

Structure of Manganese(II) Sodium Dihydrogenphosphite Monohydrate

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Abstract. $\text{MnNa}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$, $M_r = 338.9$, orthorhombic, $Pbca$, $a = 9.156$ (1), $b = 14.960$ (2), $c = 14.899$ (2) Å, $V = 2040.8$ (5) Å³, $Z = 8$, $D_m = 2.13$ (4), $D_x = 2.206$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.90$ mm⁻¹, $F(000) = 1352$, $T = 295$ K, $R = 0.042$, 2974 unique reflections. The structure consists of three crystallographically non-equivalent H_2PO_3 tetrahedra, the water molecule and hexacoordinated Mn and Na atoms. The hydrogen bonds give rise to a three-dimensional network. All values of the interatomic distances and angles are in accordance with data in the literature.

Introduction. The study of the title compound was undertaken as part of an investigation of phosphorous acid–phosphites–water systems (Eysseltová & Ebert, 1972).

Experimental. The crystals were prepared by crystallization from a concentrated aqueous solution of manganese(II) phosphite, phosphorous acid and sodium phosphite. Colourless prismatic crystals were obtained with well developed {021} and {001} faces, stable in air and to X-rays. A spherical crystal with $r = 0.15$ mm was used. Flotation method for measuring D_m (mixture of diiodomethane and toluene). Hilger & Watts four-circle diffractometer controlled by computer M7000, learnt profile method (Diamond, 1969; Clegg, 1981) for obtaining integrated intensities and their e.s.d.'s; ω – 2θ scan; 42 reflections with θ from 2.72 to 22.79° for measuring lattice parameters; absorption ignored; max. $\sin\theta/\lambda = 0.7035$ Å⁻¹; $h_{\max} = 12$, $k_{\max} = 20$, $l_{\max} = 20$; three standard reflections with no significant variation; 2974 measured unique reflections; 585 unobserved reflections with $I < 1.96\sigma(I)$; heavy-atom method; F magnitudes in full-matrix least-squares refinement; H atoms localized from a $\Delta\rho$ map; all positional parameters were refined; anisotropic thermal parameters of all non-hydrogen atoms and isotropic thermal parameters of all H atoms

(with exception of thermal parameters of H atoms in the crystalline water, which were fixed); $R = 0.042$, $wR = 0.058$, $S = 1.32$, $w = 1/\sigma^2(F_o)$, σ derived from $\sigma_2(I) = [\sigma_1(I) + (0.015I)^2]^{1/2}$, $\sigma_1(I)$ after Clegg (1981) and Diamond (1969); max. $\Delta/\sigma = 0.11$; max. and min. heights in final $\Delta\rho$ map 0.65 and -0.64 e Å⁻³; atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); no correction for secondary extinction; programs *TLS* modified for Siemens 7536 (Petříček, Malý & Novák, 1983) and *ORTEP* (Johnson, 1965).†

Discussion. The final atomic parameters are given in Table 1. The intramolecular and selected intermolecular bond distances and angles are given in Table 2. The molecule is depicted in Fig. 1. The projection of the structure along X is depicted in Fig. 2.

The Mn atoms are octahedrally coordinated by non-hydroxyl O atoms of three phosphites (5×) and by the water O atom with average distance Mn–O = 2.18 (5) Å and angles O–Mn–O = 90 (4) and 174 (1)°.

The Na atoms are also octahedrally coordinated by non-hydroxyl (4×) and hydroxyl (1×) O atoms of three phosphites and by the water O atom with average distance Na–O = 2.4 (1) Å and angles O–Na–O = 89 (12) and 163 (3)°.

The average distances and angles in phosphites are P–O(H) = 1.574 (8), P–O = 1.500 (6), P–H = 1.26 (2), O(H)–H = 0.81 (7) Å and O(H)–P–O = 109 (1), O–P–O = 115.9 (7), O(H)–P–H = 104.7 (6), O–P–H = 109 (1) and P–O(H)–H = 110 (2)°.

† Lists of atomic coordinates and isotropic thermal parameters and bond distances and angles for the hydrogen atoms, of anisotropic thermal parameters for the non-hydrogen atoms and of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43034 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The phosphite anions and the water molecules are connected by hydrogen bonds with average distances O(H)···O = 2.7 (2), H···O = 1.9 (2) Å and angle O(H)—H—O = 169 (5)° so that all hydroxyl groups act as H donors and non-hydroxyl O(12,32,33) and hydroxyl O(11,21) atoms act as H acceptors. The Mn and Na octahedra are linked by three O atoms of two phosphites and by the water O atom.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

| | x | y | z | B_{eq} (Å ²) |
|-------|------------|------------|------------|----------------------------|
| Mn | 4464.6 (5) | 8402.6 (3) | 5453.5 (3) | 1.20 (1) |
| Na | 5574 (1) | 6532.4 (9) | 4367 (1) | 2.13 (3) |
| P(1) | 2343.6 (8) | 5317.1 (5) | 5080.7 (5) | 1.33 (2) |
| P(2) | 7380.8 (8) | 7245.2 (5) | 6218.5 (5) | 1.22 (1) |
| P(3) | 4601.2 (8) | 5312.0 (5) | 2392.5 (5) | 1.33 (2) |
| O(11) | 3741 (3) | 5728 (2) | 5535 (2) | 2.95 (6) |
| O(12) | 1019 (3) | 5847 (2) | 5349 (2) | 2.04 (5) |
| O(13) | 2285 (2) | 4335 (1) | 5259 (2) | 1.89 (5) |
| O(21) | 7354 (3) | 7943 (2) | 7017 (2) | 2.13 (5) |
| O(22) | 6027 (2) | 7362 (1) | 5664 (1) | 1.69 (5) |
| O(23) | 8808 (2) | 7331 (1) | 5734 (1) | 1.66 (4) |
| O(31) | 5011 (4) | 4356 (2) | 2046 (2) | 2.93 (7) |
| O(32) | 5169 (3) | 5392 (2) | 3329 (2) | 2.07 (5) |
| O(33) | 5120 (3) | 6026 (2) | 1752 (2) | 2.06 (5) |
| O(4) | 7731 (3) | 7400 (2) | 3817 (2) | 2.11 (5) |

Table 2. Bond distances (Å) and angles (°) for Mn···O and Na···O < 3.2 Å

| | | | |
|--|------------|---|------------|
| P(1)—O(11) | 1.573 (3) | Mn—O(33 ^{iv}) | 2.199 (3) |
| P(1)—O(12) | 1.503 (3) | Mn—O(4) | 2.268 (3) |
| P(1)—O(13) | 1.494 (2) | Na—O(32) | 2.332 (3) |
| P(2)—O(21) | 1.583 (3) | Na—O(22) | 2.334 (2) |
| P(2)—O(22) | 1.500 (2) | Na—O(23) | 2.351 (2) |
| P(2)—O(23) | 1.498 (2) | Na—O(13 ^v) | 2.416 (2) |
| P(3)—O(31) | 1.566 (3) | Na—O(4) | 2.501 (3) |
| P(3)—O(32) | 1.494 (3) | Na—O(11) | 2.701 (3) |
| P(3)—O(33) | 1.509 (3) | O(11)—O(32 ^v) | 2.582 (4) |
| Mn—O(22) | 2.137 (2) | O(21)—O(33 ^{iv}) | 2.592 (4) |
| Mn—O(13 ⁱⁱⁱ) | 2.144 (2) | O(31)—O(12 ^{iv}) | 2.716 (4) |
| Mn—O(23 ^v) | 2.167 (2) | O(4)—O(21 ⁱⁱⁱ) | 2.752 (4) |
| Mn—O(12 ⁱⁱ) | 2.171 (3) | O(4)—O(11 ⁱⁱⁱ) | 3.103 (4) |
| O(11)—P(1)—O(12) | 109.6 (2) | O(4)—Mn—O(33 ^{iv}) | 88.6 (1) |
| O(11)—P(1)—O(13) | 109.7 (1) | O(4)—Mn—O(12 ⁱⁱ) | 175.1 (1) |
| O(12)—P(1)—O(13) | 116.3 (1) | O(12 ⁱⁱ)—Mn—O(13 ⁱⁱⁱ) | 94.5 (1) |
| O(21)—P(2)—O(22) | 108.9 (1) | O(12 ⁱⁱ)—Mn—O(33 ^{iv}) | 96.0 (1) |
| O(21)—P(2)—O(23) | 108.6 (1) | O(13 ⁱⁱⁱ)—Mn—O(33 ^{iv}) | 94.0 (1) |
| O(22)—P(2)—O(23) | 116.4 (1) | O(11)—Na—O(22) | 79.27 (9) |
| O(31)—P(3)—O(32) | 107.3 (2) | O(11)—Na—O(32) | 90.1 (1) |
| O(31)—P(3)—O(33) | 111.2 (2) | O(11)—Na—O(23 ^v) | 86.34 (8) |
| O(32)—P(3)—O(33) | 115.1 (2) | O(11)—Na—O(13 ^v) | 96.7 (1) |
| O(22)—Mn—O(23 ^v) | 86.37 (6) | O(11)—Na—O(4) | 158.9 (1) |
| O(22)—Mn—O(4) | 90.72 (9) | O(22)—Na—O(4) | 81.66 (9) |
| O(22)—Mn—O(12 ⁱⁱ) | 91.07 (9) | O(22)—Na—O(23 ^v) | 77.91 (7) |
| O(22)—Mn—O(33 ^{iv}) | 88.36 (9) | O(22)—Na—O(13 ^v) | 87.16 (9) |
| O(22)—Mn—O(13 ⁱⁱⁱ) | 173.66 (7) | O(22)—Na—O(32) | 165.1 (1) |
| O(23 ^v)—Mn—O(4) | 85.93 (9) | O(32)—Na—O(13 ^v) | 83.6 (1) |
| O(23 ^v)—Mn—O(12 ⁱⁱ) | 89.66 (9) | O(32)—Na—O(4) | 106.7 (1) |
| O(23 ^v)—Mn—O(13 ⁱⁱⁱ) | 90.68 (8) | O(32)—Na—O(23 ^v) | 112.16 (9) |
| O(23 ^v)—Mn—O(33 ^{iv}) | 172.33 (9) | O(4)—Na—O(13 ^v) | 73.36 (8) |
| O(4)—Mn—O(13 ⁱⁱⁱ) | 83.47 (9) | O(4)—Na—O(23 ^v) | 98.44 (9) |
| | | O(23 ^v)—Na—O(13 ^v) | 163.98 (9) |

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

The title compound is isostructural with cobalt(II) sodium dihydrogenphosphite monohydrate (Kratochvíl, Podlahová, Habibpur, Petříček & Malý, 1982). The P—O, P—H and Na—O distances and angles are practically the same, the Mn—O distances are longer than Co—O distances, the average value Co—O = 2.10 (4) Å. The Mn—O distances are also longer than the distances Mn—O in MnH₃P₂O₆·2H₂O (Cisárová, Novák, Petříček, Kratochvíl & Loub, 1982) with the average distance Mn^{III}—O = 2.01 (15) Å. The values of Na—O are comparable with that in Na₂HPO₃·5H₂O (Brodalla, Goeters, Kniep, Mootz & Wunderlich, 1978) or in Na_{0.5}H_{2.5}PO₃ (Hazell, Hazell & Kratochvíl, 1982). The distances P—H, O—H and angles O—P—H, P—O—H are in accordance with the literature data, e.g. for LiH₂PO₃ (Johansson & Lindqvist, 1976).

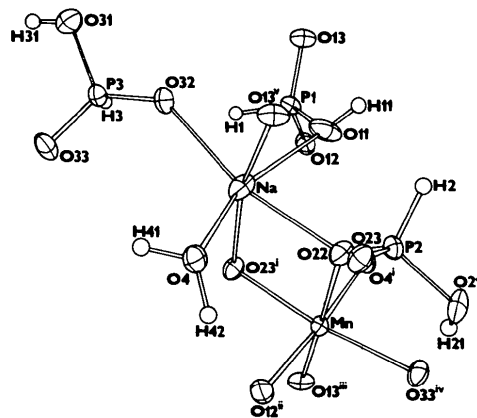


Fig. 1. The molecule of the title compound. The Mn, Na, P and O atoms are represented by thermal ellipsoids at the 50% level (Johnson, 1965).

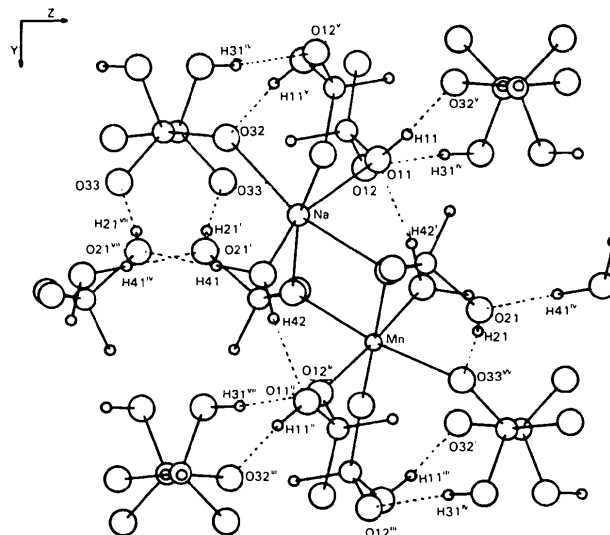


Fig. 2. A view of part of the structure of the title compound along X. The hydrogen bonds are indicated by dotted lines.

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cis-Diamminedicyanopalladium(II)

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Abstract. $[\text{Pd}(\text{CN})_2(\text{NH}_3)_2]$, $M_r = 192.5$, monoclinic, $P2_1/n$, $a = 6.825$ (2), $b = 12.733$ (3), $c = 6.779$ (2) Å, $\beta = 111.82$ (2)°, $V = 546.9$ (3) Å³, $Z = 4$, $D_m = 2.41$, $D_x = 2.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 37.6$ cm⁻¹, $F(000) = 368$, room temperature, final $R = 0.030$ for 1414 independent observed reflections. The structure is built up of independent molecules linked together by N–H...N hydrogen bonds. The Pd atom is bonded to two NH₃ and two CN ligands in a square-planar coordination. The two ligands of each pair are *cis* to each other. The PdC₂N₂ fragment is almost planar.

Introduction. The title compound was prepared in the course of our attempts to prepare tetraamminepalladium(II) tetracyanopalladate(II) – the cyanide analogue of the Vauquelin Red Salt, $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$, the successful solution and refinement of the structure showing that *cis*-diamminedicyanopalladium(II) was obtained instead. Compounds with the same overall composition have been known for a long time, Fehling (1841) describing a compound formulated as Pd(CN)₂·2NH₃. Later on Feigl & Heisig (1951) obtained [by warming palladium(II) cyanide in an excess of ammonia] diamminedicyanopalladium(II),

Gillard (1965) claiming (on the basis of his IR results) to have studied the *trans* isomer.

Experimental. The freshly prepared equimolar aqueous solutions of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $\text{K}_2[\text{Pd}(\text{CN})_4]$ were mixed and left for several days. The reaction product was filtered off and recrystallized from hot water. Density determined pycnometrically. Needle-like crystals of dimensions 0.65 × 0.07 × 0.07 mm, Philips PW 1100 diffractometer, graphite monochromator, Mo $K\alpha$, ω – 2θ scan technique, 18 reflections in range $6 \leq \theta \leq 10^\circ$ used to determine cell parameters. Data collected within range $3 < \theta < 31^\circ$, h –9→8, k 0→16, l 0→9, 1414 unique observed reflections used in structure determination. Three standard reflections measured every 2 h of exposure time showed no significant change with time. Data corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous-dispersion corrections for Pd atom from *International Tables for X-ray Crystallography* (1974). Patterson map indicated position of Pd; positions of other atoms (except H) obtained by Fourier-map calculations; H-atom positions from difference Fourier synthesis; least-squares refinement (on F) assuming anisotropic thermal parameters for non-H atoms and isotropic temperature factors for all H atoms. Refinement converged with

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