

molécules d'eau comportant les oxygènes de type O(5) et O(6) ne sont liées à aucun cation. La cohésion de l'édifice cristallin est assurée par des liaisons hydrogène.

Dans le Tableau 4, figurent les atomes d'oxygène et de chlore qui se trouvent à des distances inférieures à 3,45 Å des oxygènes des molécules d'eau et qui, dans le cas des oxygènes O(1), O(2), O(3) et O(4), ne sont pas liés au même cation. Pour les oxygènes O(1), O(3), O(4), O(5) et O(6), les entourages permettent de prévoir sans ambiguïté les liaisons hydrogène. L'oxygène O(2) a pour plus proches voisins trois atomes de chlore. En se référant aux critères angulaires de Baur & Khan (1970), la molécule H₂O(2) ne peut réaliser de liaisons hydrogène qu'avec Cl(3^v) et Cl(3) bien que la distance O(2)—Cl(1^{xl}) soit inférieure à la distance O(2)—Cl(3). Or l'affinement des coordonnées de l'hydrogène, qu'elles soient au départ données pour diriger O—H vers Cl(3) ou vers Cl(1^{xl}), converge vers les mêmes valeurs qui placent l'hydrogène en position intermédiaire et fournissent une distance O(2)—H = 0,82 (7) Å. Ce résultat est en faveur de l'existence d'une liaison hydrogène bifurquée que l'on peut admettre d'après les valeurs angulaires trouvées dans d'autres structures (Falk & Knop, 1973). On rencontre une situation similaire dans le composé CdMg₂Cl₆.2H₂O

(Ledésert & Monier, 1981) pour l'oxygène O(2) et les chlorures Cl(2^x) et Cl(1^{xl}).

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Structure of Mercury Sodium Phosphate

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Abstract. HgNaPO₄, orthorhombic, *Cmcm*, $a = 5.883$ (1), $b = 9.401$ (3), $c = 6.448$ (1) Å, $Z = 4$. Crystals were grown by hydrothermal reaction of Hg(NO₃)₂, Na₂HPO₄ and NaOH solution at 473 K for 2 weeks. Structure refinement was carried out by the full-matrix least-squares method to $R = 0.054$ with 722 independent X-ray reflection data. The structure is similar to that of olivine except for the arrangement of the PO₄ tetrahedra.

Introduction. Mercury, a member of Group IIb, has chemical properties somewhat different from those of the remaining elements of the same group. This

suggests the possibility that mercury can show different crystal chemical behavior from cadmium in formation of phosphates. However, there are few reports on the crystal structure of mercury phosphates to date. In the course of studies on divalent metal phosphates, we obtained single crystals of HgNaPO₄ and determined its crystal structure. Although the structure is similar to that of CdNaPO₄ (Ivanov, Simonov & Belov, 1974; Hata, Okada, Aoki, Akao & Iwai, 1979), they are not isomorphous, as shown later.

Single crystals of HgNaPO₄ were prepared by hydrothermal reaction of Hg(NO₃)₂, Na₂HPO₄ and NaOH solution with initial pH values in the range 6–8

at 473 K for 2 weeks. The crystals obtained were colorless, transparent, hexagonal prisms of 0.2–1.0 mm in length and 0.1–0.5 mm in diameter or hexagonal plates of 0.05–0.1 mm in thickness and 0.5–1.0 mm in diameter. The pinacoidal faces are perpendicular to the *c* axis and cleavages parallel to (010) are perfect.

The lattice constants were refined from the 2θ values of 29 reflections measured on a four-circle diffractometer (Philips PW 1100/20) with the program *RLC-3* (Sakurai, 1967). The crystals are orthorhombic and from the systematic absences observed on Weissenberg photographs, the possible space groups are restricted to *Cmcm*, *Cmc2₁* and *C2cm*.

Intensities were measured on the automated four-circle diffractometer with Mo *K* α radiation, using a crystal of dimensions 0.15 \times 0.10 \times 0.05 mm. The ω – 2θ scan mode was employed with a scan speed of 2° min⁻¹ in ω . A total of 722 independent reflection data which satisfied the relation $|F_o| > 3\sigma|F_o|$ were obtained within the range $2\theta \leq 90^\circ$ (σ : the standard deviation due to the counting statistics). Intensities were corrected for Lorentz and polarization factors. Absorption corrections ($\mu = 44.56$ mm⁻¹ for Mo *K* α) were made with the program *FDINCOR*. The structure was solved by a three-dimensional Patterson and consecutive difference Fourier syntheses, and refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). For the first step, the space group was assumed to be *Cmcm*, and then the remaining two were tested. The calculation gave the reliability factors $R = 0.0592$ for *C2cm*, $R = 0.0588$ for *Cmc2₁* and $R = 0.0594$ for *Cmcm* with anisotropic temperature factors for Hg, P and Na atoms. Since all the structure models were essentially identical and there was no significant difference between the R values obtained, the space group *Cmcm* with the highest symmetry of the three was adopted for the space group of this crystal. The calculation converged to $R = 0.054$ and $R_w = 0.064$ with anisotropic temperature factors for all the atoms, where $R_w = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. The weighting scheme employed was that proposed by Hughes (1941): $w = 1$ if $|F_o| < 124$ and $w = (124/|F_o|)^2$ if $|F_o| \geq 124$. The atomic scattering factors for Hg, P, Na and O atoms and the anomalous-

dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

The final positional and thermal parameters are given in Table 1.*

Discussion. The structure projected on (001) and (100) is shown in Fig. 1(a) and (b) respectively. The selected interatomic distances and bond angles are listed in Table 2.

As seen in Fig. 1, the structure of HgNaPO₄ is related to that of olivine, (Mg,Fe)₂SiO₄. The main difference is in the orientation of the tetrahedral anions. We can derive the latter structure from the former if we rotate the respective tetrahedral anions around the line $x = y = 0$ or its equivalents (Fig. 1a). Because of this rotation, the packing of O atoms is different in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36282 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

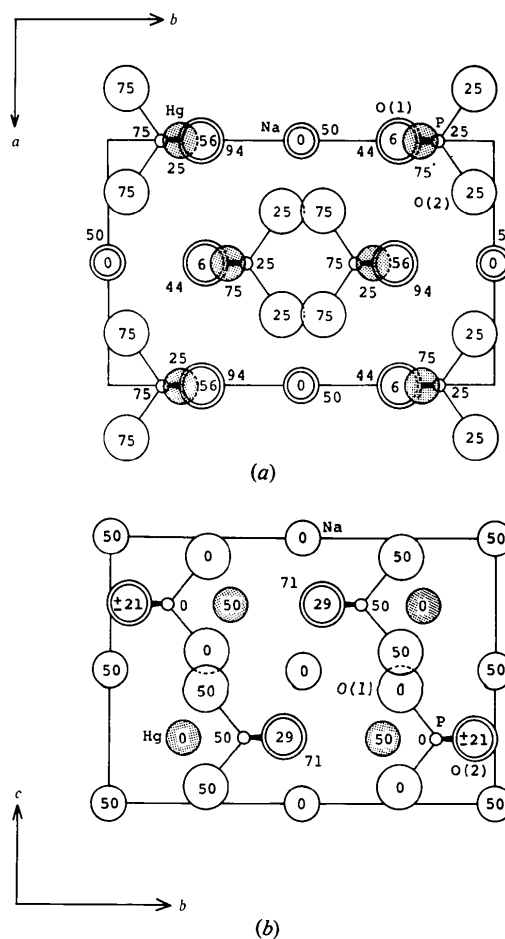


Fig. 1. The structure of HgNaPO₄ projected on (a) (001) and (b) (100). Numbers are $z \times 10^2$, and $x \times 10^2$ respectively.

Table 1. Final positional ($\times 10^4$) and equivalent isotropic temperature factors calculated from the anisotropic *U* values for HgNaPO₄

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Hg	0	1905 (1)	2500	0.99 (2)
Na	0	5000	0	1.14 (7)
P	0	8599 (3)	2500	0.55 (16)
O(1)	0	7552 (7)	4366 (11)	1.01 (17)
O(2)	2145 (12)	9536 (7)	2500	1.15 (18)

Table 2. *Interatomic distances (Å) and bond angles (°)*

Symmetry codes: (0) x, y, z ; (i) \bar{x}, y, z ; (ii) $x, y, \frac{1}{2} - z$; (iii) $x, y - 1, z$; (iv) $\bar{x}, y - 1, z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (vi) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (vii) $\frac{1}{2} - x, \frac{3}{2} - y, z - \frac{1}{2}$; (viii) $\bar{x}, 1 - y, 1 - z$; (ix) $\bar{x}, 1 - y, z - \frac{1}{2}$; (x) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

NaO₆ octahedron

Na—O(1 ^{ii,ix})	2.434 (6)	O(1 ⁱⁱ)—O(2 ^v) (×8)	3.280 (8)
Na—O(2 ^{v,vi,vii,x})	2.368 (5)	O(2 ^{vi})—O(2 ^v) (×2)	3.359 (10)
Mean	2.390	O(2 ^v)—O(2 ⁱⁱ) (×2)	3.340 (3)
		O(1 ⁱⁱ)—O(1 ^{ix})	4.868 (9)

HgO₄ tetrahedron

Hg—O(1 ^{viii,ix})	2.084 (7)	O(1 ^{viii})—O(1 ^{ix})	4.042 (10)
Hg—O(2 ^{iii,iv})	2.559 (7)	O(2 ⁱⁱⁱ)—O(2 ^{iv})	2.524 (10)
Mean	2.321	O(1 ^{ix})—O(2 ⁱⁱⁱ) (×4)	3.629 (8)
		O(1 ^{viii})—Hg—O(1 ^{ix})	151.6 (2)

PO₄ tetrahedron

P—O(1 ^{0,ii})	1.554 (7)	O(1 ⁰)—O(1 ⁱⁱ)	2.406 (10)
P—O(2 ^{0,i})	1.539 (7)	O(1 ⁰)—O(2 ⁰) (×4)	2.553 (8)
Mean	1.546	O(2 ⁰)—O(2 ⁱ)	2.524 (10)
		O(1 ⁰)—P—O(1 ⁱⁱ)	101.4 (4)
		O(1 ⁰)—P—O(2 ⁰) (×4)	111.2 (2)
		O(2 ⁰)—P—O(2 ⁱ)	110.1 (4)

these two crystals. Mg and Fe atoms in olivine are replaced by Na and Hg atoms in HgNaPO₄. Na atoms occupy *M*(1) sites and Hg atoms *M*(2) sites. In contrast to the octahedral coordination of the *M*(2) atom in olivine, the Hg atom is surrounded by two O(1) and two O(2) atoms, forming a strongly distorted HgO₄ tetrahedron with the mean Hg—O distance of 2.321 Å. The Hg—O(1) bond [2.084 (7) Å] is markedly shorter than Hg—O(2) [2.559 (7) Å] and than the sum of the crystal radii for Hg²⁺ (fourfold coordination) (1.10 Å) and O²⁻ (sixfold coordination) (1.26 Å) (Shannon, 1976), indicating the covalent character of the Hg—O(1) bonds. The larger O(1)—Hg—O(1) angle [151.6 (2)°] also suggests preference of the Hg atoms to form linear twofold coordination.

The Na atom is surrounded octahedrally by two O(1) and four O(2) atoms with the mean Na—O distance 2.390 Å. The NaO₆ octahedra share edges with one another to form ribbons parallel to [001] lying at $x = 0$ and $x = 0.5$. Since the Hg²⁺ ion attracts the O(1) atom more strongly than does the Na⁺ ion, the Na—O(2) distance [2.368 (5) Å] is shorter than that of Na—O(1) [2.434 (6) Å] whose O(1) atom is not involved in a shared edge. The perfect cleavages parallel to (010) are well explained by the rather long Hg—O(2) and Na—O(1) bonds.

The PO₄ tetrahedron is almost regular. The P—O(1) and P—O(2) bond lengths are 1.554 (7) and 1.539 (7) Å respectively, with the mean value of 1.546 Å. The symmetry of the PO₄ tetrahedron is *m2m*, and this is a rare example according to Baur (1974). The PO₄ tetrahedra share edges [O(2)—O(2)] with the neighboring HgO₄ tetrahedra, lying alternately with the latter along [001]. The longer P—O(1) length is probably due to the stronger covalency in the Hg—O(1) bond than in Hg—O(2).

Although both Cd and Hg atoms belong to Group IIb, having similar crystal radii, the structures of HgNaPO₄ and CdNaPO₄ are significantly different. Though the metal ions occupy almost the same positions in both crystals, the O atoms arrange approximately in hexagonal closest packing in CdNaPO₄ as in the structure of olivine, whereas they arrange so as to yield a twofold coordination for Hg atoms in HgNaPO₄ in consequence of the rotation of PO₄ groups about 45° around the line $x = y = 0$ or its equivalents (Fig. 1a). This causes the differences in symmetry and lattice parameters between these two compounds. Although the mean P—O lengths are nearly equal in both crystals, the distortion of the PO₄ tetrahedron in HgNaPO₄ estimated in terms of Baur's DI(PO), DI(OO) and DI(OPO) (Baur, 1974) is a little smaller than that in CdNaPO₄.

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