

Structure of Guanidinium Pentamolybdobis(*n*-propylarsenate) Dihydrate

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Abstract. $[\text{CN}_3\text{H}_6]_4[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_5\text{O}_{21}] \cdot 2\text{H}_2\text{O}$, $M_r = 1328.06$, monoclinic, $C2/c$, $a = 10.653(2)$, $b = 27.966(2)$, $c = 13.277(2)$ Å, $\beta = 96.19(2)^\circ$, $V = 3932.7$ Å³, $Z = 4$, $D_x = 2.243$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 32.704$ cm⁻¹, $F(000) = 2584$, $T = 293$ K, $R = 0.025$ for 3017 observed reflections with $F^2 > 3\sigma(F^2)$. In the anion, five MoO_6 octahedra are joined together to form an Mo_5 ring with four edge-sharing and one corner-sharing. Both sides of the ring are capped by two $n\text{-C}_3\text{H}_7\text{AsO}_3$ groups to build up a cage structure. In comparison with the phosphate analogue, the Mo_5 ring is spanned and the $n\text{-C}_3\text{H}_7\text{AsO}_3$ group is distorted. There are $\text{NH}\cdots\text{O}$ and $\text{OH}\cdots\text{O}$ hydrogen bonds among cations, anions and water molecules.

Introduction. As part of our program to explore and develop organic derivatives of heteropoly complexes, we have previously determined the structure of $[\text{CN}_3\text{H}_6]_4[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_6\text{O}_{24}]$ (Wang, Zheng, Liu & Gu, 1987). We now report the structure of a new type of heteropolyanion — $[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_5\text{O}_{21}]^{4-}$. Both complexes were prepared under the same pH conditions in the same solution (Liu, Gu, Wang & Zheng, 1988). Although the structure of $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{4-}$ (where R is an organic group) has been determined, Stalick & Quicksall (1976) have predicted that the arsenate analogue does not exist owing to the larger covalent radius of arsenic. Kwak, Rajkovic, Stalick, Pope & Quicksall (1976) and Filowitz & Klemperer (1976) have pointed out that the Mo_5 ring is favorably condensed with the phosphate whereas the Mo_6 ring incorporates the arsenate. We now confirm the presence of the As_2Mo_5 anion and the structure of the present complex should help to provide information on the geometric requirements for the formation of new organo heteropolyanions.

Experimental. Colourless crystal, $0.3 \times 0.2 \times 0.2$ mm. D_m not measured. Intensity data collected at 293 K with an Enraf–Nonius CAD-4 diffractometer and graphite-monochromated $\text{Mo } K\alpha$ radiation. Cell constants refined from 25 reflections (θ range $14.5\text{--}16^\circ$).

3451 reflections recorded with $2\theta_{\text{max}} = 50^\circ$, $h = 0$ to 12, $k = 0$ to 33, $l = -15$ to 15, 3017 reflections with $F^2 > 3\sigma(F^2)$ used for the structural refinement. Intensities of three standard reflections ($2, 20, 2, 2, 12, 7$ and 288) were recorded every 3600 s (1.4% variation). Empirical correction for absorption, min., max. transmission factors 89.44, 99.82%. Systematic absences, $hkl: h + k = 2n + 1, h0l: l = 2n + 1$, space group $C2/c$. The positions of the Mo and As atoms were found by direct method. Disorder of the water molecule and two carbon atoms of the *n*-propyl group appeared when successive difference Fourier syntheses were employed to locate the light atoms. The occupancies of the disordered atoms were obtained from peak heights in the difference maps. The disordered atoms with isotropic temperature factors and other atoms with anisotropic temperature factors were refined on F using the full-matrix least-squares method. In the final stage of the refinement, 250 variables, $(\Delta/\sigma)_{\text{max}} = 0.02$, isotropic extinction coefficient $= 1.34 \times 10^{-7}$, $R = 0.025$, $wR = 0.029$ where $w = 1$ for $F^2 > 3\sigma(F^2)$, $w = 0$ for $F^2 < 3\sigma(F^2)$. Max. value in final difference density map 0.79 e Å⁻³. Calculation performed on a PDP11/44 computer with the *SDP* program supplied by Enraf–Nonius (1983). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates of the non-H atoms are given in Table 1. The bond distances and angles are listed in Table 2. The structure of the heteropolyanion is shown in Fig. 1.*

The heteropolyanion $[(n\text{-C}_3\text{H}_7\text{As})_2\text{Mo}_5\text{O}_{21}]^{4-}$ possesses a twofold axis through Mo(1) and O(10). Five distorted MoO_6 octahedra are joined together to form an Mo_5 ring with four edge-sharing and one corner-sharing. Two tetrahedral $n\text{-C}_3\text{H}_7\text{AsO}_3$ groups

* Lists of observed and calculated structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44966 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + a\cos\beta B(1,3) + b\cos\alpha B(2,3)].$$

| | x | y | z | B _{eq} (Å ²) | Occupancy |
|--------|-------------|-------------|-------------|-----------------------------------|-----------|
| Mo(1) | 0.000 | 0.02322 (2) | 0.250 | 2.50 (1) | 1 |
| Mo(2) | 0.25318 (4) | 0.09477 (1) | 0.31743 (3) | 2.234 (7) | 1 |
| Mo(3) | 0.17437 (3) | 0.20999 (1) | 0.26967 (3) | 1.808 (7) | 1 |
| As | 0.03434 (4) | 0.12824 (2) | 0.10658 (3) | 1.886 (8) | 1 |
| O(1) | 0.1104 (3) | 0.0839 (1) | 0.1757 (2) | 2.34 (6) | 1 |
| O(2) | 0.0987 (3) | 0.1424 (1) | 0.3394 (2) | 2.11 (6) | 1 |
| O(3) | 0.1219 (3) | 0.1776 (1) | 0.1149 (2) | 2.28 (6) | 1 |
| O(4) | 0.3543 (3) | 0.0606 (1) | 0.2564 (3) | 3.54 (8) | 1 |
| O(5) | -0.1322 (3) | 0.0453 (1) | 0.1507 (2) | 2.65 (6) | 1 |
| O(6) | 0.2960 (3) | 0.1571 (1) | 0.2669 (2) | 2.23 (6) | 1 |
| O(7) | -0.0794 (4) | -0.0145 (1) | 0.3214 (3) | 3.83 (8) | 1 |
| O(8) | 0.3260 (3) | 0.0983 (1) | 0.4383 (3) | 3.25 (7) | 1 |
| O(9) | 0.2457 (3) | 0.2522 (1) | 0.2025 (2) | 2.67 (7) | 1 |
| O(10) | 0.000 | 0.2294 (2) | 0.250 | 2.23 (8) | 1 |
| O(11) | 0.2168 (3) | 0.2280 (1) | 0.3914 (2) | 2.74 (7) | 1 |
| O(12) | 0.385 (1) | 0.0681 (4) | 0.6504 (9) | 10.0 (3) | 0.64 |
| O(12*) | 0.449 (2) | 0.0992 (8) | 0.644 (2) | 9.8 (5) | 0.36 |
| N(1) | 0.5342 (4) | 0.1791 (2) | 0.3838 (3) | 3.11 (9) | 1 |
| N(2) | 0.6858 (4) | 0.1982 (2) | 0.5136 (3) | 3.6 (1) | 1 |
| N(3) | 0.4749 (4) | 0.2124 (2) | 0.5307 (4) | 4.7 (1) | 1 |
| N(4) | 0.5919 (6) | 0.0633 (2) | 0.4516 (5) | 6.0 (1) | 1 |
| N(5) | 0.7679 (5) | 0.0159 (2) | 0.4882 (4) | 5.2 (1) | 1 |
| N(6) | 0.6423 (7) | 0.0345 (2) | 0.6132 (4) | 6.5 (2) | 1 |
| C(1) | -0.0079 (6) | 0.1073 (2) | -0.0310 (4) | 3.8 (1) | 1 |
| C(2) | -0.0971 (9) | 0.1467 (3) | -0.0931 (7) | 5.5 (2) | 0.78 |
| C(2*) | -0.012 (3) | 0.139 (1) | -0.110 (2) | 5.2 (6) | 0.22 |
| C(3) | -0.045 (2) | 0.1844 (6) | -0.116 (1) | 8.0 (4) | 0.61 |
| C(3*) | -0.148 (2) | 0.136 (1) | -0.188 (2) | 8.4 (6) | 0.39 |
| C(4) | 0.5656 (5) | 0.1967 (2) | 0.4753 (4) | 2.9 (1) | 1 |
| C(5) | 0.6676 (6) | 0.0379 (2) | 0.5173 (5) | 4.4 (1) | 1 |

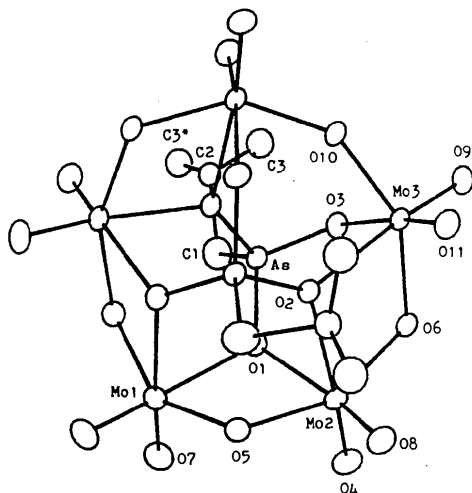


Fig. 1. View and atomic numbering of the heteropolyanion.

cap both sides of the ring to build up a cage structure. Two *n*-propyl groups protrude out of the cage.

The average bond distance between Mo and terminal O is 1.707 Å, that between Mo and O which links to two Mo is 1.946 Å, that between Mo and O which links to two Mo and one As is 2.276 Å and that between Mo and O which links to one Mo and one As is 2.260 Å. The Mo...Mo distances of the heteropolyanion are similar to those reported by Stalick & Quicksall (1976). However, the bond distances between Mo and O linked to two Mo range from 1.924 to 1.970 Å, of which

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

| | | | |
|------------------|------------|--------------------|------------|
| Mo—O(1) | 2.342 (2) | As—O(1) | 1.696 (2) |
| Mo(1)—O(5) | 1.924 (2) | As—O(2) | 1.703 (2) |
| Mo(1)—O(7) | 1.703 (2) | As—O(3) | 1.664 (2) |
| Mo(2)—O(1) | 2.309 (2) | As—C(1) | 1.924 (3) |
| Mo(2)—O(2) | 2.161 (2) | N(1)—C(4) | 1.321 (3) |
| Mo(2)—O(4) | 1.708 (2) | N(2)—C(4) | 1.326 (3) |
| Mo(2)—O(5) | 1.969 (2) | N(3)—C(4) | 1.348 (3) |
| Mo(2)—O(6) | 1.939 (2) | N(4)—C(5) | 1.328 (5) |
| Mo(2)—O(8) | 1.709 (2) | N(5)—C(5) | 1.326 (5) |
| Mo(3)—O(2) | 2.290 (2) | N(6)—C(5) | 1.333 (4) |
| Mo(3)—O(3) | 2.260 (2) | C(1)—C(2) | 1.620 (6) |
| Mo(3)—O(6) | 1.970 (2) | C(1)—C(2*) | 1.36 (2) |
| Mo(3)—O(9) | 1.707 (2) | C(2)—C(3) | 1.24 (2) |
| Mo(3)—O(10) | 1.9261 (7) | C(2)—C(3*) | 1.35 (1) |
| Mo(3)—O(11) | 1.707 (2) | | |
| O(1)—Mo(1)—O(1') | 87.16 (8) | O(6)—Mo(3)—O(9) | 100.36 (8) |
| O(1)—Mo(1)—O(5) | 80.98 (6) | O(6)—Mo(3)—O(10) | 146.73 (8) |
| O(1)—Mo(1)—O(5') | 72.11 (6) | O(6)—Mo(3)—O(11) | 97.57 (7) |
| O(1)—Mo(1)—O(7) | 170.20 (9) | O(9)—Mo(3)—O(10) | 102.17 (8) |
| O(1)—Mo(1)—O(7') | 84.96 (8) | O(9)—Mo(3)—O(11) | 101.73 (9) |
| O(5)—Mo(1)—O(5') | 142.6 (2) | O(10)—Mo(3)—O(11) | 101.44 (6) |
| O(5)—Mo(1)—O(7) | 102.05 (9) | O(1)—As—O(2) | 108.24 (8) |
| O(5)—Mo(1)—O(7') | 100.84 (9) | O(1)—As—O(3) | 109.84 (8) |
| O(7)—Mo(1)—O(7') | 103.4 (1) | O(1)—As—C(1) | 110.0 (2) |
| O(1)—Mo(2)—O(2) | 75.34 (6) | O(2)—As—O(3) | 105.39 (7) |
| O(1)—Mo(2)—O(4) | 86.16 (7) | O(2)—As—C(1) | 110.5 (2) |
| O(1)—Mo(2)—O(5) | 72.15 (6) | O(3)—As—C(1) | 112.8 (2) |
| O(1)—Mo(2)—O(6) | 89.71 (7) | Mo(1)—O(1)—Mo(2) | 93.92 (6) |
| O(1)—Mo(2)—O(8) | 164.97 (7) | Mo(1)—O(1)—As | 121.69 (8) |
| O(2)—Mo(2)—O(4) | 159.52 (8) | Mo(2)—O(1)—As | 125.39 (8) |
| O(2)—Mo(2)—O(5) | 83.06 (6) | Mo(2)—O(2)—Mo(3) | 98.52 (6) |
| O(2)—Mo(2)—O(6) | 72.77 (7) | Mo(2)—O(2)—As | 126.44 (8) |
| O(2)—Mo(2)—O(8) | 96.48 (7) | Mo(3)—O(2)—As | 135.04 (8) |
| O(4)—Mo(2)—O(5) | 99.78 (8) | Mo(3)—O(3)—As | 118.34 (8) |
| O(4)—Mo(2)—O(6) | 98.84 (8) | Mo(1)—O(5)—Mo(2) | 121.75 (9) |
| O(4)—Mo(2)—O(8) | 103.5 (1) | Mo(2)—O(6)—Mo(3) | 119.26 (8) |
| O(5)—Mo(2)—O(6) | 152.93 (7) | Mo(3)—O(10)—Mo(3') | 147.2 (1) |
| O(5)—Mo(2)—O(8) | 94.59 (8) | As—C(1)—C(2) | 110.0 (2) |
| O(6)—Mo(2)—O(8) | 100.00 (8) | As—C(1)—C(2*) | 121.0 (7) |
| O(2)—Mo(3)—O(3) | 88.49 (6) | C(1)—C(2)—C(3) | 116.6 (6) |
| O(2)—Mo(3)—O(6) | 69.39 (6) | C(1)—C(2)—C(3*) | 119.0 (8) |
| O(2)—Mo(3)—O(9) | 168.14 (7) | N(1) C(4)—N(2) | 120.2 (2) |
| O(2)—Mo(3)—O(10) | 84.92 (7) | N(1)—C(4)—N(3) | 119.9 (2) |
| O(2)—Mo(3)—O(11) | 85.94 (8) | N(2)—C(4)—N(3) | 119.9 (2) |
| O(3)—Mo(3)—O(6) | 77.33 (7) | N(4)—C(5)—N(5) | 120.5 (4) |
| O(3)—Mo(3)—O(9) | 83.26 (7) | N(4)—C(5)—N(6) | 119.6 (3) |
| O(3)—Mo(3)—O(10) | 81.33 (5) | N(5)—C(5)—N(6) | 119.8 (4) |
| O(3)—Mo(3)—O(11) | 173.52 (7) | | |

A prime denotes the corresponding atom related by the twofold axis.

Mo(2)—O(5) and Mo(3)—O(6) are especially long (1.969 and 1.970 Å, respectively). All these distances are longer than those in the phosphate analogues (Stalick & Quicksall, 1976). Obviously, the Mo₅O₁₅ ring is enlarged by the coordination of the arsenate groups.

The average As—O bond distance is 1.688 Å and the bond angles about As range from 105.4 to 110.7°. As—O(3) is shorter than the other As—O because O(3) is a terminal oxygen (Stalick & Quicksall, 1976; Strandberg, 1973). In the *n*-C₃H₇AsO₃ group of the [(*n*-C₃H₇As)₂Mo₆O₂₄]⁴⁻ anion (Wang *et al.*, 1987) and CH₃AsO₃ of [(CH₃AsO₃)₂Mo₆O₂₄]⁴⁻ (Kwak *et al.*, 1976) the average As—O distances are 1.713 and 1.701 Å, respectively, and the average O—As—O angles 110.4 and 111.1°. Comparison clearly shows that the *n*-C₃H₇AsO₃ group is distorted through the condensation with the Mo₅ ring.

As pointed out by Kwak *et al.* (1976) and Filowitz & Klemperer (1976), the appropriate O...O distances

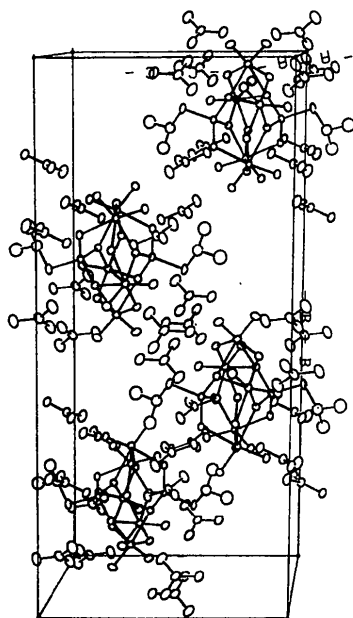


Fig. 2. A view of the unit cell.

across the six-membered Mo_6O_{24} ring closely match the non-bonded $\text{O}\cdots\text{O}$ separation in the AsO_3 tetrahedron (2.86 Å), whereas the corresponding distances in the Mo_5O_{21} ring are too small to accommodate arsenate groups. The present study has indicated that this criterion is not so strict. Expansion of the Mo_5O_{21} ring and distortion of the arsenate tetrahedron make the $\text{O}\cdots\text{O}$ distance 2.74 Å.

In the cations, the average N–C bond distance is 1.330 Å, the bond angles range from 119.6 to 120.5° as usual.

Fig. 2 shows the crystal structure. There are $\text{NH}\cdots\text{O}$ and $\text{OH}\cdots\text{O}$ hydrogen bonds among the cations,

Table 3. Hydrogen bonds

E.s.d.'s are ~0.004 Å.

| Donor | Acceptor | $d(\text{Å})$ | Donor | Acceptor | $d(\text{Å})$ |
|-------|----------|---------------|--------|----------|---------------|
| N(1) | O(6) | 2.895 | N(4) | O(8) | 2.985 |
| N(1) | O(6') | 2.904 | N(5) | O(5'') | 2.867 |
| N(2) | O(3) | 2.862 | N(5) | O(7') | 3.008 |
| N(2) | O(9'') | 2.876 | N(6) | O(4'') | 3.173 |
| N(3) | O(11) | 3.174 | N(6) | O(12) | 2.989 |
| N(3) | O(11''') | 2.912 | O(12) | O(8) | 2.941 |
| N(4) | O(4) | 2.880 | O(12*) | O(8) | 2.902 |

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

anions and water molecules. The hydrogen bonds are listed in Table 3. Each anion is surrounded by eight cations, and each cation has two anions as the first neighbours in the range 5.8–6.4 Å. The crystal is stabilized by Coulomb forces and hydrogen bonds.

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Structure of ScBO_3

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Abstract. Scandium borate, $M_r = 103.76$, trigonal, $R\bar{3}c$, $a = 4.748(1)$, $c = 15.262(2)$ Å, $V = 298.0$ Å³, $Z = 6$, $D_x = 3.47$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 33.95$ cm⁻¹, $F(000) = 300$, $T = 298$ K, $R = 0.017$ for 444 averaged reflections. The octahedral environment of O anions about the Sc^{III} ion exhibits a small

trigonal elongation, as demonstrated by the value of 92.28 (1)° for the bond angle O–Sc–O.

Introduction. As part of our program in new optical materials, we have recently synthesized and structurally characterized a number of new ternary and quaternary