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Synthesis and Characterization of the Second Example of a New Type of Heteropolyanion: Pentamolybdobis(allylarsonate)

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Abstract

The second example of a new type of heteropolyanion – pentamolybdobis(allylarsonate) – has been synthesized and characterized as a guanidinium salt. It belongs to the monoclinic space group $C2/c, Z = 4$, $a = 10.623(1)$, $b = 27.258(2)$, $c = 13.530(1)$ Å, $\beta = 95.32(2)°$, $V = 3900.9$ Å^3, $\mu = 157.8$ cm^{-1}, $R = 0.063$. Its IR spectra, cyclic voltammogram and single-crystal X-ray diffraction data have been reported and discussed. The larger arsenic atom has a considerable effect on the geometry of the Mo_5O_{15} ring in a similar way to the first example $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$. Furthermore, the allyl groups enable this new type of heteropolyanion to be easier formed and stabilized. It is demonstrated that the stable existence of the anions of the $[(RAs)_2Mo_5O_{21}]^{4-}$ type is by no means a fortuitous phenomenon.

Introduction

Although salts of the anions $[(RP)_2Mo_5O_{21}]^{4-}$ and $[(RAs)_2Mo_6O_{24}]^{4-}$ have been synthesized and characterized since 1975 [1–3], the first example of arsenic complexes analogous to $[(RP)_2Mo_5O_{21}]^{4-}$ has just been reported by us in 1988 [4, 5]. Before 1988 it was predicted that the corresponding As_2Mo_5 anion did not exist due to the larger covalent radius of the arsenic atom. Some papers have also stated that the Mo_5O_{21} ring is suitable to accommodate PO_4^{3-} or RPO_3^{2-} groups and the Mo_6O_{24} ring is suitable to accommodate $RAsO_3^{2-}$ groups [3, 6]. After the X-ray crystal structural investigation of the two organophosphorus polymolybdates $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$ and $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$, Stalick and Quicksall accounted for the inability to isolate the corresponding As_2Mo_5 ions. They said that the larger covalent radius of arsenic might sterically inhibit the formation of heteropolyanions of this type with molybdenum [7]. We have been able, however, to prepare both $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_5O_{21}]\cdot 2H_2O$ (**A**) and $(CN_3H_6)_4[(n\text{-}C_3H_7As)_2Mo_6O_{24}]$ (**B**) on mixing aqueous solutions of Na_2MoO_4 and $n\text{-}C_3H_7AsO(OH)_2$ (2:1 molar ratio) at pH 4–5 [4]. Although **B** is more thermostable than **A**, the latter is a rather stable crystal that remains transparent for a long time in the presence of oxygen and moisture [4]. The existence of **A** clearly demonstrates that $[(RAs)_2Mo_5O_{21}]^{4-}$ polyanions can be formed in spite of earlier speculations about molecular dimensions. In our previous paper [4] we hoped that some other compounds belonging to the $[(RAs)_2Mo_5O_{21}]^{4-}$ type would soon be synthesized and characterized. Now we wish to report the second example of this new type: $(CN_3H_6)_4[(CH_2{=}CH{-}CH_2{-}As)_2Mo_5O_{21}]^{4-}$ (**C**) and its easier formation than **A**.

Experimental

Allylarsonic acid was prepared according to ref. 8. IR measurement was made on a Nicolet FTIR-5DX instrument (KBr pellet). UV spectra were obtained on a Hitachi-557 instrument. The thermogravity curve was obtained on a LCT-2 analyzer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 240-C analyzer. Arsenic and molybdenum analyses were performed by the ICP method on a Jarrell-Ash 2000 ICP instrument. The selected wavelengths are $\lambda = 202.3$ and 228.8 nm for Mo and As, respectively. The cyclic voltammograms were performed on an F-78 pulse-polarograph (platinum electrode, area 2.5 mm^2, reference electrode Ag/AgCl, supporting electrolyte 1 M KNO_3, scan rate 50 mV/s.)

Preparation and Properties of C

Ten ml of cold aqueous solution of 0.33 g (2 mmol) allylarsonic acid were mixed with 10 ml of aqueous solution of 0.48 g (2 mmol) sodium

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molybdate dihydrate, then 6 M hydrochloride solution was added drop by drop until the pH value was adjusted from 6.7 to about 4.5. The mixture was boiled for 1 h. After it was cooled to room temperature, it was filtered to remove a small amount of insoluble residue. A colorless transparent solution was then obtained. Tests for cations show that sodium, potassium, ammonium, tetramethylammonium, tetraethylammonium, magnesium, calcium and even cesium or barium salts are very soluble in water. The solubility of the guanidinium salt is comparatively small. Ten drops of 2:1 guanidinium hydrochloride solution were added to the hot colorless solution mentioned above. When the solution was gradually cooled to room temperature, colorless needles were obtained. It can be recrystallized from 15 ml of hot water (pH = 4–5). The yield is 82%. *Anal.* Calc. for $C_{10}H_{34}N_{12}As_2Mo_5O_{21}$: C, 9.33; H, 2.66; N, 13.05; As, 11.63; Mo, 37.24. Found for compound **C**: C, 9.54; H, 2.81; N, 13.18; As, 11.36; Mo, 37.66%. $\lambda_{max}(H_2O)$: 208 nm. ν_{max}(KBr): 3360(s), 3180(s), 1650–1640(vs, C=N), 1560(w), 1390(w), 1130(w), 1050(w), 1010(w), 990(w), 940(s), 930, 902(vs), 895(vs), 870(s), 835(s), 820(s), 670(br, s), 559, 520, 487 cm^{-1}. The thermogravimetry (TG) curve shows that compound **C** decomposes at 242 °C. It lost 26.1% of its weight (calc. 26.1%) when heated from 242 to 352 °C. This is an endothermic process because of the decomposition of the guanidinium salt. When heated from 352 to 470 °C, it lost its organoarsenic groups (17.5% of its weight, calc. 18.0%) and released a great deal of heat. The final product was MoO_3 (56.1% of its weight, calc. 55.9%). The cyclic voltammogram of a 1.00 mM solution of **C** shows that **C** has no reversible redox procedure from –0.9 to +0.5 V.

Structural Determination of C

The crystal structure of **C** was determined by single-crystal X-ray diffraction studies. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) at 298 K. **C** is monoclinic, space group $C2/c$, $Z = 4$, $a = 10.623(1)$, $b = 27.258(2)$, $c = 13.530(1)$ Å, $\beta = 95.32(2)°$, $V = 3900.9$ $Å^3$, $\mu = 157.8$ cm^{-1}. The positions of all the molybdenum and arsenic atoms were determined by the direct method. The positions of the non-H atoms were revealed by difference Fourier syntheses. A total of 3428 unique reflections was measured with $3° < 2\theta < 130°$; 3182 reflections with $I > 3\sigma(I)$ were used in the refinement. The structure was refined by full-matrix least-squares to a final $R = 0.063$. Table 1 lists the atomic positional parameters. The bond distances

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

Atom	x	y	z	B_{eq} ($Å^2$)[a]
Mo(1)	0.500	0.02040(6)	0.750	1.96(3)
Mo(2)	0.2472(1)	0.09389(4)	0.6857(1)	1.65(2)
Mo(3)	0.3256(1)	0.21195(4)	0.73249(9)	1.22(2)
As(1)	0.5355(1)	0.12828(6)	0.6104(1)	1.26(3)
O(1)	0.422(1)	–0.0185(4)	0.820(1)	3.1(3)
O(2)	0.369(1)	0.0427(4)	0.6540(8)	2.0(2)
O(3)	0.6109(9)	0.0828(3)	0.6757(8)	1.4(4)
O(4)	0.4040(9)	0.1426(4)	0.6648(8)	1.7(2)
O(5)	0.2040(9)	0.1557(4)	0.7355(8)	2.0(2)
O(6)	0.176(1)	0.0979(5)	0.569(1)	3.0(3)
O(7)	0.147(1)	0.0601(4)	0.747(1)	2.7(2)
O(8)	0.622(1)	0.1793(4)	0.6166(8)	1.6(2)
O(9)	0.500	0.2307(6)	0.750	1.6(3)
O(10)	0.255(1)	0.2541(4)	0.7976(8)	2.0(2)
O(11)	0.282(1)	0.2288(4)	0.6134(9)	2.2(2)
N(11)	0.591(2)	0.4377(8)	0.450(2)	5.4(5)
N(12)	0.769(2)	0.4832(7)	0.492(1)	4.4(4)
N(13)	0.631(2)	0.4649(8)	0.608(2)	6.0(6)
N(21)	0.533(1)	0.3192(6)	0.382(1)	2.6(3)
N(22)	0.471(1)	0.2858(7)	0.526(1)	3.9(4)
N(23)	0.682(1)	0.3015(6)	0.510(1)	2.8(3)
C(A)	0.665(2)	0.4612(7)	0.517(2)	3.6(4)
C(B)	0.562(1)	0.3020(6)	0.471(1)	2.1(3)
C(1)	0.491(2)	0.1104(7)	0.473(1)	2.9(4)
C(2)	0.426(3)	0.150(1)	0.418(2)	6.6(7)
C(3)	0.464(5)	0.182(1)	0.365(3)	13(1)

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

TABLE 2. Bond distances (A) with e.s.d.s in parentheses

Mo(1)–O(1)	1.690(3)	Mo(3)–O(11)	1.698(3)
Mo(1)–O(2)	1.912(3)	As(1)–O(3)	1.682(2)
Mo(1)–O(3)	2.347(2)	As(1)–O(4′)	1.685(3)
Mo(2)–O(2)	1.979(3)	As(1)–O(8)	1.662(3)
Mo(2)–O(3)	2.315(3)	As(1)–C(1)	1.937(4)
Mo(2)–O(4)	2.168(2)	N(11)–C(A)	1.307(7)
Mo(2)–O(5)	1.887(3)	N(12)–C(A)	1.320(7)
Mo(2)–O(6)	1.694(3)	N(13)–C(A)	1.320(8)
Mo(2)–O(7)	1.685(3)	N(21)–C(B)	1.301(6)
Mo(3)–O(4)	2.291(3)	N(22)–C(B)	1.356(6)
Mo(3)–O(5)	2.007(3)	N(23)–C(B)	1.325(6)
Mo(3)–O(8)	2.250(3)	C(1)–C(2)	1.445(8)
Mo(3)–O(9)	1.915(1)	C(2)–C(3)	1.239(14)
Mo(3)–O(10)	1.667(3)		

and bond angles are given in Tables 2 and 3 respectively. The structure and atomic numbering of the anion of **C** is shown in Fig. 1. It is similar to $[(RP)_2Mo_5O_{21}]^{4-}$ reported by Stalick and Quicksall [7] and to $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$ reported by us [4, 5]. Different from its phosphorus congener, the anion of **C** possesses 2-fold axis symmetry. Different from its propylarsenic congener, no disorder of carbon atoms appears. It consists of a ring of five MoO_6 octahedra (four edge-shared and one corner-shared) capped on either side by two allylarsenic groups. The asymmetric unit of the structure contains half a $[(C_3H_5As)_2Mo_5O_{21}]^{4-}$ anion and two $CN_3H_6^+$ cations.

Discussion

The synthesis and characterization of **C** and **A** demonstrate that the existence of the anions of $[(RAs)_2Mo_5O_{21}]^{4-}$ type is by no means a fortuitous phenomenon. The larger arsenic atom has a considerable effect on the geometry of the Mo_5O_{15} ring in a very similar way to the first example $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$.

TABLE 3. Bond angles (°) with e.s.d.s in parentheses

O(1)–Mo(1)–O(1′)	102.3(3)	O(5)–Mo(3)–O(8)	77.7(1)
O(1)–Mo(1)–O(2)	102.5(1)	O(5)–Mo(3)–O(9)	144.9(1)
O(1)–Mo(1)–O(2′)	100.5(1)	O(5)–Mo(3)–O(10)	101.1(1)
O(1)–Mo(1)–O(3′)	170.6(1)	O(5)–Mo(3)–O(11)	96.2(1)
O(1)–Mo(1)–O(3)	85.5(1)	O(8)–Mo(3)–O(9)	80.54(9)
O(1′)–Mo(1)–O(2)	100.5(1)	O(8)–Mo(3)–O(10)	83.1(1)
O(1′)–Mo(1)–O(2′)	102.5(1)	O(8)–Mo(3)–O(11)	172.4(1)
O(1′)–Mo(1)–O(3′)	85.5(1)	O(9)–Mo(3)–O(10)	103.2(1)
O(1′)–Mo(1)–O(3)	170.6(1)	O(9)–Mo(3)–O(11)	102.7(1)
O(2)–Mo(1)–O(2′)	142.9(2)	O(10)–Mo(3)–O(11)	102.6(1)
O(2)–Mo(1)–O(3)	80.8(1)	O(3)–As(1)–O(4′)	108.4(1)
O(2)–Mo(1)–O(3′)	72.5(1)	O(3)–As(1)–O(8)	111.0(1)
O(2′)–Mo(1)–O(3)	72.5(1)	O(3)–As(1)–C(1)	112.3(2)
O(2′)–Mo(1)–O(3′)	80.8(1)	O(4′)–As(1)–O(8)	105.0(1)
O(3)–Mo(1)–O(3′)	87.2(1)	O(4′)–As(1)–C(1)	109.9(2)
O(2)–Mo(2)–O(3)	72.1(1)	O(8)–As(1)–C(1)	110.0(2)
O(2)–Mo(2)–O(4)	82.9(1)	Mo(1)–O(2)–Mo(2)	121.8(1)
O(2)–Mo(2)–O(5)	153.3(1)	Mo(1)–O(3)–Mo(2)	93.61(9)
O(2)–Mo(2)–O(6)	95.0(1)	Mo(1)–O(3)–As(1)	121.7(1)
O(2)–Mo(2)–O(7)	100.3(1)	Mo(2)–O(3)–As(1)	124.8(1)
O(3)–Mo(2)–O(4)	74.6(1)	Mo(2)–O(4)–Mo(3)	98.1(1)
O(3)–Mo(2)–O(5)	89.4(1)	Mo(2)–O(4′)–As(1)	126.4(1)
O(3)–Mo(2)–O(6)	165.2(1)	Mo(3)–O(4)–As(1′)	135.5(1)
O(3)–Mo(2)–O(7)	85.7(1)	Mo(2)–O(5)–Mo(3)	119.8(1)
O(4)–Mo(2)–O(5)	73.4(1)	Mo(3)–O(8)–As(1)	117.8(1)
O(4)–Mo(2)–O(6)	97.0(1)	Mo(3)–O(9)–Mo(3′)	149.1(2)
O(4)–Mo(2)–O(7)	158.1(1)	N(11)–C(A)–N(12)	120.9(6)
O(5)–Mo(2)–O(6)	100.1(1)	N(11)–C(A)–N(13)	118.9(6)
O(5)–Mo(2)–O(7)	97.3(1)	N(12)–C(A)–N(13)	120.1(6)
O(6)–Mo(2)–O(7)	104.3(2)	N(21)–C(B)–N(22)	120.0(4)
O(4)–Mo(3)–O(5)	68.7(1)	N(21)–C(B)–N(23)	120.9(4)
O(4)–Mo(3)–O(8)	88.1(1)	N(22)–C(B)–N(23)	119.0(4)
O(4)–Mo(3)–O(9)	83.5(1)	As(1)–C(1)–C(2)	111.7(4)
O(4)–Mo(3)–O(10)	167.8(1)	C(1)–C(2)–C(3)	131.0(1)
O(4)–Mo(3)–O(11)	85.5(1)		

A prime denotes the corresponding atom related by the 2-fold axis.

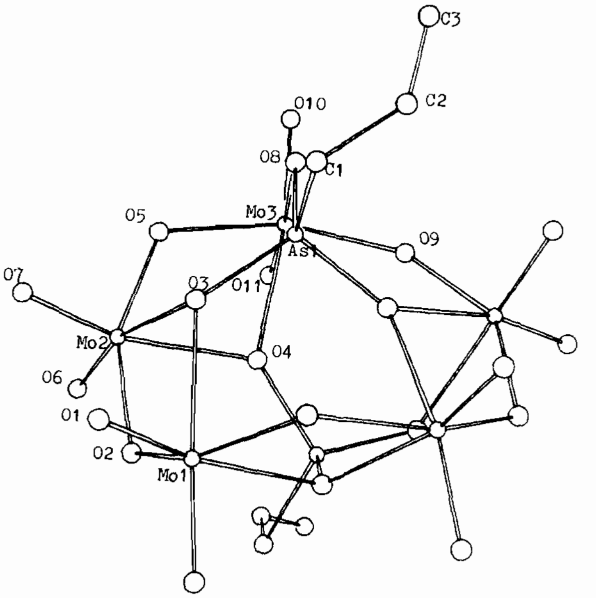

Fig. 1. Structure and atomic numbering of the anion of C, $[(C_3H_5As)_2Mo_5O_{21}]^{4-}$.

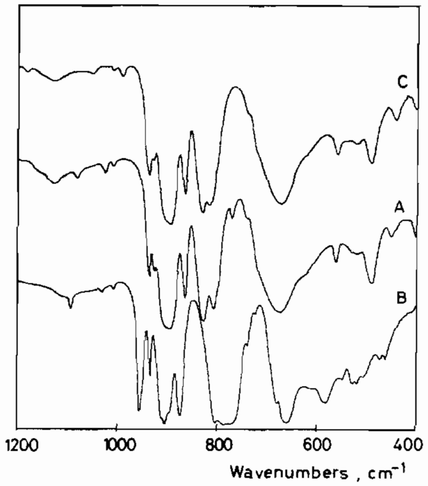

Fig. 2. Infrared spectra of compounds C, A and B.

The infrared spectra of **C** and **A** are very similar in the entire region, whereas those of **C**, **A** and **B** are only very similar above 1200 cm^{-1} in the N–H, C–H, C=N stretching regions. Figure 2 shows the IR spectra of **C**, **A** and **B** below 1200 cm^{-1}. The most interesting region is around 760 cm^{-1} near which **B** has a strong absorption while **C** and **A** have a minimum absorption. This phenomenon is a result of the different ring structures. The absorption character near 760 cm^{-1} can be regarded as a criterion to judge whether the compound belongs to the $(RAs)_2Mo_5$ or the $(RAs)_2Mo_6$ type. The wavenumbers 940, 930, 902, 895 cm^{-1} in **C**, 936, 925, 895 cm^{-1} in **A** and 953, 933, 905 cm^{-1} in **B** have been assigned to the molybdenum–oxygen(terminal) stretching frequencies. The difference between them is rather small because the Mo–O_t bond lengths are around 1.70 Å in **C**, **A** and **B**. The wavenumbers 870, 835, 820 cm^{-1} in **C**, 864, 826, 806 cm^{-1} in **A** and 873, 801, 786 cm^{-1} in **B** have been assigned to the arsenic–oxygen stretching frequencies. From the structural data the As–O bond lengths are 1.682, 1.683, 1.662 Å in **C**, 1.696, 1.703, 1.664 Å in **A** [5] and 1.75, 1.709, 1.75 Å in **B** [9]. The hypsochromic shifts of absorption peaks in **C** and **A** have reached 34 and 20–25 cm^{-1} respectively in comparison with those in **B**. This is why **B** has a strong absorption near 760 cm^{-1} region while **C** and **A** have a minimum absorption. The wavenumbers 670, 559 cm^{-1} in **C**, 673, 558 cm^{-1} in **A** and 681, 659, 581 cm^{-1} in **B** have been assigned to the molybdenum–oxygen(bridging) stretching frequencies. Structural data show that the Mo–O_b bond lengths are 1.912, 1.887, 1.979, 2.007, 1.915 Å in **C**, 1.924, 1.939, 1.969, 1.970, 1.926 Å in **A** [5] and 1.905, 1.910, 1.943 Å in **B** [9]. The Mo_5O_{15} ring in both **C** and **A** must be enlarged in order to accommodate the larger arsenic atoms and the bathochromic shifts of absorption peaks in **C** and **A** take place.

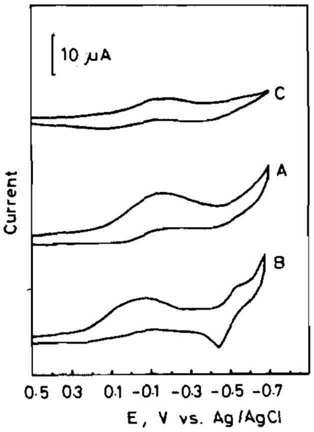

Fig. 3. Cyclic voltammograms of 1.00, 1.43 and 1.22 mM solutions of C, A and B in 1 M KNO_3 (scan initiated at 0.5 V vs. Ag/AgCl in negative direction at 50 mV/s; platinum electrode, area 2.5 mm^2).

Figure 3 shows the cyclic voltammograms for **C**, **A** and **B**. The CV curves of **C** and **A** are also very similar; they have no reversible redox behavior within the potential region from −0.4 to −0.6 V. It is also verified that **C** and **A** belong to the same new type. The almost reversible redox procedure of **B** most probably results from the high symmetry of its anion.

We compare bond lengths and angles of $[(C_3H_5As)_2Mo_5O_{21}]^{4-}$ with those of $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$ and $[(RP)_2Mo_5O_{21}]^{4-}$. The following conclusions can be obtained.

First, on one side of the ring, the oxygen triangle O(3′)O(4)O(8′) which accommodates the 'organic handle', is very close to that for **A**, close to that for **B** and much larger than that in the $[(RP)_2Mo_5O_{21}]^{4-}$ anion. The corresponding average O–O distances are 2.71, 2.73, 2.81 and 2.52 Å for **C**, **A**, **B** and $[(RP)_2Mo_5O_{21}]^{4-}$ anions respectively. It is not surprising that the corresponding oxygen triangle in **B** is the largest one because it is connected to the Mo_6O_{18} ring. The oxygen triangle in **C** and **A**, however, are much larger than that in the $[(RP)_2Mo_5O_{21}]^{4-}$ anion, although they are connected to quite similar Mo_5O_{15} rings. In a sense, this triangle can represent the coordination space for arsenic or phosphorus tetrahedra. It is obvious that this coordination space in **C** and **A** must be larger than that in the $[(RP)_2Mo_5O_{21}]^{4-}$ anion and close to that in **B**. On the other side of the ring the situation is quite similar. Furthermore, it is noticed that the average O–O distance for **C** is slightly smaller than that for **A**.

Second, apart from the two oxygen triangles (six oxygen atoms altogether), the Mo_5O_{15} rings in **C** and **A** are markedly enlarged in order to accommodate the larger arsenic atom. The dimensions of the Mo_5O_{15} rings are mainly determined by ten $Mo-O_b$ distances. In the anion of **C**, the $Mo-O_b$ bond lengths range from 1.912 to 2.007 Å, the average is 1.940 Å. In the anion of **A**, the $Mo-O_b$ bond lengths range from 1.924 to 1.970 Å, the average is 1.946 Å. Both Mo_5O_{15} rings are much larger than that in the $[(RP)_2Mo_5O_{21}]^{4-}$ anion, in which the $Mo-O_b$ bond lengths range from 1.889 to 1.956 Å, the average is only 1.926 Å. It must be emphasized that the four corresponding $Mo-O_b$ bond lengths in **C** and **A** are especially long. The distances of Mo(2)O(2), Mo(3)O(5), Mo(2')O(2'), Mo(3')O(5') in **C** are 1.979, 2.007, 1.979, 2.007 Å respectively. The corresponding distances of Mo(2)O(5), Mo(3)O(6), Mo(2')O(5'), Mo(3')O(6') in **A** are 1.969, 1.970, 1.969, 1.970 Å respectively. This is by no means an accidental phenomenon although we do not know the reason for this so far. Furthermore, although these four $Mo-O_b$ distances in **C** are longer than those in **A**, the other six $Mo-O_b$ distances in **C** are shorter than those in **A**. After all, the Mo_5O_{15} ring in **C** is slightly smaller than that in **A**.

Third, the Mo_5O_{15} ring also has an effect on the organoarsenic tetrahedra. The O–As–O average angles are 108.1°, 107.8°, 110.4° and 110.6° for **C**, **A**, **B** and $[(RP)_2Mo_5O_{21}]^{4-}$ anions, respectively. Both O–As–O average angles in **C** and **A** are less than the regular angle for a tetrahedron (109°28'), while those in **B** and $[(RP)_2Mo_5O_{21}]^{4-}$ anions are larger than the regular one. It is obvious that the tetrahedral $RAsO_3$ groups in **C** and **A** has been distorted to suit the above mentioned oxygen triangles. We can see the effect of the larger arsenic atom on the Mo_5O_{15} ring and vice versa: on the one hand, the Mo_5O_{15} rings have been enlarged to accommodate two larger arsenic groups, on the other hand, the organoarsenic groups have been slightly compressed to fit in the Mo_5O_{15} rings. Furthermore, we can also see that the organoarsenic groups are less compressed in **C** than in **A**.

TABLE 4. Corresponding arsenic–oxygen distances (Å) for C and A

Atoms	As–O distances	
	C	A
As(1')–O(3')	1.682	1.692
As(1')–O(4)	1.685	1.703
As(1')–O(8')	1.662	1.664

Fourth, it is noticed that the As–O bond lengths in **C** are shorter than those in **A**. Table 4 lists the corresponding As–O bond lengths for **C** and **A**. From this accurate comparison it can be seen that the allyl group has a certain influence on this new system. Because of the shorter As–O distances the allylarsenic tetrahedron can be less compressed to fit in the Mo_5O_{15} ring. In addition, the Mo_5O_{15} ring and oxygen triangles are less enlarged as indicated above. It is easily understood that this new system is more stabilized by the less enlarged Mo_5O_{15} ring and less compressed organoarsenic tetrahedra when the n-propyl group is replaced by an electron-richer allyl group. In fact, we tested the reaction of sodium molybdate with allylarsonic acid at various molar ratios Mo/As = 1, 2 and 3 respectively; only the anions of $[(RAs)_2Mo_5O_{21}]^{4-}$ type were obtained. Different from the n-propyl case, no two types of crystals appeared in the same solution. The analogous compound to **B** has not been isolated yet. The stable existence of the anions of the $[(RAs)_2Mo_5O_{21}]^{4-}$ type, however, is by no means a fortuitous phenomenon. The previous views that phosphorus atoms always prefer the $(RP)_2Mo_5$ type and larger arsenic atoms always prefer the $(RAs)_2Mo_6$ type must be changed.

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