# METAL-ORGANIC COMPOUNDS

## Sodium 1,6-Hexanediammonium Cyclotriphosphate Dihydrate

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### Abstract

The mineral entities $P_3O_9$ and $NaO_6$ are connected by $OW1$ water molecules in the title compound, $Na^+.C_6H_{18}N_2^{2+}.P_3O_9^{3-}.2H_2O$, to form ribbons running parallel to the $c$ axis. Four ribbons create a channel which holds the organic cation.

### Comment

Organic compounds resulting from the interaction of cyclotriphosphoric acid with organic molecules have not been studied extensively. Only seven have been structurally well characterized (Durif, 1995; Thabet & Jouini, 1996). Among these compounds, only $K^+.C_2H_{10}N_2^{2+}.P_3O_9^{3-}$ was found to have a monovalent cation. In this work, we describe the crystal structure of sodium 1,6-hexanediammonium cyclotriphosphate dihydrate, (I), giving the second example of a compound obtained during the systematic investigation of the $H_3P_3O_9$–organic–$M_2^IO$–$H_2O$ system.

$$Na^+.\left[H_3N\diagdown\diagup\diagdown\diagup NH_3\right]^{2+}.\left[P_3O_9\right]^{3-}.2H_2O$$

(I)
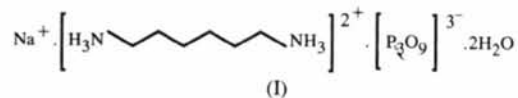
The atomic arrangement in projection along the **c** direction and the formation of channels by four ribbons of mineral entities are shown in Fig. 1. Organic cations reside in these channels. Fig. 2 represents, in projection along the **b** direction, the ribbons resulting from the connection, along the $c$ axis, of four $P_3O_9$ groups and two $NaO_6$ distorted octahedra. One of the two water molecules is located near the $Na^+$ cation; the second one, $OW1$, links ribbons *via* hydrogen bonding with the organic cations along the [101] direction. Two $NaO_6$ octahedra, sharing the $OE31$—$OE31(2 - x, 1 - y, -1 - z)$ edge, are associated in pairs. The $P_3O_9$ group observed in this arrangement has no internal symmetry. The P—P distances and the corresponding P—P—P angles range from 2.867 (1) to 2.873 (1) Å and from

59.88 (2) to 60.12 (2)°, respectively, corroborating the regular conformation of the $P_3O_9$ group.

The (N—C, C—C) distances and (N—C—C, C—C—C) angles, are similar to those reported previously for condensed phosphates with this organic cation (Loiseau & Férey, 1994; Charfi & Jouini, 1996; Thabet, Bdiri & Jouini, 1997), *i.e.* they lie within the ranges 1.489 (3)–1.530 Å and 111.2 (2)–112.9 (2)°, respectively. All hydrogen bonds, establishing cohesion between the different components of this atomic arrangement, are weak since the corresponding $O(N)\cdots O$ distances are 2.729–3.010 Å (Blessing, 1986; Brown, 1976).
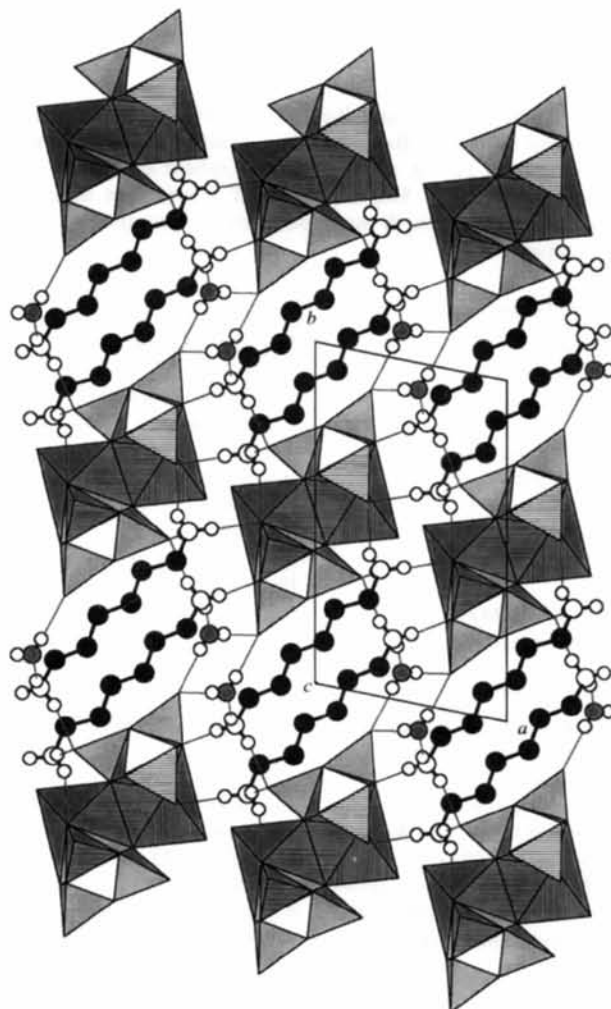


Fig. 1. Projection along the **c** direction of the the atomic arrangement. $P_3O_9$ and $NaO_6$ are given in polyhedral representation. Large empty circles represent N atoms, grey circles O water atoms, black ones C atoms and small empty circles H atoms. Hydrogen bonds are denoted by full and dotted lines.
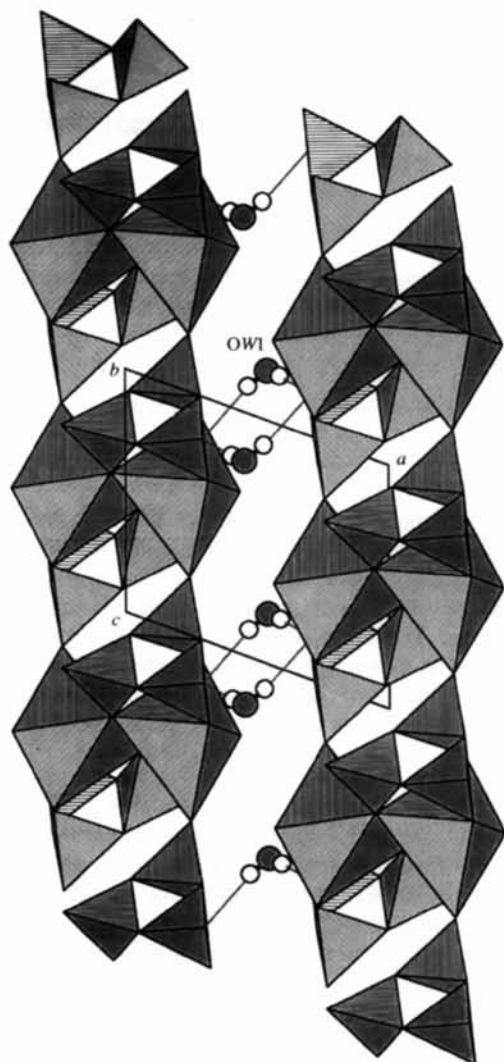
Fig. 2. The b-axis projection of two ribbons linked by OW1 molecules along the [101] direction. $P_3O_9$ and $NaO_6$ groups are in polyhedral representation.

## Experimental

$Na[NH_3(CH_{26}NH_3].P_3O_9.2H_2O$ was prepared by action of cyclotriphosphoric acid, $H_3P_3O_9$, with an aqueous solution of 1,4-diaminohexane (purity >97%) and sodium carbonate (purity >99.5%). The obtained solution was slowly evaporated at room temperature for two weaks. Crystals obtained in this way are stable under normal conditions of temperature and hygrometry. We note that $H_3P_3O_9$ was synthesized using an aqueous solution of $Na_3P_3O_9$ and ion-exchange resin Amberlite IR 120. Studied by TG–DTA and DSC techniques, the title compound was dehydrated in two steps at 384 and 409 K. The overall $\Delta H$ of the dehydration is 84.2 kJ mol$^{-1}$. It is to be noted that this compound decomposes before melting.

### Crystal data

$Na^+.C_6H_{18}N_2^{2+}.P_3O_9^{3-}.2H_2O$
$M_r = 414.16$
Triclinic
$P\bar{1}$
$a = 8.619\,(1)$ Å
$b = 13.983\,(1)$ Å
$c = 7.344\,(1)$ Å
$\alpha = 94.17\,(1)°$
$\beta = 68.69\,(1)°$
$\gamma = 102.14\,(1)°$
$V = 806.19\,(13)$ Å$^3$
$Z = 2$
$D_x = 1.706$ Mg m$^{-3}$
$D_m = 1.697$ Mg m$^{-3}$
$D_m$ measured by pycnometry
  (toluene as pycnometric
  liquid)

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
  reflections
$\theta = 13–14°$
$\mu = 0.453$ mm$^{-1}$
$T = 293\,(2)$ K
Transparent
$0.25 \times 0.20 \times 0.18$ mm
Colourless

### Data collection

Enraf–Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3076 measured reflections
2832 independent reflections
2396 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.010$
$\theta_{max} = 25°$
$h = -10 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 0$
1 standard reflection
  frequency: 120 min
  intensity decay: 0.78%

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.075$
$S = 1.050$
2832 reflections
297 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.332P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.260$ e Å$^{-3}$
$\Delta\rho_{min} = -0.290$ e Å$^{-3}$
Extinction correction:
  SHELXL93
Extinction coefficient:
  0.0169 (19)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|---|---|---|---|
| P1—OE12 | 1.464 (2) | P3—Na$^i$ | 3.4554 (9) |
| P1—OE11 | 1.490 (2) | Na—OE31 | 2.361 (2) |
| P1—OL13 | 1.617 (1) | Na—OE12$^{ii}$ | 2.373 (2) |
| P1—OL12 | 1.621 (1) | Na—OE31$^i$ | 2.389 (2) |
| P2—OE22 | 1.473 (1) | Na—OE21 | 2.449 (2) |
| P2—OE21 | 1.486 (2) | Na—OW2 | 2.472 (2) |
| P2—OL12 | 1.611 (1) | Na—OE11 | 2.637 (2) |
| P2—OL23 | 1.613 (1) | Na—P3$^i$ | 3.4554 (9) |
| P3—OE31 | 1.476 (1) | Na—Na$^i$ | 3.611 (2) |
| P3—OE32 | 1.490 (1) | N1—C1 | 1.496 (3) |
| P3—OL13 | 1.608 (1) | N2—C6 | 1.489 (3) |
| P3—OL23 | 1.610 (1) | C1—C2$^{iii}$ | 1.515 (3) |
| P1—P2 | 2.867 (1) | C2—C3$^{iv}$ | 1.523 (3) |
| P1—P3 | 2.873 (1) | C3—C4 | 1.519 (3) |
| P2—P3 | 2.870 (1) | C4—C5 | 1.530 (3) |
| P3—Na | 3.399 (1) | C5—C6$^v$ | 1.511 (3) |
| | | | |
| OE12—P1—OE11 | 120.11 (9) | OE31—Na—OW2 | 144.96 (6) |
| OE12—P1—OL13 | 109.11 (8) | OE12$^{ii}$—Na—OW2 | 93.05 (6) |
| OE11—P1—OL13 | 109.55 (8) | OE31$^i$—Na—OW2 | 77.13 (6) |
| OE12—P1—OL12 | 108.66 (8) | OE21—Na—OW2 | 111.99 (6) |
| OE11—P1—OL12 | 107.51 (8) | OE31—Na—OE11 | 81.75 (5) |
| OL13—P1—OL12 | 100.02 (7) | OE12$^{ii}$—Na—OE11 | 161.02 (6) |
| OE22—P2—OE21 | 120.13 (9) | OE31$^i$—Na—OE11 | 99.05 (5) |
| OE22—P2—OL12 | 106.97 (8) | OE21—Na—OE11 | 75.12 (5) |
| OE21—P2—OL12 | 109.86 (8) | OW2—Na—OE11 | 75.08 (5) |

| | | | |
|---|---|---|---|
| OE22—P2—OL23 | 107.75 (8) | P2—OL12—P1 | 124.97 (8) |
| OE21—P2—OL23 | 109.85 (8) | P3—OL13—P1 | 126.01 (8) |
| OL12—P2—OL23 | 100.46 (7) | P3—OL23—P2 | 125.91 (8) |
| OE31—P3—OE32 | 118.65 (8) | P1—P2—P3 | 60.12 (2) |
| OE31—P3—OL13 | 111.59 (7) | P1—P3—P2 | 59.88 (2) |
| OE32—P3—OL13 | 107.25 (7) | P2—P1—P3 | 60.00 (2) |
| OE31—P3—OL23 | 110.23 (8) | H1W1—OW1—H2W1 | 108 (3) |
| OE32—P3—OL23 | 106.23 (8) | H1W2—OW2—H2W2 | 102 (4) |
| OL13—P3—OL23 | 101.38 (7) | N1—C1—C2$^{iii}$ | 112.7 (2) |
| OE31—Na—OE12$^{ii}$ | 115.11 (6) | C1$^{vi}$—C2—C3$^{iv}$ | 111.9 (2) |
| OE31—Na—OE31$^i$ | 81.04 (5) | C4—C3—C2$^{ii}$ | 112.9 (2) |
| OE12$^{ii}$—Na—OE31$^i$ | 92.49 (6) | C3—C4—C5 | 112.7 (2) |
| OE31—Na—OE21 | 86.33 (5) | C6$^v$—C5—C4 | 111.2 (2) |
| OE12$^{ii}$—Na—OE21 | 96.42 (6) | N2—C6—C5$^v$ | 112.9 (2) |
| OE31$^i$—Na—OE21 | 166.78 (6) | | |

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

### Table 2. Hydrogen-bonding geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| OW1—H1W1···OE22$^i$ | 0.74 (3) | 1.99 (3) | 2.729 (2) | 176 (3) |
| OW1—H2W1···OE22$^{ii}$ | 0.74 (3) | 2.08 (3) | 2.816 (2) | 170 (3) |
| OW2—H1W2···OE12$^{iii}$ | 0.80 (3) | 2.26 (3) | 3.010 (2) | 156 (3) |
| OW2—H2W2···OE32$^{iv}$ | 0.78 (5) | 2.22 (5) | 2.988 (2) | 172 (4) |
| N1—H1N1···OE11$^{iii}$ | 0.83 (3) | 2.16 (3) | 2.825 (2) | 138 (3) |
| N1—H2N1···OE32$^v$ | 0.89 (3) | 1.98 (3) | 2.861 (2) | 172 (2) |
| N1—H3N1···OE11 | 0.96 (3) | 2.05 (3) | 3.006 (2) | 177 (3) |
| N2—H1N2···OE21 | 0.87 (3) | 1.91 (3) | 2.775 (2) | 169 (2) |
| N2—H2N2···OE32$^v$ | 0.89 (3) | 1.99 (3) | 2.852 (2) | 164 (2) |
| N2—H3N2···OW1 | 0.88 (3) | 1.89 (3) | 2.740 (3) | 163 (2) |

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1172). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1997). C53, 1184–1186

# catena-Poly[[(5-ethyl-2-methylpyridine-N)copper(II)]-μ-(N-salicylideneglycinato-O,N,O':O'')]

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## Abstract

The title complex, [Cu(C$_9$H$_7$NO$_3$)(C$_8$H$_{11}$N)]$_n$, adopts a square-pyramidal Cu$^{II}$ coordination with the tridentate N-salicylideneglycinato Schiff base dianion (TSB$^{2-}$) and the 5-ethyl-2-methylpyridine ligand bound in the basal plane. The apex of the pyramid is occupied by the carboxylic O atom from the neighbouring chelate at an apical distance of 2.268 (2) Å, which is the shortest apical distance in this class of substances.

## Comment

Copper(II) complexes with tridentate Schiff base dianions of the N-salicylideneaminoalkanoato type (TSB$^{2-}$) represent a relatively simple model for studies of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes, which are of the general type [Cu(TSB)(*L*)]$_n$ (Warda, 1994), three donor atoms (O, N, O) of the Schiff base and a fourth donor atom from the neutral ligand *L* (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the Cu coordination can be square planar or square pyramidal when a neutral donor ligand is located in the apical site ($n = 1$; Ueki, Ashida, Sasada & Kakudo, 1969; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). If a phenolic O atom from a neighbouring molecule is apically coordinated, dimeric structures are formed ($n = 2$; Warda, 1994; Warda, Dahlke, Wocadlo, Massa & Friebel, 1997). $n = 4$ is found in the case of (4-ethylpyridine)(N-salicylideneglycinato)copper(II) (Warda, 1997). Polymeric struc-



(I)