

Fig. 1. The coordination geometry of the Pt and Cu ions, surrounded by O ions.

According to Pauling's third rule (Pauling, 1939), the presence of shared edges or particularly shared faces of coordination polyhedra around highly charged ions decreases the stability of the structure. Thus, the structure of Er₂Ba₃Cu₂PtO₁₀ with face-shared polyhedra seems to be less stable than the structure of Er₂Ba₂CuPtO₈ which is composed of corner-shared polyhedra. In the solid-state reaction at 1323 K, Er₂Ba₃Cu₂PtO₁₀ is formed first but gradually reacts with platinum and changes into Er₂Ba₂CuPtO₈ after a long period (Saito, Shishido, Toyota, Ukei, Sasaki & Fukuda, 1991).

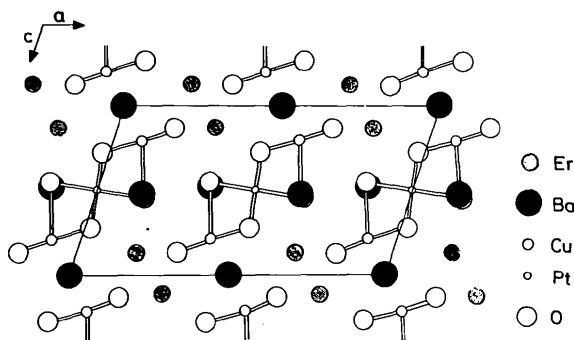


Fig. 2. Projection of the atomic arrangement of Er₂Ba₃Cu₂PtO₁₀ along the *b* axis.

while in R₂Ba₂CuPtO₈ the coordination polyhedra of Cu^{II} and Pt^{IV} are alternately connected sharing corners of the polyhedra to form one-dimensional chains (Saito *et al.*, 1990).

References

- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
 GEISER, U., PORTER, L. C., WANG, H. H., ALLEN, T. A. & WILLIAMS, J. M. (1988). *J. Solid State Chem.* **73**, 243–251.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 LALIGANT, Y., FERREY, G., HERVIEU, M. & RAVEAU, B. (1987). *Europhysics Lett.* **4**, 1023–1029.
 PAULING, L. (1939). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, pp. 396–400. New York: Cornell Univ. Press.
 SAITO, Y., SHISHIDO, T., TOYOTA, N., UKEI, K., SASAKI, T. & FUKUDA, T. (1991). *J. Cryst. Growth.* **109**, 426–431.
 SAITO, Y., UKEI, K., SHISHIDO, T. & FUKUDA, T. (1990). *Acta Cryst.* **C46**, 970–972.
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
 SHISHIDO, T., FUKUDA, T., TOYOTA, N., UKEI, K. & SASAKI, T. (1987). *J. Cryst. Growth*, **85**, 599–601.
 SWINNEA, J. S. & STEINFINK, H. (1987). *Acta Cryst.* **C43**, 2436–2437.
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
 UKEI, K., SHISHIDO, T. & FUKUDA, T. (1988). *Acta Cryst.* **C44**, 958–959.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1991). **C47**, 1368–1370

Structure of Ammonium Trithio-cyclo-triphosphate

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(Received 7 January 1991; accepted 28 January 1991)

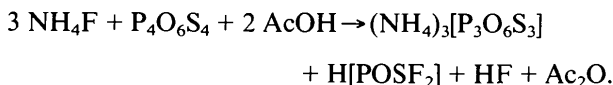
Abstract. (NH₄)₃[P₃O₆S₃], *M_r* = 339.225, orthorhombic, *Pnma*, *a* = 12.450 (8), *b* = 12.755 (8), *c* = 8.154 (6) Å, *V* = 1294.9 Å³, *Z* = 4, *D_x* = 1.739 Mg m⁻³, λ(Ag *Kα*) = 0.5608 Å, μ =

0.480 mm⁻¹, *F*(000) = 696, room temperature, final *R* = 0.041 for 1071 reflections. The P₃O₆S₃ ring anion has mirror symmetry. The S atoms are external atoms of the ring; two of them are located above the

ring plane, while one is below. The two different P atoms of the ring have a highly distorted tetrahedral coordination involving three O atoms and one S atom. The ammonium groups are connected to the ring anions by weak hydrogen bonds.

Introduction. In contrast to the chemistry and crystal chemistry of *cyclo*-triphosphates (for reviews see, for example, Kalliney, 1972; Durif, 1987), knowledge of thio-*cyclo*-phosphates is very poor. Up to now only some structural data on tetrathio-*cyclo*-tetrathosphates have been reported (Meisel, Wolf & Averbuch-Pouchot, 1990, and references therein). Ammonium trithio-*cyclo*-triphosphate was first prepared by reaction of $P_4O_6S_4$ with a saturated solution of ammonia in ethanol or methanol (Meisel, Neels & Wolf, unpublished).

Experimental. The process used to prepare crystals of the title compound is different from that mentioned above; $(NH_4)_3[P_3O_6S_3]$ was obtained by fluoridolysis of $P_4O_6S_4$ in glacial acetic acid. Fine-ground $P_4O_6S_4$ was added slowly to an ice-cooled solution of an excess of dry ammonium fluoride in glacial acetic acid. Under stirring within 2 h white crystals of $(NH_4)_3[P_3O_6S_3]$ began to precipitate. After further intensive stirring at room temperature for 1 h, the reaction was finished. To complete the crystallization the reaction mixture was stored in a refrigerator for 12 h. The crystals were isolated, washed with glacial acetic acid, ethanol and ether, twice in each case, and then dried under vacuum. The complicated reaction is described in a simple way by the following equation (for details see Wolf & Meisel, 1991):



$(NH_4)_3[P_3O_6S_3]$ was recrystallized once from a saturated aqueous solution at room temperature in the presence of undissolved crystals. The crystals appear as elongated prisms with a diamond-like section. Crystal size: $0.16 \times 0.24 \times 0.16$ mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 16 reflections ($10.0 < \theta < 11.0^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.20° , scan speed $0.02^\circ s^{-1}$. Total background measuring time 8 s. 1245 reflections collected ($3 < \theta < 25^\circ$), hkl ; $h_{max} = 20$, $k_{max} = 18$, $l_{max} = 10$. Two orientation and intensity control reflections ($50\bar{4}$, 504) measured every 6 h without any significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods with *MULTAN77* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F), isotropic

Table 1. Final atomic coordinates, B_{eq} for non-H atoms and B_{iso} for H atoms, with e.s.d.'s in parentheses

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

	x	y	z	B_{eq}/B_{iso} (\AA^2)
P(1)	0.88066 (8)	0.13484 (8)	0.1602 (1)	2.03 (1)
P(2)	1.0267 (1)	0.250	-0.0660 (2)	2.09 (2)
S(1)	0.92977 (9)	0.03778 (9)	0.3279 (1)	3.13 (2)
S(2)	1.1772 (2)	0.250	-0.0104 (4)	6.33 (6)
O(1)	0.8770 (3)	0.250	0.2415 (5)	2.26 (7)
O(2)	0.7783 (2)	0.1118 (2)	0.0736 (4)	3.04 (6)
O(3)	0.9722 (3)	0.1514 (2)	0.0240 (4)	3.54 (6)
O(4)	0.9882 (4)	0.250	-0.2367 (5)	3.8 (1)
N(1)	0.4060 (5)	0.750	0.9680 (7)	4.0 (1)
N(2)	0.3198 (3)	0.4308 (4)	0.7753 (5)	4.32 (9)
H(1N1)	0.433 (8)	0.750	0.08 (1)	7 (3)
H(2N1)	0.142 (7)	0.250	0.46 (1)	4 (2)
H(3N1)	0.075 (4)	0.196 (4)	0.422 (7)	5 (2)
H(1N2)	0.300 (4)	0.436 (4)	0.685 (6)	3 (1)
H(2N2)	0.228 (7)	0.620 (7)	0.349 (9)	9 (2)
H(3N2)	0.123 (5)	0.914 (5)	0.278 (7)	5 (2)
H(4N2)	0.296 (6)	0.500 (7)	0.822 (9)	8 (2)

for H atoms. Unit weights. Final refinements with 1071 reflections corresponding to $I > 3\sigma$. Final $R = 0.041$ ($wR = 0.042$), $S = 1.382$, max. $\Delta/\sigma = 0.02$, max. peak height in the final difference Fourier synthesis = $0.652 e \text{\AA}^{-3}$. No secondary-extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX II. Table 1 reports the final atomic coordinates.*

The drawings were made using *STRUPLO* (Fischer, 1985).

Discussion. The trithio-*cyclo*-triphosphate anion has m symmetry and is made up of a ring of three PO_3S tetrahedra sharing corners. These tetrahedra are strongly distorted, the longest vertex corresponding to the P—S bond. The P—O bridging bonds (1.606 – 1.612\AA) are about 9% longer than the P—O terminal bonds (1.473 – 1.486\AA). Two of the three external S atoms of the ring are located above the ring plane while one is below. Compared with the P—S bond lengths of ionic dithiophosphates (1.96 – 1.98\AA) and with the average P—S single bond distance (2.03\AA ; Corbridge, 1974), the shortened P—S bonds (1.928 – 1.943\AA) found in $(NH_4)_3[P_3O_6S_3]$ show distinct evidence for the π character of the P—S bond, showing that there is no strong mesomeric exchange of charge between the external P—O

* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53951 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Main interatomic distances (Å) and bond angles (°) in the atomic arrangement of $(\text{NH}_4)_3[\text{P}_3\text{O}_6\text{S}_3]$, with e.s.d.'s in parentheses

The $\text{P}_3\text{O}_6\text{S}_3$ ring anion

The P(1)O₃S tetrahedron

P(1)	S(1)	O(1)	O(2)	O(3)
S(1)	1.943 (1)	2.873 (2)	2.957 (3)	2.919 (3)
O(1)	107.5 (1)	1.612 (2)	2.548 (4)	2.476 (4)
O(2)	118.6 (1)	110.6 (2)	1.486 (3)	2.500 (4)
O(3)	110.3 (1)	100.6 (2)	107.9 (2)	1.605 (3)

The P(2)O₃S tetrahedron

P(2)	S(2)	O(3)	O(3)	O(4)
S(2)	1.928 (2)	2.859 (4)	2.859 (4)	2.991 (5)
O(3)	107.7 (1)	1.606 (3)	2.515 (4)	2.478 (5)
O(3)	107.7 (1)	103.0 (2)	1.606 (3)	2.478 (5)
O(4)	122.6 (2)	107.1 (2)	107.1 (2)	1.473 (5)

P(1)—P(1)	2.938 (1)	P(1)—O(1)—P(1)	131.3 (2)
P(1)—P(2)	2.977 (2)	P(1)—O(3)—P(2)	136.0 (2)

P(1)—P(1)—P(2)	60.44 (3)
P(1)—P(2)—P(1)	59.12 (4)

The N(1)O₆ polyhedron

N(1)—O(1)	3.273 (7)	(× 2)
N(1)—O(2)	2.913 (5)	(× 2)
N(1)—O(4)	2.744 (7)	(× 2)

The N(2)O₇ polyhedron

N(2)—S(1)	3.430 (4)	N(2)—S(1)	3.497 (4)
N(2)—S(2)	3.395 (5)	N(2)—O(2)	2.942 (5)
N(2)—O(2)	2.882 (5)	N(2)—O(3)	3.264 (5)
N(2)—O(4)	3.132 (6)		

The hydrogen bonds

N—H...O(S)	N—H	H...O(S)	N—O(S)	N—H...O(S)
N(1)—H(1N1)...O(4)	1.0 (1)	1.75 (10)	2.744 (7)	166 (9)
N(1)—H(2N1)...O(2)	0.61 (8)	2.45 (6)	2.913 (5)	134 (1)
N(1)—H(3N1)...S(1)	0.82 (5)	2.81 (5)	3.580 (4)	156 (5)
N(2)—H(1N2)...O(2)	0.78 (2)	2.21 (5)	2.942 (5)	157 (5)
N(2)—H(2N2)...S(2)	1.06 (8)	2.33 (8)	3.395 (5)	173 (7)
N(2)—H(3N2)...O(4)	0.74 (6)	2.53 (6)	3.132 (6)	139 (6)
N(2)—H(4N2)...O(2)	1.06 (8)	1.90 (8)	2.888 (5)	166 (7)

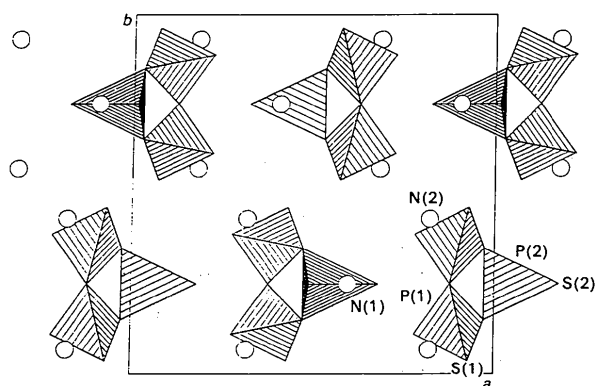


Fig. 1. Projection along the *c* direction of the atomic arrangement of $(\text{NH}_4)_3[\text{P}_3\text{O}_6\text{S}_3]$. H atoms have been omitted.

and P—S linkages [most of the observed P=S bond lengths in thiophosphoryl compounds lie in the range 1.85–1.96 Å; the average P=S bond distance is 1.92 Å (Corbridge, 1974)]. The main geometrical

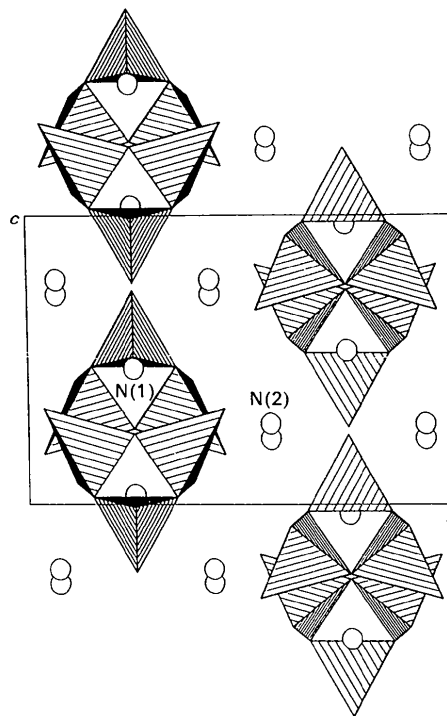


Fig. 2. Projection along the *a* direction of the atomic arrangement of $(\text{NH}_4)_3[\text{P}_3\text{O}_6\text{S}_3]$. H atoms have been omitted.

features of the $\text{P}_3\text{O}_6\text{S}_3$ ring anion are reported in Table 2. As expected each H atom is involved in a hydrogen bridge either to an O atom or to an S atom. Three bridges terminate on O(2), two on O(4), two on S(1) and one on S(2). The main geometrical features of the hydrogen-bond scheme are given in Table 2. Most of the distances lie in the normal range except the relatively short N(2)—H(2N2)...S(2) bond [2.33 (8) Å] compared with the relatively long N(2)—H(3N2)...O(4) bond [2.53 (6) Å]. Figs. 1 and 2 show, respectively, the projection along *c* and *a* of the atomic arrangement of $(\text{NH}_4)_3[\text{P}_3\text{O}_6\text{S}_3]$.

References

- CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*. Amsterdam: Elsevier.
- DURIF, A. (1987). *The Chemistry of Inorganic Homo- and Heterocycles*, Vol. 2. pp. 659–679. London: Academic Press.
- Enraf-Nonius (1977). *Structure Determination Package*, version RSX11M. Enraf-Nonius, Delft, The Netherlands.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- KALLINEY, S. Y. (1972). In *Topics in Phosphorus Chemistry*, Vol. 7, pp. 255–310. New York: Interscience.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MEISEL, M., WOLF, G. U. & AVERBUCH-POUCHOT, M. T. (1990). *Acta Cryst.* **C46**, 2239–2241.
- WOLF, G.-U. & MEISEL, M. (1991). In preparation.