent Hg^{2+} ions form dimers, $[\mathrm{Hg1_2O_{10}}]$ and $[\mathrm{Hg2_2O_{10}}]$, by edge sharing. The common edge is O4—O4 in the case of Hg1, and O2—O2 for Hg2 (Fig. 2). The dimers are linked *via* common edges (O2 and O3) and vertices (O5) thus forming the layers. In contrast to the thortveitite-type structures, where adjacent metal–oxygen layers (*e.g.* $Mn_2P_2O_7$; Stefanidis & Nord, 1984) are joined only by diphosphate groups, additional contacts from one [Hg—O] layer to another *via* common vertices (O6) occur in $Hg_2P_2O_7$ (Fig. 1).

The diphosphate anion (Fig. 3) displays an eclipsed conformation with a dihedral angle of 7.2° along O4, P2, O1, P1 and O3. The P—O—P bridging angle is 133.4 (4)°. Both values agree with those generally observed for $[X_2O_7]$ anions in dichromate-type structures, where the eclipsed conformation is stabilized by chelate-type coordination to the two divalent cations. Bond lengths from the P atoms to the terminal and bridging O atoms are in the typical range observed for diphosphates of divalent cations [d_b(P—O) = 1.596 (6) and 1.611 (6) Å, $\bar{d}_t$(P1—O) = 1.528 Å and $\bar{d}_t$(P2—O) = 1.519 Å].

Hg1 and Hg2 are coordinated by six O atoms (Fig. 2), with the nearest 'non-bonding' O atom 3.177 Å from Hg1 and 3.280 Å from Hg2. The $[\mathrm{Hg1O_6}]$ group can be described as a highly compressed octahedron (2 + 4 coordination) with two short axial bonds, $\bar{d}_{\mathrm{ax}}$ = 2.132 Å, and four longer equatorial bonds, $\bar{d}_{\mathrm{eq}}$ = 2.583 Å. The coordination around Hg2 may be described as (4 + 2) with $\bar{d}_{\mathrm{eq}}$ = 2.28 Å and $\bar{d}_{\mathrm{ax}}$ = 2.49 Å. The $[\mathrm{Hg2O_6}]$ octahedron is less distorted than the $[\mathrm{Hg1O_6}]$ octahedron. The Hg—O bond lengths found in $Hg_2P_2O_7$ are in the same range as those found in $Hg_3(PO_4)_2$ (Aurivillius & Nilsson, 1975) and $HgSO_4$ (Aurivillius & Stålhandske, 1980). The $[\mathrm{HgO}_x]$ polyhedra in mercury(II) orthophosphate have Hg—O distances from 2.06 to 2.80 Å (five- and

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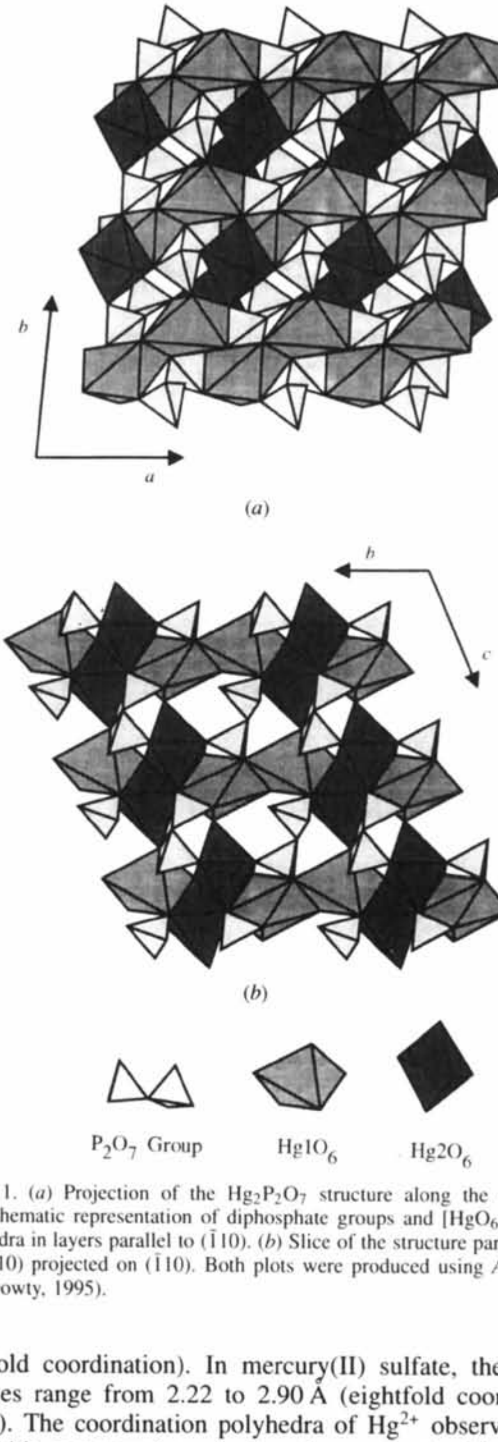

Fig. 1. (*a*) Projection of the $Hg_2P_2O_7$ structure along the *c* axis. Schematic representation of diphosphate groups and $[HgO_6]$ polyhedra in layers parallel to $(\bar{1}10)$. (*b*) Slice of the structure parallel to $(\bar{1}10)$ projected on $(\bar{1}10)$. Both plots were produced using *ATOMS* (Dowty, 1995).

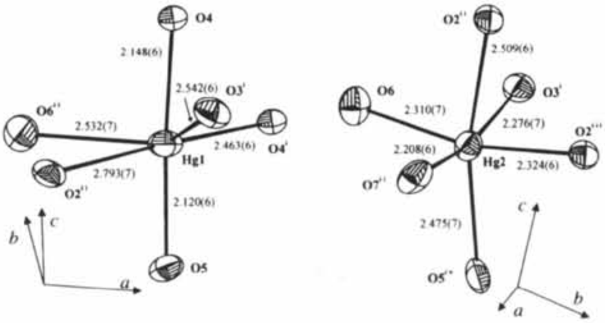

Fig. 2. *ORTEP*II (Johnson, 1976) plot of $Hg1O_6$ and $Hg2O_6$. Displacement ellipsoids are drawn at the 85% probability level; distances are in Å. Symmetry codes are as given in Table 1.

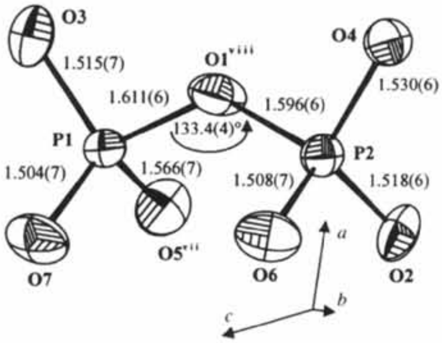

Fig. 3. *ORTEP*II (Johnson, 1976) plot of the diphosphate group. Displacement ellipsoids are drawn at the 85% probability level; distances are in Å. Symmetry codes are as given in Table 1.

sixfold coordination). In mercury(II) sulfate, the distances range from 2.22 to 2.90 Å (eightfold coordination). The coordination polyhedra of Hg^{2+} observed in the title compound are in broad agreement with other $[HgO_x]$ complexes reviewed by Wessels (1996). Bond length–bond strength considerations (Brese & O'Keeffe, 1991) led to a coordination number (CN) of 6 for both Hg^{2+} ions. Taking all six Hg—O contacts with $d(Hg—O) < 3.00$ Å into account gives valence sums of 1.88 and 2.01 for Hg1 and Hg2, respectively. Calculations of the effective coordination number ECN, following a concept described by Hoppe (1979), led to ECN(Hg1) = 4.03 and ECN(Hg2) = 5.60, thus showing an even larger difference in the bonding situation for the two independent Hg^{2+} ions. The Madelung part of the lattice energy (MAPLE) (Hoppe, 1995) calculated with the actual structural data for $Hg_2P_2O_7$ differs by only 0.4% from the sum of the MAPLE values of the binary oxides HgO (Wyckoff, 1965) and P_4O_{10} [MAPLE($Hg_2P_2O_7$) = 12 531 kcal mol^{-1}; 1 kcal = 4.184 kJ]. MAPLE(P_4O_{10}) was calculated as the difference 2 × MAPLE($Na_4P_2O_7$) − 4 × MAPLE(Na_2O). Crystallographic data for $Na_4P_2O_7$ and Na_2O were taken from the literature (Leung & Calvo, 1972; Wyckoff, 1965).

The coordination numbers of the O atoms range from 2 to 4. The P—O—P bridging atom O1 has no additional coordination partner, differing from other dichromate-type structures with X^{n+} cations of lower charge (Clark & Morley, 1976). For the terminal O atom, O7, twofold coordination is also observed, with relatively short Hg—O and P—O distances. Atoms O3, O4, O5 and O6 are three-coordinate, showing comparatively short bond distances to one Hg atom and longer distances to the other, as well as a P—O bond. Only O2 shows fourfold coordination (1 P + 3 Hg) with a longer Hg1—O2 bond of 2.793 (7) Å.

Experimental

A powder of $Hg_2P_2O_7$ was prepared by heating a solution of HgO (Merck, *p.a.*) in half-concentrated nitric acid with a small excess (*ca* 5%) of phosphoric acid (Merck, 85% pure). To remove water and remaining nitrogen oxides the residue was subsequently heated in a silica crucible in air to 693 K (4 d). The product was white and microcrystalline. Similar experiments using $(NH_4)_2HPO_4$ instead of phosphoric acid, following the procedure given in the literature for $Cd_2P_2O_7$ (Calvo & Au, 1969), led to yellowish powders presumably still containing small amounts of nitrogen. Single crystals suitable for X-ray investigations could be obtained by chemical vapour transport reactions in evacuated silica ampoules (*e.g.* 177 mg $Hg_2P_2O_7$, temperature gradient 823–773 K, 19 d), adding 14 mg PCl_5 per ampoule as a transport agent. The experiments led to the deposition of colourless plate-like crystals with an edge-length up to 2 mm in the cooler zone of the ampoule.

From temperature-dependent X-ray powder photographs, the melting point of the diphosphate was determined to be 933 (10) K, which is in agreement with the value given in the literature (Gmelin, 1969). These investigations also revealed two phase transitions, at 482 (10) and 843 (10) K, which are accompanied by only slight changes in the diffraction pattern. The lattice constants for $Hg_2P_2O_7$ given below were derived from Guinier photographs using the program *SOS* (Soose, 1980).

Crystal data

$Hg_2P_2O_7$
$M_r = 575.12$
Triclinic
$P\bar{1}$
$a = 6.706$ (1) Å
$b = 6.806$ (1) Å
$c = 6.997$ (1) Å
$\alpha = 100.73$ (2)°
$\beta = 113.33$ (2)°
$\gamma = 80.53$ (2)°
$V = 286.65$ (7) Å^3
$Z = 2$
$D_x = 6.668$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections from a Guinier photograph
$\theta = 6.94$–21.42°
$\mu = 54.036$ mm^{-1}
$T = 293$ (2) K
Irregular
0.1 × 0.1 × 0.1 mm
Colourless

Data collection

Siemens AED-2 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993)
$T_{\min} = 0.045$, $T_{\max} = 0.092$
3372 measured reflections
1686 independent reflections

1411 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0492$
$\theta_{\max} = 30.02°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on . ^{2}
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 1.091$

$\Delta\rho_{\max} = 2.41$ e Å^{-3}
$\Delta\rho_{\min} = -2.36$ e Å^{-3}
Extinction correction: *SHELXL*93

1685 reflections
101 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

Extinction coefficient: 0.0369 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Hg1—O5	2.120 (6)	Hg2—O5$^{\rm iv}$	2.475 (7)
Hg1—O4	2.148 (6)	Hg2—O2$^{\rm ii}$	2.509 (6)
Hg1—O4$^{\rm i}$	2.463 (6)	Hg2—O1$^{\rm v}$	3.280 (6)
Hg1—O6$^{\rm ii}$	2.532 (7)	Hg2—P1$^{\rm i}$	3.388 (2)
Hg1—O3$^{\rm i}$	2.542 (6)	Hg2—Hg2$^{\rm vi}$	3.7431 (12)
Hg1—O2$^{\rm ii}$	2.793 (7)	P1—O7	1.504 (7)
Hg1—P1$^{\rm iii}$	3.159 (2)	P1—O3	1.515 (7)
Hg1—O7	3.177 (7)	P1—O5$^{\rm vii}$	1.566 (7)
Hg1—Hg1$^{\rm i}$	3.5975 (11)	P1—O1$^{\rm viii}$	1.611 (6)
Hg1—Hg2	3.7979 (7)	P1—P2$^{\rm viii}$	2.945 (3)
Hg2—O7$^{\rm ii}$	2.208 (6)	P2—O6	1.508 (7)
Hg2—O3$^{\rm i}$	2.276 (7)	P2—O2	1.518 (6)
Hg2—O6	2.310 (7)	P2—O4	1.530 (6)
Hg2—O2$^{\rm iii}$	2.324 (6)	P2—O1	1.596 (6)
O5—Hg1—O4	176.1 (2)	O3$^{\rm i}$—Hg2—O5$^{\rm iv}$	102.2 (2)
O5—Hg1—O4$^{\rm i}$	99.4 (2)	O6—Hg2—O5$^{\rm iv}$	108.0 (2)
O4—Hg1—O4$^{\rm i}$	77.6 (2)	O2$^{\rm iii}$—Hg2—O5$^{\rm iv}$	87.5 (2)
O5—Hg1—O6$^{\rm ii}$	95.0 (2)	O7$^{\rm ii}$—Hg2—O2$^{\rm ii}$	89.8 (2)
O4—Hg1—O6$^{\rm ii}$	88.8 (2)	O3$^{\rm i}$—Hg2—O2$^{\rm ii}$	78.4 (2)
O4$^{\rm i}$—Hg1—O6$^{\rm ii}$	127.3 (2)	O6—Hg2—O2$^{\rm ii}$	85.8 (2)
O5—Hg1—O3$^{\rm i}$	99.6 (2)	O2$^{\rm iii}$—Hg2—O2$^{\rm ii}$	78.6 (2)
O4—Hg1—O3$^{\rm i}$	79.2 (2)	O5$^{\rm iv}$—Hg2—O2$^{\rm ii}$	166.0 (2)
O4$^{\rm i}$—Hg1—O3$^{\rm i}$	109.8 (2)	O7—P1—O3	114.3 (4)
O6$^{\rm ii}$—Hg1—O3$^{\rm i}$	117.3 (2)	O7—P1—O5$^{\rm vii}$	113.5 (4)
O5—Hg1—O2$^{\rm ii}$	78.6 (2)	O3—P1—O5$^{\rm vii}$	110.9 (4)
O4—Hg1—O2$^{\rm ii}$	104.3 (2)	O7—P1—O1$^{\rm viii}$	108.4 (4)
O4$^{\rm i}$—Hg1—O2$^{\rm ii}$	177.3 (2)	O3—P1—O1$^{\rm viii}$	103.8 (4)
O6$^{\rm ii}$—Hg1—O2$^{\rm ii}$	55.0 (2)	O5$^{\rm vii}$—P1—O1$^{\rm viii}$	105.1 (4)
O3$^{\rm i}$—Hg1—O2$^{\rm ii}$	69.0 (2)	O6—P2—O2	109.3 (4)
O7$^{\rm ii}$—Hg2—O3$^{\rm i}$	167.5 (2)	O6—P2—O4	114.1 (4)
O7$^{\rm ii}$—Hg2—O6	83.4 (2)	O2—P2—O4	113.8 (4)
O3$^{\rm i}$—Hg2—O6	91.8 (2)	O6—P2—O1	110.2 (4)
O7$^{\rm ii}$—Hg2—O2$^{\rm iii}$	94.2 (2)	O2—P2—O1	108.0 (4)
O3$^{\rm i}$—Hg2—O2$^{\rm iii}$	87.3 (2)	O4—P2—O1	101.0 (3)
O6—Hg2—O2$^{\rm iii}$	164.2 (2)	P2—O1—P1$^{\rm iv}$	133.4 (4)
O7$^{\rm ii}$—Hg2—O5$^{\rm iv}$	90.3 (2)		
O4—P2—O1—P1$^{\rm iv}$	−177.0 (6)	O3—P1—O1$^{\rm viii}$—P2$^{\rm viii}$	171.1 (6)

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

The crystal shape was optimized by minimizing the internal *R* value of ψ-scan data for 16 selected reflections using the program *HABITUS* (Herrendorf, 1993). The habitus so derived was used for the numerical absorption correction.

Data collection: *STADI*4 (Stoe & Cie, 1995). Cell refinement: *STADI*4. Data reduction: *STADI*4. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995) and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1174). Services for accessing these data are described at the back of the journal.

References

Aurivillius, K. & Nilsson, B. A. (1975). *Z. Kristallogr.* **141**, 1–10.

Aurivillius, K. & Stålhandske, C. (1980). *Z. Kristallogr.* **153**, 121–129.

Beucher, M. & Tordjman, I. (1968). *Bull. Soc. Fr. Mineral. Cristallogr.* **91**, 207–209.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. & Calvo, C. (1970). *J. Solid State Chem.* **1**, 173–179.

Calvo, C. & Au, P. K. L. (1969). *Can. J. Chem.* **47**, 3409–3416.

Clark, G. M. & Morley, M. (1976). *Chem. Soc. Rev.* **5**, 269–295.

Dowty, E. (1995). *ATOMS for Windows.* Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Gmelin's Handbuch der anorganische Chemie (1969). 8th ed., Vol. 34, Part B4, *Quecksilber*, 1357*f.* Weinheim: Verlag Chemie.

Herrendorf, W. (1993). *HABITUS. Programm zur Optimierung der Kristallgestalt für die numerische Absorptionskorrektur anhand geeigneter ψ-abgetasteter Reflexe.* University of Karlsruhe, Germany.

Hoppe, R. (1979). *Z. Kristallogr.* **150**, 23–52.

Hoppe, R. (1995). *Z. Naturforsch. Teil A*, **50**, 555–567.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Leung, K. Y. & Calvo, C. (1972). *Can. J. Chem.* **50**, 2519–2526.

Nord, A. G. & Kierkegaard, P. (1980). *Chem. Scr.* **15**, 27–39.

Schwarzenberg, A. (1848). *Liebigs Ann. Chem.* **65**, 133–163.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Soose, J. (1980). *SOS. Programme zur Auswertung von Guinier-Aufnahmen.* University of Gießen, Germany.

Stefanidis, T. & Nord, A. G. (1984). *Acta Cryst.* C**40**, 1995–1999.

Stoe & Cie (1995). *STADI4. Data Collection Program for Windows.* Version 1.04. Stoe & Cie, Darmstadt, Germany.

Weil, M. (1997). Thesis. University of Gießen, Germany. In preparation.

Wessels, A. (1996). *Darstellung und strukturelle Charakterisierung ternärer Quecksilberoxide.* University of Münster, Germany.

Wyckoff, R. W. G. (1965). In *Crystal Structures.* Vol. 1, second edition. New York: John Wiley & Sons.