Acta Cryst. (1996). C**52**, 2645–2647

Triammonium Trimetaphosphimate Monohydrate

Norbert Stock and Wolfgang Schnick

Laboratorium für Anorganische Chemie der Universität, Universitätsstrasse 30, D-95440 Bayreuth, Germany. E-mail: wolfgang.schnick@uni-bayreuth.de

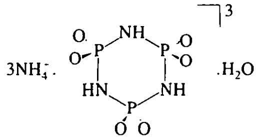
(*Received 23 April 1996; accepted 24 May 1996*)

Abstract

Crystals of triammonium *cyclo*-tri-μ-imido-triphosphate monohydrate, $(NH_4)_3(PO_2NH)_3.H_2O$, are composed of three ammonium cations, a trimetaphosphimate anion with a chair conformation and a water molecule per asymmetric unit. A three-dimensional network is formed by N—H···O and O—H···O hydrogen bonds.

Comment

In order to synthesize silicate-analogous framework structures built up from PN_4 tetrahedra (Schnick, Horstmann & Häser, 1996) with a defined partial substitution of nitrogen by oxygen, we have started a systematic investigation of soluble P–O–N compounds (Stock & Schnick, 1996) and have now isolated the title compound, (I).



(I)

Although many salts of trimetaphosphimic acid with monovalent cations have been described from as early as 1895 (Stokes, 1895) and characterized (Herzog & Nielsen, 1958), only the crystal structures of $Na_3(PO_2NH)_3.4H_2O$, $H_3(PO_2NH)_3.2H_2O$ and $(NH_4)H_2(PO_2NH)_3.CH_3OH$ have been reported (Attig & Mootz, 1976; Olthof, Migchelsen & Vos, 1965). Trimetaphosphimate salts with divalent and trivalent cations have also been described (Sokol, Porai-Koshits, Berdnikov, Rozanov & Butman, 1979; Rozanov, Medvedeva, Beresnev, Sokolov & Sokol, 1981).

The molecular structure of the title compound is shown in Fig. 1. In contrast to $H_3(PO_2NH)_3.2H_2O$ and $(NH_4)H_2(PO_2NH)_3.CH_3OH$ but in analogy to $Na_3(PO_2NH)_3.4H_2O$, the P–N ring in the title compound exhibits the approximate symmetry $3m$, as may be seen from the bond lengths and valence angles. As observed in the sodium salt, one imido H atom causes a reduction of the symmetry of the anion to m. This arises from intermolecular hydrogen bonds (Attig & Mootz, 1976). Each H atom of the imido groups is involved in N—H···O hydrogen bonding [N···O 2.884 (1), 2.910 (1), 2.813 (1) Å], thus forming a three-dimensional network (Fig. 2). In addition, all the H atoms of the water molecule and the ammonium cations form O—H···O and O—H···N hydrogen bonds [N···O 2.731 (1)–2.997 (1) Å; O···O 2.862 (1) and 2.812 (1) Å] (Table 3). In analogy to $(NH_4)H_2(PO_2NH)_3.CH_3OH$, the ammonium cations are distorted from ideal tetrahedral geometry.

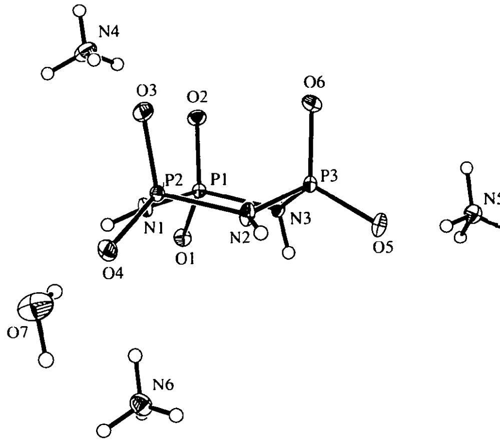


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary size.

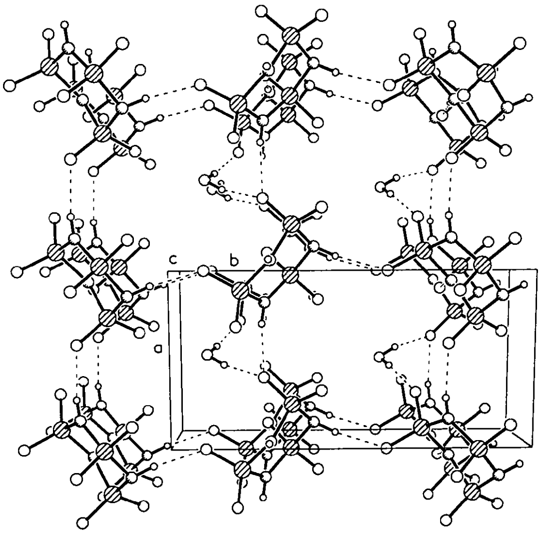


Fig. 2. View of the crystal packing of the trimetaphosphimate rings and the water molecules illustrating the hydrogen bonds. The ammonium ions are omitted for clarity.

Experimental

The starting material $Na_3(PO_2NH)_3.4H_2O$ was obtained according to the method of Nielsen & Morrow (1960). Ammonium trimetaphosphimate was prepared by a similar method to that of Stokes (1896). To a 3×10^{-4} *M* solution of $Ag_3(PO_2NH)_3$ in water and ammonia a stoichiometric amount of NH_4Br was added and the precipitated AgBr was removed. $Ag_3(PO_2NH)_3$ was obtained by the addition of excess 0.1 *M* $AgNO_3$ to a 3×10^{-4} *M* solution of $Na_3(PO_2NH)_3.4H_2O$. Suitable crystals were grown by diffusion-controlled addition of methanol to a 1×10^{-4} *M* solution of trimetaphosphimate monohydrate in water.

Crystal data

$(NH_4)_3(PO_2NH)_3.H_2O$
$M_r = 306.11$
Monoclinic
$P2_1$
$a = 6.5712\ (6)$ Å
$b = 12.9917\ (6)$ Å
$c = 6.9237\ (3)$ Å
$\beta = 102.133\ (6)°$
$V = 577.88\ (6)$ Å^3
$Z = 2$
$D_x = 1.759$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 49 reflections
$\theta = 6.1–15.16°$
$\mu = 0.549$ mm^{-1}
$T = 153\ (2)$ K
Platelet
$0.50 \times 0.45 \times 0.2$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3517 measured reflections
3106 independent reflections
3048 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0129$

$\theta_{\rm max} = 29.28°$
$h = -9 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 97 reflections intensity decay: 4.22%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0167$
$wR(F^2) = 0.0447$
$S = 1.129$
3106 reflections
163 parameters
H atoms refined using a riding model starting from Fourier coordinates
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.9697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.385$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.266$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.169 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.07 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P1	0.02535 (4)	0.33316 (2)	0.72015 (4)	0.00744 (6)
P2	0.10742 (4)	0.19652 (2)	1.07928 (4)	0.00771 (7)
P3	−0.25397 (4)	0.33577 (2)	0.99785 (4)	0.00800 (6)
O1	0.16375 (13)	0.41095 (7)	0.64863 (12)	0.0119 (2)
O2	−0.10457 (13)	0.26666 (7)	0.56206 (11)	0.0118 (2)
O3	−0.0006 (2)	0.09673 (6)	1.00781 (14)	0.0131 (2)
O4	0.30004 (13)	0.18524 (7)	1.24027 (12)	0.0136 (2)
O5	−0.34141 (14)	0.41494 (7)	1.11523 (13)	0.0133 (2)
O6	−0.39934 (13)	0.25751 (7)	0.88222 (13)	0.0136 (2)
O7	0.4847 (2)	0.09424 (8)	1.60331 (15)	0.0241 (2)
N1	0.17490 (15)	0.25983 (8)	0.89190 (14)	0.0094 (2)
N2	−0.0590 (2)	0.27646 (8)	1.15341 (14)	0.0117 (2)
N3	−0.1355 (2)	0.39647 (8)	0.83702 (14)	0.0085 (2)
N4	0.0383 (2)	0.06228 (8)	0.6223 (2)	0.0170 (2)
N5	−0.6011 (2)	0.55749 (8)	0.9022 (2)	0.0147 (2)
N6	0.4845 (2)	0.35738 (8)	1.4433 (2)	0.0156 (2)

Table 2. *Selected geometric parameters (Å, °)*

P1—O2	1.5101 (8)	P2—N2	1.6654 (10)
P1—O1	1.5110 (9)	P2—N1	1.6728 (10)
P1—N1	1.6721 (10)	P3—O5	1.4983 (9)
P1—N3	1.6758 (10)	P3—O6	1.5052 (9)
P2—O4	1.5077 (9)	P3—N2	1.6779 (10)
P2—O3	1.5104 (9)	P3—N3	1.6830 (10)
O2—P1—O1	115.63 (5)	N2—P2—N1	103.34 (5)
O2—P1—N1	110.35 (5)	O5—P3—O6	118.64 (5)
O1—P1—N1	108.05 (5)	O5—P3—N2	107.17 (5)
O2—P1—N3	108.24 (5)	O6—P3—N2	110.17 (5)
O1—P1—N3	108.31 (5)	O5—P3—N3	108.70 (5)
N1—P1—N3	105.80 (5)	O6—P3—N3	107.14 (5)
O4—P2—O3	114.98 (6)	N2—P3—N3	104.06 (5)
O4—P2—N2	109.66 (5)	P1—N1—P2	128.29 (6)
O3—P2—N2	110.03 (6)	P2—N2—P3	123.42 (6)
O4—P2—N1	107.64 (5)	P1—N3—P3	121.06 (6)
O3—P2—N1	110.54 (5)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	D···A	H···A	D—H···A
N1—H1···O6$^{\rm i}$	0.799 (1)	2.813 (1)	2.021 (1)	171.1 (1)
N2—H2···O2$^{\rm ii}$	0.872 (1)	2.910 (1)	2.043 (1)	172.9 (1)
N3—H3···O3$^{\rm iii}$	0.887 (1)	2.884 (1)	2.003 (1)	172.2 (1)
N4—H4A···O1$^{\rm iv}$	0.830 (1)	2.846 (1)	2.016 (1)	177.2 (1)
N4—H4B···O3	0.840 (1)	2.771 (1)	1.985 (1)	155.4 (1)
N4—H4C···O2	0.795 (1)	2.818 (1)	2.052 (1)	161.8 (1)
N4—H4D···O7$^{\rm v}$	0.855 (1)	2.993 (2)	2.157 (2)	165.8 (1)
N5—H5A···O4$^{\rm iii}$	0.908 (1)	2.909 (1)	2.043 (1)	158.9 (1)
N5—H5B···O1$^{\rm vi}$	0.934 (1)	2.820 (1)	1.903 (1)	167.1 (1)
N5—H5C···O5	0.913 (1)	2.731 (1)	1.842 (1)	163.7 (1)
N5—H5D···O6$^{\rm iii}$	0.747 (1)	2.997 (1)	2.371 (1)	142.3 (1)
N5—H5D···O3$^{\rm iii}$	0.747 (1)	2.861 (1)	2.343 (1)	127.7 (1)
N6—H6A···O1$^{\rm ii}$	0.761 (1)	2.865 (1)	2.127 (1)	163.8 (1)
N6—H6B···O5$^{\rm i}$	0.893 (1)	2.849 (1)	2.089 (1)	142.4 (1)
N6—H6C···O4	0.865 (1)	2.780 (1)	1.936 (1)	164.8 (1)
N6—H6D···O2$^{\rm vii}$	0.809 (1)	2.902 (1)	2.137 (1)	157.7 (1)
O7—H7A···O4	0.776 (1)	2.812 (1)	2.038 (1)	175.3 (1)
O7—H7B···O6$^{\rm vii}$	0.855 (1)	2.862 (1)	2.030 (1)	164.0 (1)

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

The absolute structure was checked by refinement of the Flack (1983) parameter and revealed to be correct. The origin was fixed by the method of Flack & Schwarzenbach (1988). All H atoms could be unambiguously located after the anisotropic refinement of all non-H atoms. The ω-scan width was 1.2° with an ω-scan rate of 2.5° min^{-1}. The background-to-signal ratio was 0.5.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Financial support by the Deutsche Forschungsgemeinschaft (project SCHN 377/6-1 and Gottfried Wilhelm Leibniz program) and the Fonds der Chemischen Industrie is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Attig, R. & Mootz, D. (1976). *Z. Anorg. Allg. Chem.* **419**, 139–156.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.

Herzog, A. H. & Nielsen, M. L. (1958). *Anal. Chem.* **30**, 1490–1496.

Nielsen, M. L. & Morrow, T. J. (1960). *Inorg. Synth.* **6**, 99.

Olthof, R., Migchelsen, T. & Vos, A. (1965). *Acta Cryst.* **19**, 596–603.

Rozanov, I. A., Medvedeva, Y. La., Beresnev, E. N., Sokolov, Yu. A. & Sokol, V. I. (1981). *Zh. Neorg. Khim.* **26**, 668–676.

Schnick, W., Horstmann, S. & Häser, M. (1996). *Phosphorus Sulfur*, **109/110**, 93–96.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1994). *SHELXTL/PC.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sokol, V. I., Porai-Koshits, M. A., Berdnikov, V. R., Rozanov, I. A. & Butman, L. A. (1979). *Koord. Khim.* **5**, 1093–1102.

Stock, N. & Schnick, W. (1996). *Z. Naturforsch. Teil B.* In the press.

Stokes, H. N. (1895). *Ber. Dtsch. Chem. Ges.* **28**, 437.

Stokes, H. N. (1896). *Am. Chem. J.* **18**, 629–663.

Acta Cryst. (1996). **C52**, 2647-2650

Refinement of the Superstructure of *C*-Type Chromium(III) Tris(metaphosphate), $Cr(PO_3)_3$

Michael Gruss and Robert Glaum

Institut für Anorganische und Analytische Chemie, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany. E-mail: robert.glaum@anorg.chemie.uni-giessen.de

(*Received 10 April 1996; accepted 29 May 1996*)

Abstract

Single crystals of $Cr(PO_3)_3$ suitable for X-ray investigations were obtained under various experimental conditions that favour volatilization of the phosphate and its recrystallization from the gas phase. The compound belongs to the series of phosphates $M(PO_3)_3$ (M^{3+} = Al, In, Sc, Ti, V, Fe, Mo, Rh, Ru) which adopt the *C*-type structure, characterized by one-dimensional infinite metaphosphate chains and isolated MO_6 octahedra. Associated with the superstructure generally found for this structure type, in which the monoclinic *b* axis is tripled, three crystallographically different CrO_6 octahedra of almost ideal geometry [d_{ave}(Cr—O) = 1.96 (2) Å] were observed. Within the two independent metaphosphate chains distinctly different bond distances from P to bridging and terminal O atoms were found [d_{ave}(P—O_b) = 1.58 (1), d_{ave}(P—O_t) = 1.49 (1) Å].

Comment

C-Type $Cr(PO_3)_3$ is one of the six polymorphic modifications of this compound that have been reported in the literature (Rémy & Boullé, 1972). Up to now only the *B*-type structure (described as $Cr_2P_6O_{18}$; Bagieu-Beucher & Guitel, 1977) and the atomic arrangement of the subcell of *C*-$Cr(PO_3)_3$ (Yakubovich, Dimitrova & Savina, 1991) have been refined using X-ray single crystal data. In the paper by Yakubovich *et al.* (1991), anomalously high displacement coefficients for some atoms together with unreasonable P—O distances indicate the necessity of a refinement of the complete structure to obtain reliable information on interatomic distances and bond angles. The unit cell of the substructure of *C*-$Cr(PO_3)_3$ given by Yakubovich *et al.* (1991) [*Ia*, $Z = 4$, $a = 9.367\,(6)$, $b = 6.344\,(8)$, $c = 10.544\,(8)$ Å, $\beta = 98.00\,(6)°$] is related by the transformation matrix $T = (-1\ 0\ -1,\ 0\ 3\ 0,\ 1\ 0\ 0)$ to the cell of the superstructure reported here.

Additional motivation for a detailed structure investigation of *C*-$Cr(PO_3)_3$ was drawn from polarized single-crystal UV/visible spectra of *C*-$Ti(PO_3)_3$ (Glaum & Hitchman, 1996). These measurements revealed the existence of three slightly differently distorted TiO_6 octahedra in agreement with a structure refinement published recently (Harrison, Gier & Stucky, 1994). This observation convincingly demonstrates once more that understanding of structure–property relationships can be reached only on the basis of complete structural information.

C-$Cr(PO_3)_3$ is a member of a series of isotypical tris(metaphosphates) $M(PO_3)_3$ [M = Al (van der Meer, 1976), In (Bentama, Durand & Cot, 1988), Sc (Domanskii, Shepelev, Smolin & Litvin, 1982), Ti (Harrison, Gier & Stucky, 1994), V (Middlemiss, Hawthorne & Calvo, 1977), Mo (Watson, Borel, Chardon & Leclaire, 1994), Ru (Fukuoka, Imoto & Saito, 1995), Rh (Rittner & Glaum, 1994)] for which the structures have been refined from single crystal data. *C*-$Fe(PO_3)_3$ also belongs to this series, but has been characterized so far from powder data only (Rémy & Boullé, 1972). The general aspects of the structure type have been described and discussed extensively in the references above, so apart from the specific crystallographic parameters found in this work, only a short discussion of the structure is appropriate.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996