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Structures of Ethylenediammonium Monohydrogentetraoxophosphate(V) and Ethylenediammonium Monohydrogentetraoxoarsenate(V)

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USTMG, 166X, 38042 Grenoble CEDEX, France

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Abstract. (I): C₂H₁₀N₂⁺.HPO₄²⁻, *M_r* = 158.09, monoclinic, *P*2₁/*a*, *a* = 8.059 (3), *b* = 11.819 (5), *c* = 7.513 (3) Å, β = 110.12 (5)°, *V* = 672 (1) Å³, *Z* = 4, *D_x* = 1.562 Mg m⁻³, λ(Ag Kα) = 0.5608 Å, μ = 0.198 mm⁻¹, *F*(000) = 336, *T* = 295 K, final *R* = 0.030 for 1286 unique reflexions. (II): C₂H₁₀N₂⁺.HAsO₄²⁻, *M_r* = 202.04, monoclinic, *P*2₁/*c*, *a* = 10.433 (9), *b* = 8.163 (6), *c* = 8.062 (6) Å, β = 90.33 (7)°, *V* = 687 (2) Å³, *Z* = 4, *D_x* = 1.953 Mg m⁻³, λ(Ag Kα) = 0.5608 Å, μ = 2.740 mm⁻¹, *F*(000) = 408, *T* = 295 K, final *R* = 0.038 for 1499 unique reflexions. In both cases planes of XO₄H²⁻ tetrahedra alternate with planes of (CH₂)₂(NH₃)₂⁺ groups. In the first type of planes, XO₄H tetrahedra are associated in pairs forming X₂O₈H₂⁺ groups. (CH₂)₂(NH₃)₂⁺ groups are centrosymmetric for *X* = As, pseudocentrosymmetric for *X* = P.

Introduction. During investigations of interactions of ethylenediamine with various kinds of acidic monophosphates or monoarsenates we very often observed the formation of very stable compounds corresponding to the formula H₃XO₄(CH₂)₂(NH₂)₂ (*X* = P, As). These compounds appeared later to be interesting starting materials for further syntheses. The present work is devoted to a detailed structural investigation of these two species.

Experimental. (I) C₂H₁₀N₂⁺.HPO₄²⁻. Single crystals are easily prepared by slow evaporation at room temperature of an aqueous solution of H₃PO₄ and ethylenediamine in stoichiometric ratio. Crystals appear as stout, multifaceted, monoclinic prisms. Crystal size: 0.24 × 0.24 × 0.30 mm. Density not measured. Philips

PW 1100 diffractometer, graphite monochromator. Systematic absences: *h*0*l*: *h* = 2*n*; 0*k*0: *k* = 2*n*. 24 reflexions (10 < θ < 14°) for refining unit-cell dimensions. ω scan. 2229 non-zero unique reflexions collected (3 < θ < 30°), ±*h*,*k*,*l*, *h*_{max} = 13, *k*_{max} = 20, *l*_{max} = 12. Scan width 1.40°, scan speed 0.03° s⁻¹, total background measuring time 10 s. Two intensity and orientation reference reflexions ($\bar{6}52$ and 652), no variation. Lorentz and polarization correction, no absorption correction. Structure solved by classical methods (Patterson and successive Fourier syntheses). H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement (on *F*), isotropic for H atoms. Unit weights. Final refinement cycles with 1286 reflexions corresponding to *I* > 6σ_{*I*}. Final *R* = 0.030 (*ωR* = 0.035). *S* = 0.655. Max. Δ/σ = 0.00. Max. peak height in the final difference Fourier synthesis 0.39 e Å⁻³. No extinction correction. *R* = 0.054 for the complete set of 2229 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: PDP 11/70.

(II) C₂H₁₀N₂⁺.HAsO₄²⁻. The chemical preparation from H₃AsO₄ and ethylenediamine is identical to that described for (I). The morphology of the crystals obtained is close to that of the phosphorus complex. Crystal size: 0.30 × 0.30 × 0.24 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: *h*0*l*: *l* = 2*n*; 0*k*0: *k* = 2*n*. 18 reflexions (10 < θ < 12°) for refining unit-cell dimensions. ω scan. 2804 non-zero unique reflexions collected (3 < θ < 30°), ±*h*,*k*,*l*, *h*_{max} = 16, *k*_{max} = 14, *l*_{max} = 14. Scan width 1.30°, scan speed

0.03° s⁻¹, total background measuring time 10 s. Two intensity and orientation reference reflexions (130 and $\bar{1}\bar{3}0$) measured every 2 h without significant variation. Lorentz and polarization correction, no absorption correction. Structure solved by classical methods (Patterson and successive Fourier syntheses). H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 1499 reflexions corresponding to $I > 9\sigma_I$. Final $R = 0.038$ ($wR = 0.043$). $S = 1.485$. Max. $\Delta/\sigma = 0.06$ [B of H(2N2)].

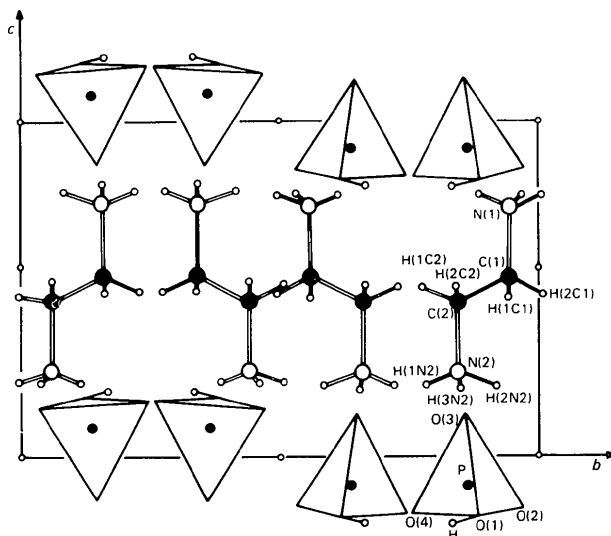


Fig. 1. Projection along the a direction of the atomic arrangement of $\text{HPO}_4(\text{NH}_3)_2(\text{CH}_2)_2$.

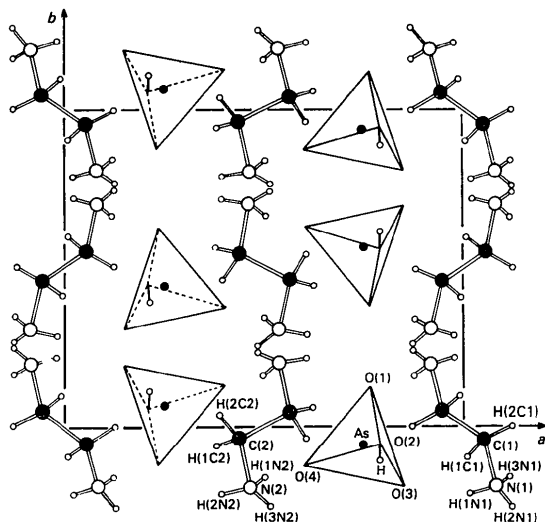


Fig. 2. Projection along the c direction of the atomic arrangement of $\text{HAsO}_4(\text{NH}_3)_2(\text{CH}_2)_2$.

Table 1. Final atomic coordinates, B_{eq} for non-H atoms and B_{iso} for H atoms in $\text{HPO}_4(\text{NH}_3)_2(\text{CH}_2)_2$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
P	0.24191 (7)	0.13601 (5)	0.08489 (7)	1.126 (8)
O(1)	0.9061 (2)	0.8820 (1)	0.8223 (2)	2.00 (3)
O(2)	0.6426 (2)	0.9694 (1)	0.8584 (2)	1.67 (3)
O(3)	0.3473 (2)	0.6450 (2)	0.1307 (2)	1.72 (3)
O(4)	0.8422 (2)	0.2559 (1)	0.1652 (2)	1.97 (3)
N(1)	0.2861 (2)	0.9430 (2)	0.7436 (3)	1.64 (4)
N(2)	0.2211 (2)	0.8427 (2)	0.2487 (2)	1.58 (4)
O(1)	0.2814 (3)	0.4394 (2)	0.4646 (3)	2.18 (5)
O(2)	0.2926 (3)	0.8410 (2)	0.4593 (3)	1.85 (5)
H	0.042 (5)	0.166 (4)	0.183 (6)	6.6 (12)
H(1C1)	0.919 (5)	0.060 (4)	0.524 (6)	6.3 (11)
H(2C1)	0.738 (5)	0.494 (3)	0.484 (5)	4.1 (8)
H(1C2)	0.726 (4)	0.227 (3)	0.493 (4)	3.3 (8)
H(2C2)	0.073 (4)	0.338 (3)	0.499 (5)	4.2 (8)
H(1N1)	0.749 (3)	0.114 (3)	0.219 (4)	2.1 (6)
H(2N1)	0.101 (4)	0.457 (3)	0.236 (5)	3.9 (8)
H(3N1)	0.262 (4)	0.505 (3)	0.221 (4)	2.9 (7)
H(1N2)	0.238 (4)	0.280 (3)	0.790 (4)	3.1 (7)
H(2N2)	0.219 (4)	0.415 (3)	0.791 (5)	4.4 (9)
H(3N2)	0.402 (4)	0.343 (3)	0.780 (5)	4.0 (8)

Table 2. Final atomic coordinates, B_{eq} for non-H atoms and B_{iso} for H atoms in $\text{HAsO}_4(\text{NH}_3)_2(\text{CH}_2)_2$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
As	0.24979 (5)	0.06941 (6)	0.09305 (6)	1.212 (9)
O(1)	0.2323 (3)	0.8743 (4)	0.1546 (4)	1.60 (8)
O(2)	0.7903 (5)	0.5566 (5)	0.6155 (4)	2.9 (1)
O(3)	0.1847 (4)	0.3050 (5)	0.6909 (5)	2.4 (1)
O(4)	0.5991 (4)	0.6297 (5)	0.3887 (5)	2.3 (1)
N(1)	0.0816 (4)	0.6939 (5)	0.9306 (5)	1.51 (9)
N(2)	0.5379 (4)	0.1983 (6)	0.3905 (5)	1.8 (1)
C(1)	0.9449 (5)	0.4517 (6)	0.9660 (6)	1.8 (1)
C(2)	0.4375 (5)	0.5402 (6)	0.0247 (6)	1.9 (1)
H	0.211 (6)	0.388 (8)	0.328 (8)	3. (1)
H(1C1)	0.009 (10)	0.597 (14)	0.136 (12)	8. (3)
H(2C1)	0.876 (8)	0.498 (11)	0.975 (10)	5. (2)
H(1C2)	0.622 (11)	0.060 (5)	0.549 (13)	8. (3)
H(2C2)	0.606 (6)	0.539 (8)	0.907 (8)	3. (1)
H(1N1)	-0.022 (6)	0.216 (8)	0.574 (8)	2. (1)
H(2N1)	0.125 (6)	0.744 (8)	0.488 (7)	2. (1)
H(3N1)	0.878 (6)	0.159 (7)	0.658 (7)	1. (1)
H(1N2)	0.497 (9)	0.340 (11)	0.822 (10)	6. (2)
H(2N2)	0.607 (5)	0.287 (7)	0.861 (7)	1. (1)
H(3N2)	0.485 (6)	0.254 (8)	0.454 (7)	2. (1)

Max. peak height in final difference Fourier synthesis 1.97 e \AA^{-3} . No extinction correction, $R = 0.039$ for the complete set of 2804 reflexions. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) SDP used for all calculations. Computer: PDP 11/70.

Discussion. Examination of the results obtained from the crystal structure determinations shows clearly that these two compounds are not simple adducts, *i.e.*, $\text{H}_3\text{XO}_4 \cdot (\text{NH}_3)_2(\text{CH}_2)_2$, but have atomic arrangements built up by a stacking of HXO_4^{2-} and $(\text{NH}_3)_2(\text{CH}_2)_2^{2+}$

Table 3. Main interatomic distances (Å) and bond angles (°) in HPO₄(NH₃)₂(CH₂)₂

PO ₄ tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.590 (2)	2.459 (3)	2.540 (3)	2.523 (3)
O(2)	104.3 (1)	1.525 (2)	2.532 (3)	2.535 (3)
O(3)	108.8 (1)	111.8 (1)	1.533 (2)	2.512 (3)
O(4)	108.4 (1)	112.7 (1)	110.7 (1)	1.521 (2)

$$\overline{P-O} = 1.542 (2)$$

NH₃-(CH₂)₂-NH₃ group

N(1)-C(1)	1.469 (4)	N(1)-C(1)-C(2)	112.1 (3)
C(1)-C(2)	1.507 (4)	C(1)-C(2)-N(2)	109.6 (2)
C(2)-N(2)	1.486 (4)		

Hydrogen bonds

	(O,N)-H	H...O	(O,N)-O	∠(O,N)-H...O
O(1)-H...O(4)	0.71 (6)	1.90 (6)	2.578 (3)	160 (7)
N(1)-H(1N1)...O(4)	0.82 (4)	1.93 (4)	2.747 (4)	173 (4)
N(1)-H(2N1)...O(2)	0.88 (5)	1.85 (5)	2.719 (4)	167 (5)
N(1)-H(3N1)...O(3)	0.91 (4)	2.00 (5)	2.906 (4)	176 (4)
N(2)-H(1N2)...O(3)	0.90 (4)	1.91 (5)	2.810 (4)	178 (4)
N(2)-H(2N2)...O(2)	1.08 (5)	1.65 (5)	2.720 (4)	176 (4)
N(2)-H(3N2)...O(3)	0.94 (5)	1.90 (5)	2.836 (4)	172 (4)

groups. In both structures one observes a layer arrangement: planes of HXO₄ tetrahedra alternate with planes of (CH₂)₂(NH₃)₂²⁺ groups, as depicted in Figs. 1 and 2.

Another common feature for these two arrangements is the internal repartition of the HXO₄²⁻ tetrahedra in their planes; they are associated in pairs forming H₂X₂O₈ clusters with rather short X-X distances (P-P = 4.847, As-As = 4.994 Å). The two HXO₄ groups in such a cluster are linked by a double hydrogen bridge.

In the case of the phosphorus compound the (NH₃)₂(CH₂)₂ entities are strongly pseudocentrosymmetric while they are centrosymmetric in the arsenic compound. This implies the existence of two crystallographically independent (NH₃)₂(CH₂)₂ units.

Table 4. Main interatomic distances (Å) and bond angles (°) in HASO₄(NH₃)₂(CH₂)₂

AsO ₄ tetrahedron				
As	O(1)	O(2)	O(3)	O(4)
O(1)	1.678 (3)	2.647 (4)	2.775 (4)	2.751 (4)
O(2)	101.7 (2)	1.734 (3)	2.793 (5)	2.763 (5)
O(3)	111.9 (2)	110.2 (2)	1.672 (3)	2.763 (5)
O(4)	111.1 (2)	109.1 (2)	112.2 (2)	1.657 (3)

$$\overline{As-O} = 1.685 (3)$$

NH₃-(CH₂)₂-NH₃ groups

C(1)-C(1)	1.496 (8)	C(2)-C(2)	1.516 (9)
C(1)-N(1)	1.479 (5)	C(2)-N(2)	1.482 (6)
C(1)-C(1)-N(1)	111.3 (4)	C(2)-C(2)-N(2)	110.6 (5)

Hydrogen bonds

	(O,N)-H	H...O	(O,N)-O	∠(O,N)-H...O
O(2)-H...O(3)	0.64 (6)	2.03 (6)	2.634 (5)	158 (8)
N(1)-H(1N1)...O(3)	0.64 (6)	2.14 (6)	2.744 (5)	157 (7)
N(1)-H(2N1)...O(1)	0.82 (6)	1.99 (6)	2.805 (5)	170 (5)
N(1)-H(3N1)...O(1)	0.88 (5)	1.92 (5)	2.788 (5)	168 (5)
N(2)-H(1N2)...O(4)	0.76 (8)	1.98 (8)	2.718 (5)	162 (8)
N(2)-H(2N2)...O(1)	0.77 (5)	2.14 (6)	2.820 (5)	148 (5)
N(2)-H(3N2)...O(4)	0.88 (6)	1.81 (6)	2.686 (5)	170 (5)

Tables 1 and 2* report the final atomic coordinates, while Tables 3 and 4 give the main interatomic distances, bond angles and details of the hydrogen-bond scheme.

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44090 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Disodium Ethylenediammonium Bis[monohydrogentetraoxophosphate(V)] Hexahydrate

BY M. T. AVERBUCH-POUCHOT, A. DURIF AND J. C. GUITEL

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USTMG, 166X, 38042 Grenoble CEDEX, France

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Abstract. C₂H₁₀N₂²⁺.2Na⁺.2HPO₄²⁻.6H₂O, *M_r* = 408.15, monoclinic, *P*2₁/*c*, *a* = 11.699 (9), *b* = 10.164 (9), *c* = 6.835 (4) Å, β = 105.00 (5)°, *V* = 785 (2) Å³, *Z* = 2, *D_x* = 1.727 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 0.415 mm⁻¹, *F*(000) = 428, *T* = 295 K, final *R* = 0.022 for 1823 independent reflexions. HPO₄²⁻ and (CH₂)₂(NH₃)₂²⁺ groups alternate in planes perpendicular to the *a* axis. In these planes, HPO₄²⁻

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