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Structure of Diammonium Disodium Mercury(II) Trimetaphosphate

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Abstract. $Hg(NH_4)_2Na_2(P_3O_9)_2$, $M_r = 756{\cdot}47$, monoclinic, $C2/c$, $a = 13{\cdot}524\ (8)$, $b = 8{\cdot}362\ (5)$, $c = 14{\cdot}390\ (8)$ Å, $\beta = 92{\cdot}58\ (5)°$, $V = 1625{\cdot}7$ Å^3, $Z = 4$, $D_x = 3{\cdot}090$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5608$ Å, $\mu = 5{\cdot}72$ mm^{-1}, $F(000) = 1432$, $T = 293$ K, final $R = 0{\cdot}030$ for 1401 independent reflexions. The cyclic phosphate anion has pseudo mirror symmetry. Sodium and mercury atoms are disordered on two different crystallographic positions. The $(Na,Hg)O_6$ distorted octahedra are linked to form infinite chains of edge-shared octahedra approximately in the (101) planes. The two types of $(Na,Hg)O_6$ octahedra have average (Na,Hg)–O distances of 2·403 and 2·420 Å.

Introduction. $HgNa_4(P_3O_9)_2$ is the only compound observed during the determination of the $Hg(PO_3)_2$–$NaPO_3$ phase equilibrium diagram (Raholison, 1970). $HgNa_4(P_3O_9)_2$ powder diagrams suggest that this compound is probably isotypic with $CdNa_4(P_3O_9)_2$ (Averbuch–Pouchot & Durif, 1969) and $CaNa_4(P_3O_9)_2$ (Grenier, Martin & Durif, 1970).

During attempts to produce good quality crystals of $HgNa_4(P_3O_9)_2$ we obtained crystals whose unit-cell dimensions are comparable to those of $CdNa_4(P_3O_9)_2$ suggesting that the compound was $HgNa_4(P_3O_9)_2$. Owing to chemical interaction with the flux used, the correct formula of this salt is in fact $Hg(NH_4)_2Na_2(P_3O_9)_2$. The present work is devoted to the crystal structure of this new compound.

Experimental. Crystals of $Hg(NH_4)_2Na_2(P_3O_9)_2$ are prepared by adding 6g of HgO to a flux of 5 cm^3 of H_3PO_4 (85%), 12 g of $(NH_4)_2HPO_4$ and 2 g of NaH_2PO_4 kept at 623 K for 2 or 3 d. $Hg(NH_4)_2Na_2(P_3O_9)_2$ crystals look like calcite rhombohedra. Crystal size: 0·12 × 0·12 × 0·12 mm; D_m not measured; Philips PW 1100 diffractometer; graphite monochromator; systematic absences: $h0l$ ($h = 2n$), ($l = 2n$) and hkl ($h+k = 2n$); 22 reflexions ($10{\cdot}8 < \theta < 12{\cdot}9°$) for refining the unit cell; ω scan; scan speed: 0·02° s^{-1}; scan width: 1·20°; total background measuring time: 20 s; intensity and orientation reflexions 040 and $0\bar{4}0$ (no significant variation in intensity); θ range: 3–30°; 2730 reflexions measured; $h_{max} = 24$, $k_{max} = 14$, $l_{max} = 25$; Lorentz–polarization correction; no absorption correction; classical methods for structure determination: Patterson function and successive Fourier syntheses; anisotropic full-matrix least-squares refinements on F; unit weights; final refinements with 1401 independent reflexions ($I > 8\sigma_I$); final $R = 0{\cdot}030$ ($wR = 0{\cdot}037$), $S = 2{\cdot}317$; $\Delta\rho_{max} = 1{\cdot}084$ e Å^{-3}; $(\Delta/\sigma)_{max} < 0{\cdot}14$; scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations; computer used: Digital PDP 11/70.

Table 1. *Final atomic coordinates and* B_{eq} *for* $Hg(NH_4)_2Na_2(P_3O_9)_2$

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

	x	y	z	B_{eq}(Å^2)
Hg(1)Na(1)	0·1617 (4)	0·1427 (6)	0·4148 (4)	1·14 (8)
Hg(2)Na(2)	0	0·3545 (7)	¼	1·2 (1)
N	0·3489 (4)	0·1270 (9)	0·0406 (5)	1·9 (2)
P(1)	0·0810 (1)	0·0263 (2)	0·1183 (2)	1·01 (4)
P(2)	0·4038 (1)	0·1878 (2)	0·3719 (1)	0·96 (4)
P(3)	0·2720 (1)	0·3734 (2)	0·2539 (1)	0·99 (4)
O(*E*11)	−0·0036 (4)	0·1446 (7)	0·3604 (4)	1·7 (1)
O(*E*12)	0·1371 (4)	0·0472 (7)	0·0320 (4)	1·8 (1)
O(*L*12)	0·4678 (3)	0·3512 (7)	0·3802 (3)	1·2 (1)
O(*E*21)	0·3350 (4)	0·1856 (7)	0·4497 (3)	1·3 (1)
O(*E*22)	0·4728 (4)	0·0528 (7)	0·3610 (4)	1·7 (1)
O(*L*23)	0·3417 (3)	0·2194 (6)	0·2758 (3)	1·0 (1)
O(*E*31)	0·1807 (3)	0·3600 (8)	0·3083 (3)	1·6 (1)
O(*E*32)	0·2629 (4)	0·3960 (7)	0·1519 (3)	1·6 (1)
O(*L*13)	0·3416 (4)	0·5186 (7)	0·2944 (4)	1·4 (1)

Discussion. Final atomic coordinates are reported in Table 1.* Fig. 1, a projection along the a axis, presents the respective locations of the P_3O_9 ring anions and of the associated cations. The ring anion has pseudo mirror symmetry passing through P(3), O(L12), O(E31) and O(E32); its main geometrical features are given in Table 2. Sodium and mercury atoms are disordered: a general position 8(f) is occupied by 3·4 Hg and 4·6 Na while a position 4(e) is occupied by 0·6 Hg and 3·4 Na. Mercury–sodium coordination polyhedra are linked so as to build infinite chains of

* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42908 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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edge-sharing distorted octahedra spreading approximately in the (101) planes. Details of such a chain are reported in Fig. 2, while the main distances in the associated cation polyhedra are given in Table 2.

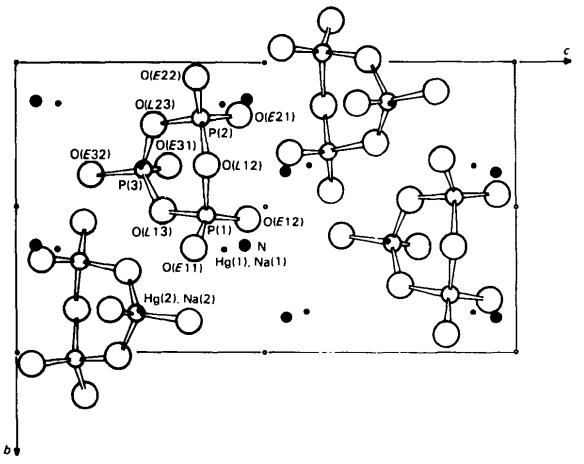

Fig. 1. Projection along the *a* axis of the atomic arrangement of $Hg(NH_4)_2Na_2(P_3O_9)_2$. Ring anions with $x > 0{\cdot}50$ are not represented.

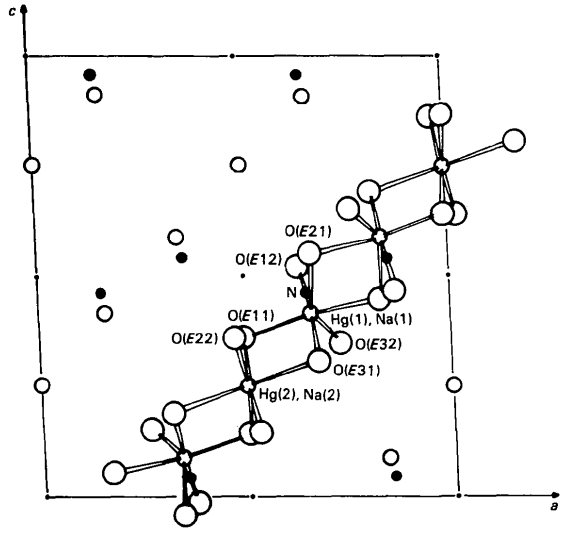

Fig. 2. Projection along the *b* axis of an $(Hg,Na)O_6$ octahedra chain.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Hg(NH_4)_2Na_2(P_3O_9)_2$

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·482 (4)	2·563 (6)	2·502 (6)	2·493 (5)
O(*E*12)	118·9 (2)	1·495 (4)	2·541 (5)	2·513 (5)
O(*L*2)	108·1 (2)	110·0 (2)	1·606 (4)	2·491 (5)
O(*L*13)	107·9 (2)	108·6 (2)	102·0 (2)	1·600 (4)

$P(2)O_4$ tetrahedron

P(2)	O(*E*21)	O(*E*22)	O(*L*12)	O(*L*23)
O(*E*21)	1·488 (4)	2·560 (6)	2·510 (5)	2·524 (5)
O(*E*22)	119·3 (2)	1·478 (4)	2·511 (5)	2·529 (5)
O(*L*12)	107·8 (2)	108·3 (2)	1·618 (4)	2·480 (4)
O(*L*23)	109·2 (2)	110·0 (2)	100·5 (2)	1·608 (3)

$P(3)O_4$ tetrahedron

P(3)	O(*E*31)	O(*E*32)	O(*L*23)	O(*L*13)
O(*E*31)	1·495 (3)	2·572 (5)	2·536 (5)	2·563 (5)
O(*E*32)	119·6 (2)	1·480 (3)	2·515 (5)	2·489 (5)
O(*L*23)	109·0 (2)	108·5 (2)	1·618 (3)	2·516 (5)
O(*L*13)	110·2 (2)	106·3 (2)	101·6 (2)	1·628 (4)

P(1)–P(2)	2·840 (2)	P(1)–P(2)–P(3)	62·03 (5)
P(2)–P(3)	2·863 (2)	P(2)–P(3)–P(1)	58·61 (4)
P(3)–P(1)	2·939 (2)	P(3)–P(1)–P(2)	59·36 (4)

P(1)–O(*L*12)–P(2)	123·5 (2)
P(2)–O(*L*23)–P(3)	125·1 (2)
P(1)–O(*L*13)–P(3)	131·2 (2)

Associated cation polyhedra

[Hg(1),Na(1)]–O(*E*11)	2·336 (3)	N–O(*E*12)	2·940 (6)
–O(*E*12)	2·351 (4)	–O(*E*12)	2·926 (6)
–O(*E*21)	2·402 (3)	–O(*E*21)	2·925 (6)
–O(*E*21)	2·420 (3)	–O(*E*22)	2·810 (6)
–O(*E*31)	2·398 (4)	–O(*E*31)	3·155 (6)
–O(*E*32)	2·510 (4)	–O(*E*32)	3·024 (6)
		–O(*E*32)	3·101 (6)

[Hg(2),Na(2)]–O(*E*11)	2×2·370 (4)
–O(*E*22)	2×2·342 (4)
–O(*E*31)	2×2·549 (3)

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