

Structure of a Strontium Ethylenediammonium *cyclo*-Tetraphosphate Hydrate

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Abstract. Sr[NH₃(CH₂)₂NH₃]P₄O₁₂·5H₂O, $M_r = 555.70$, orthorhombic, *Pbca*, $a = 17.863$ (15), $b = 15.317$ (13), $c = 13.109$ (10) Å, $V = 3587$ (9) Å³, $Z = 8$, $D_x = 2.058$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 1.959$ mm⁻¹, $F(000) = 2240$, $T = 295$ K, final $R = 0.034$ for 2898 independent reflexions. P₄O₁₂⁴⁻ and (CH₂)₂(NH₃)₂²⁺ groups alternate in planes perpendicular to the *b* axis. Strontium coordination is a distorted dodecahedron comprising four O atoms and four water molecules. P₄O₁₂ rings alternate with SrO₈ polyhedra so as to form arrays parallel to *a*. Organic groups and arrays are interconnected by hydrogen bonds in a three-dimensional network.

Introduction. The title compound has been characterized during a systematic investigation of the systems (C₂H₁₀N₂)₂P₄O₁₂—M^{II}P₄O₁₂—H₂O for M^{II} = Ba, Sr, Pb, Ca, Cd, Mn, Co, Zn, Cu, Mg, Ni. Up to now, three types of ethylenediammonium *cyclo*-tetraphosphates have been determined. They have been recently described by Averbuch-Pouchot, Durif & Guitel (1988*a,b,c*) and correspond to the following chemical formulae: [eda]₂·P₄O₁₂·H₂O, Ca[eda]P₄O₁₂·15/2 H₂O and Cu[eda]₃(P₄O₁₂)₂·14H₂O — the structure type of a series of isotopic salts with M^{II} = Cd, Mn, Co, Zn, Cu, Mg, Ni.

Experimental. The process for the preparation of the title compound is identical to that used for all the salts of the series. Crystals were prepared by adding strontium carbonate and ethylenediamine in a stoichiometric ratio to a water solution of *cyclo*-tetraphosphoric acid kept at low temperature ($T < 278$ K); after slow evaporation large prisms with rectangular section are obtained. Density not measured. Crystal size: 0.32 × 0.26 × 0.22 mm. Philips PW1100 diffractometer, graphite monochromator. Systematic absences: $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$. 25 reflexions ($20 < \theta < 25^\circ$) for refining unit-cell dimensions. ω scan; 3827 non-zero unique reflexions collected ($3 < \theta < 25^\circ$), $h_{\max} = 26$, $k_{\max} = 22$, $l_{\max} = 19$. Scan width 1.20°, scan speed 0.03° s⁻¹, total background measuring time 10 s. Two intensity and orientation reference reflexions (006 and 00 $\bar{6}$), no significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods: MULTAN77 (Main, Lessinger, Woolfson, Germain &

Table 1. Final atomic coordinates and B_{eq} values

	x	y	z	B_{eq} (Å ²)
Sr	0.47692 (2)	0.27159 (3)	0.20082 (3)	1.549 (5)
P(1)	0.15903 (6)	0.18708 (7)	0.38882 (8)	1.21 (2)
P(2)	0.17730 (6)	0.67043 (7)	0.35497 (9)	1.21 (2)
P(3)	0.29259 (6)	0.17604 (7)	0.13637 (8)	1.24 (2)
P(4)	0.36586 (6)	0.64837 (8)	0.17296 (8)	1.33 (2)
O(E11)	0.1134 (2)	0.2324 (2)	0.8760 (2)	1.64 (5)
O(E12)	0.3503 (2)	0.8700 (2)	0.9790 (2)	2.00 (6)
O(L12)	0.2446 (2)	0.2190 (2)	0.3793 (2)	1.50 (5)
O(E21)	0.3805 (2)	0.2603 (2)	0.8465 (2)	1.78 (6)
O(E22)	0.1661 (2)	0.5959 (2)	0.4255 (3)	1.97 (6)
O(L23)	0.1933 (2)	0.6282 (2)	0.2437 (2)	1.24 (5)
O(E31)	0.1617 (2)	0.7565 (2)	0.1299 (2)	1.80 (6)
O(E32)	0.2990 (2)	0.1075 (2)	0.0581 (3)	2.07 (6)
O(L34)	0.2935 (2)	0.7927 (2)	0.6455 (2)	1.33 (5)
O(E41)	0.0683 (2)	0.2937 (2)	0.6643 (3)	1.95 (6)
O(E42)	0.3626 (2)	0.5645 (2)	0.1173 (3)	2.08 (6)
O(L41)	0.3505 (2)	0.6247 (2)	0.2908 (2)	1.38 (5)
O(W1)	0.0258 (2)	0.8961 (3)	0.6668 (3)	3.25 (8)
O(W2)	-0.0209 (2)	0.2532 (4)	-0.0094 (3)	3.94 (9)
O(W3)	-0.0191 (3)	0.8928 (3)	0.3316 (3)	3.73 (9)
O(W4)	0.4194 (2)	0.4628 (3)	0.4644 (4)	3.72 (9)
O(W5)	0.0512 (3)	0.5847 (3)	0.6056 (4)	5.2 (1)
N(1)	0.2578 (2)	0.4177 (3)	0.1218 (3)	2.03 (7)
N(2)	0.2009 (2)	0.4214 (3)	0.3978 (3)	1.87 (7)
C(1)	0.2075 (3)	0.0824 (3)	0.7109 (4)	1.82 (8)
C(2)	0.2520 (3)	0.4226 (3)	0.3084 (4)	1.80 (7)

Declercq, 1977) used. H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement on F , isotropic for H atoms. Unit weights. Final refinement cycles with 2898 reflexions corresponding to $I > 3\sigma_I$. Final $R = 0.034$ ($wR = 0.036$). $S = 2.927$. Max. $\Delta/\sigma = 0.07$. Max. peak height in the final difference Fourier synthesis 0.69 e Å⁻³. No extinction correction. $R = 0.052$ for the complete set of 3827 reflexions. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) *SDP* employed for all calculations. Computer used: Micro VAXII.

Discussion. Table 1 reports the final atomic coordinates.* Fig. 1 represents a partial projection of the atomic arrangement along the *b* axis showing the mean

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51206 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane of the P₄O₁₂ ring anion perpendicular to this direction. The main interatomic distances and bond angles in the P₄O₁₂ ring are given in Table 2. As for the anion of the Cu[eda]₃(P₄O₁₂)₂·14H₂O structure type, the ring has no symmetry element. Nevertheless, its conformation is quite regular: 2.902 < P—P < 2.968 Å, 88.97 < P—P—P < 90.75°, 127.7 < P—O—P < 134.2°.

All the (CH₂)₂(NH₃)₂⁺ groups lie in planes $y \approx \pm 0.08$ and $y \approx \pm 0.042$ alternating with anionic planes $y \approx \pm 0.17$ and $y = \pm 0.33$. The projection along the *a* axis drawn in Fig. 2 shows this type of stacking. The main geometrical features are reported in Table 2.

Table 2. Main interatomic distances (Å) and bond angles (°)

The P₄O₁₂ ring anion

P(1)O₄ tetrahedron

P(1)	O(E11)	O(L12)	O(L41)	O(E12)
O(E11)	1.488 (3)	105.1 (2)	110.1 (2)	121.2 (2)
O(L12)	2.460 (4)	1.610 (3)	102.6 (2)	110.4 (2)
O(L41)	2.540 (4)	2.513 (4)	1.610 (3)	106.0 (2)
O(E12)	2.586 (5)	2.538 (5)	2.469 (4)	1.480 (4)

P(2)O₄ tetrahedron

P(2)	O(E21)	O(L12)	O(L23)	O(E22)
O(E21)	1.485 (3)	106.7 (2)	109.9 (2)	120.2 (2)
O(L12)	2.486 (4)	1.613 (3)	102.1 (2)	110.4 (2)
O(L23)	2.544 (4)	2.514 (4)	1.621 (3)	106.1 (2)
O(E22)	2.574 (5)	2.544 (5)	2.483 (5)	1.483 (4)

P(3)O₄ tetrahedron

P(3)	O(E31)	O(L23)	O(L34)	O(E32)
O(E31)	1.481 (3)	110.1 (2)	106.4 (2)	120.7 (2)
O(L23)	2.531 (4)	1.606 (3)	102.7 (2)	105.9 (2)
O(L34)	2.481 (4)	2.515 (4)	1.615 (3)	109.7 (2)
O(E32)	2.567 (5)	2.458 (5)	2.526 (5)	1.473 (4)

P(4)O₄ tetrahedron

P(4)	O(E41)	O(L34)	O(L41)	O(E42)
O(E41)	1.478 (3)	106.5 (2)	110.1 (2)	121.0 (2)
O(L34)	2.482 (4)	1.618 (3)	101.7 (2)	110.1 (2)
O(L41)	2.533 (4)	2.503 (4)	1.610 (3)	105.8 (2)
O(E42)	2.575 (5)	2.540 (5)	2.465 (5)	1.479 (4)

P(1)—P(2)	2.968 (2)	P(2)—P(1)—P(4)	89.29 (3)
P(2)—P(3)	2.917 (2)	P(1)—P(2)—P(3)	87.86 (4)
P(3)—P(4)	2.902 (2)	P(2)—P(3)—P(4)	90.75 (4)
P(4)—P(1)	2.925 (2)	P(1)—P(4)—P(3)	88.97 (4)

P(1)—O(L12)—P(2)	134.2 (2)
P(2)—O(L23)—P(3)	129.4 (2)
P(3)—O(L34)—P(4)	127.7 (2)
P(4)—O(L41)—P(1)	130.6 (2)

The environment of Sr

Sr—O(E11)	2.638 (3)	Sr—O(W1)	2.608 (4)
Sr—O(E21)	2.617 (3)	Sr—O(W2)	2.539 (4)
Sr—O(E31)	2.655 (3)	Sr—O(W3)	2.637 (4)
Sr—O(E41)	2.605 (3)	Sr—O(W5)	2.580 (5)
Sr—P(1)	3.693 (1)	Sr—N(1)	4.627 (4)
Sr—P(2)	3.752 (1)	Sr—N(2)	4.790 (4)
Sr—P(3)	3.701 (1)	Sr—C(1)	4.827 (5)
Sr—P(4)	3.767 (1)	Sr—C(2)	4.845 (5)
Sr—Sr	6.5878 (6)	Sr—H(2W5)	2.40 (7)

The ethylenediammonium group

C(1)—N(1)	1.473 (6)	N(1)—C(1)—C(2)	110.5 (4)
C(1)—C(2)	1.508 (7)	C(1)—C(2)—N(2)	110.1 (4)
C(2)—N(2)	1.485 (6)		

Table 2 (cont.)

O(N)—H...O	O(N)—H	H...O	O(N)—H—O	O(N)—O
O(W1)—H(1W1)...O(W4)	0.75 (7)	2.29 (7)	161 (7)	3.007 (7)
O(W1)—H(2W1)...O(W3)		2.56 (7)	114 (4)	3.235 (6)
	1.20 (7)			
O(W1)—H(2W1)...O(W4)		2.63 (7)	117 (5)	3.007 (7)
O(W2)—H(1W2)...O(E21)	0.82 (5)	2.00 (5)	159 (5)	2.776 (5)
O(W2)—H(2W2)...O(E41)	0.75 (5)	2.21 (5)	147 (5)	2.870 (5)
O(W3)—H(1W3)...O(E12)	0.70 (6)	2.76 (6)	160 (6)	3.424 (6)
O(W3)—H(2W3)...O(W4)	0.95 (6)	1.77 (6)	174 (5)	2.712 (6)
O(W4)—H(1W4)...O(E32)	1.00 (6)	1.71 (6)	172 (5)	2.701 (5)
O(W4)—H(2W4)...O(E12)	0.64 (6)	2.22 (6)	168 (6)	2.849 (5)
O(W5)—H(1W5)...O(E42)	1.00 (7)	1.86 (7)	149 (6)	2.759 (6)
O(W5)—H(2W5)...O(W3)	1.12 (7)	2.37 (7)	133 (5)	3.237 (7)
N(1)—H(1N1)...O(E12)	0.81 (7)	2.00 (7)	163 (7)	2.786 (5)
N(1)—H(2N1)...O(E31)	0.90 (6)	1.99 (6)	165 (5)	2.860 (5)
N(1)—H(3N1)...O(E42)	1.17 (8)	1.81 (8)	158 (6)	2.926 (5)
N(2)—H(1N2)...O(E22)	0.90 (6)	1.91 (6)	157 (5)	2.768 (5)
N(2)—H(2N2)...O(E11)	0.92 (6)	1.93 (6)	173 (6)	2.842 (5)
N(2)—H(3N2)...O(E32)	0.86 (6)	1.91 (6)	176 (6)	2.771 (5)

H(1W1)—O(W1)—H(2W1)	101 (6)
H(1W2)—O(W2)—H(2W2)	114 (5)
H(1W3)—O(W3)—H(2W3)	90 (6)
H(1W4)—O(W4)—H(2W4)	103 (6)
H(1W5)—O(W5)—H(2W5)	90 (5)

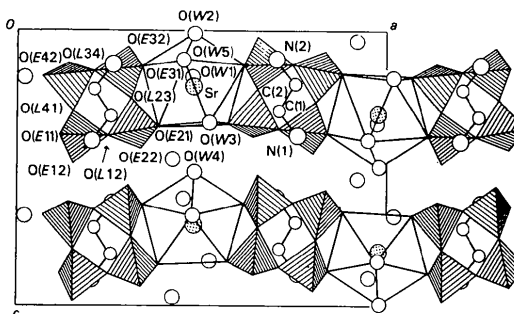


Fig. 1. Projection along the *b* axis of the atomic arrangement of Sr[(CH₂)₂(NH₃)₂]₂P₄O₁₂·5H₂O between $y = 0$ and $y = 0.50$.

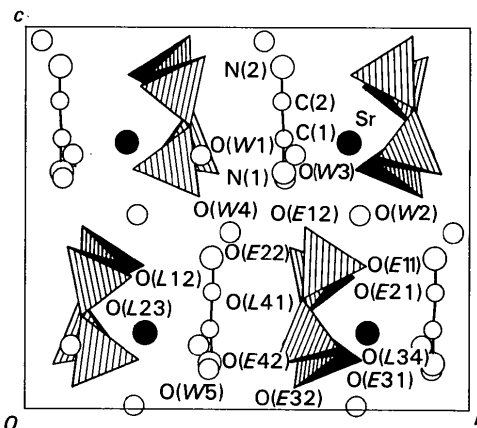


Fig. 2. Projection along the *a* axis of the atomic arrangement of Sr[(CH₂)₂(NH₃)₂]₂P₄O₁₂·5H₂O between $x = 0$ and $x = 0.50$.

The Sr atoms are located near the mirror plane c at $y \simeq \pm 0.25$. Each cation is surrounded by four O atoms and four water molecules with Sr—O distances ranging from 2.539 to 2.655 Å. The SrO_8 polyhedra are distorted dodecahedra isolated from one another by P_4O_{12} rings. The shortest Sr—Sr distance is 6.5878 (6) Å. Each dodecahedron alternates with a P_4O_{12} ring *via* two common oxygen atoms so as to form arrays along the 2_1 axis parallel to a (Fig. 1).

The four water molecules O(W1), O(W2), O(W3) and O(W5) which participate in the Sr coordination are located in planes perpendicular to the ring planes at $x \simeq 0$ and $x \simeq 0.5$, while the remaining water molecule O(W4) lies between the P_4O_{12} — SrO_8 arrays (Figs. 1 and 2).

Hydrogen bonds link together all the inorganic arrays and the organic groups. They form a three-

dimensional network, the geometrical features of which are described in Table 2.

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Structure of Guanidinium Tris(oxalato)chromate(III) Monohydrate

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Abstract. $[\text{C}(\text{NH}_2)_3]_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$, $M_r = 514.3$, monoclinic, $P2_1/n$, $a = 11.256$ (1), $b = 10.831$ (1), $c = 16.425$ (2) Å, $\beta = 91.47$ (1)°, $V = 2001.8$ (6) Å³, $Z = 4$, $D_x = 1.707$, $D_m = 1.69$ (1) Mg m⁻³ (by flotation), $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.638$ mm⁻¹, $F(000) = 1048$, $T = 293$ (1) K, $R = 0.040$ for 2539 observed reflections. The Cr atom is six-coordinated by O atoms from three slightly nonplanar oxalate groups in an octahedral configuration. The average Cr—O bond distance is 1.972 (5) Å. The coordination octahedra, guanidinium cations and one water molecule are interconnected by a net of hydrogen bonds.

Introduction. The first crystal structures of chromium(III) oxalate complexes with potassium and ammonium cations were studied by X-ray diffraction (van Niekerk & Schoening, 1952a,b). Owing to the moderate accuracy of the bond distances and the questionable water content the two structures were redetermined (Taylor, 1978; Merrachi, Mentzen & Chassagneux, 1986). Reinvestigation of ammonium tris(oxalato)chromate(III) trihydrate confirmed the presence of three water molecules as well as the expected isostructurality with ammonium tris(oxalato)gallate(III) trihydrate (Bulc, Golič & Šiftar, 1984).

X-ray structure determinations were also carried out on the chromium(III) complexes with monovalent cations (Bulc, Golič & Šiftar, 1982, 1985). In order to establish the influence of cations on the conformations and water content of the complexes, guanidinium tris(oxalato)chromate(III) monohydrate was prepared and its crystal structure determined.

Experimental. Dark violet crystals of the title compound were grown from an aqueous solution of chromium(III) oxalate and guanidinium oxalate (1:3). Crystal size 0.21 × 0.31 × 0.34 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo K α radiation. Cell parameters by least-squares refinement of 90 reflections within $9 < \theta < 16^\circ$; intensity measurement by ω – 2θ scan, ω -scan width (°) = $0.7 + 0.3 \tan \theta$, aperture (mm) = $2.4 + 0.9 \tan \theta$, max. scan time 40 s, $2\theta_{\text{max}} = 56^\circ$, $\frac{1}{4}$ sphere measured, with equality test ($\pm h, +k, -l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.66$ Å⁻¹, standard reflections 327, 2,0,10, 530; re-measured every 216 reflections, 4805 unique reflections measured ($h - 14/14, k 0/14, l - 21/0$), 2539 observed [$I > 3\sigma(I)$], no absorption correction applied. Patterson and Fourier methods, two-block-matrix least-squares refinement, anisotropic for all non-hydrogen atoms,