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Paul A. Grutsch, Charles Kutal*

Department of Chemistry, University of Georgia,
Athens, Georgia 30602

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A New Molybdoarsonate. Structure of $(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2^{4-}$ and Solution Interconversion of Heteropoly Anions That Differ by a Constitutional Water Molecule

Sir:

The mechanisms of formation and interconversion of isopoly and heteropoly oxometallate anions are not well delineated, although there is encouraging activity in this area.¹⁻³ A new heteropoly molybdate structure, described below, appears to be simply related to a previously determined structure by the insertion of a bridging water molecule. The solution interconversion of the two structures suggests that reaction pathways involving face sharing of MO_6 octahedra may be important in oxometallate hydrolyses.

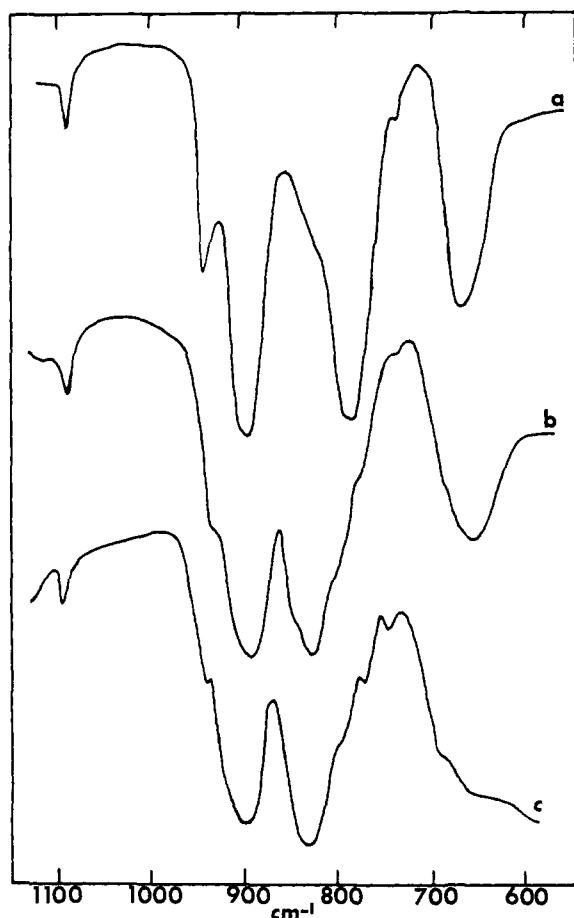


Figure 1. Infrared spectra: (a) $(\text{CN}_3\text{H}_6)_4[(\text{PhAs})_2\text{Mo}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$ (A complex); (b) $(\text{CN}_3\text{H}_6)_4[(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2] \cdot 4\text{H}_2\text{O}$ (B complex); (c) solution of PhAsO_3^{2-} and MoO_4^{2-} (1:3 molar ratio) in D_2O - DCl , pH 4.

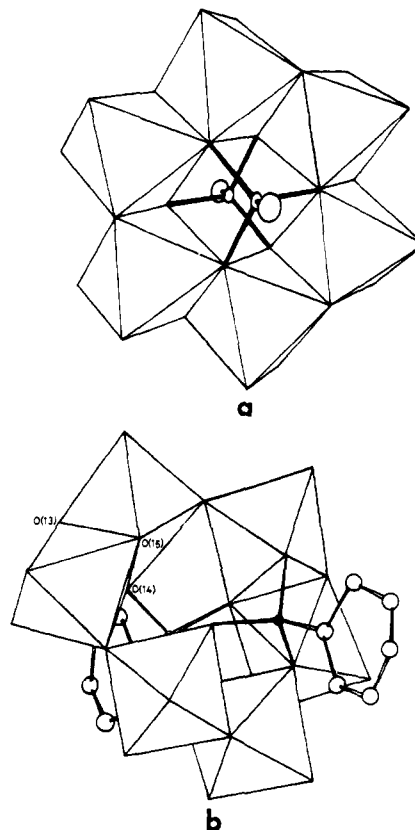


Figure 2. (a) A structure, $(\text{MeAs})_2\text{Mo}_6\text{O}_{24}^{4-}$ (ref 4); (b) B structure, $(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2^{4-}$ (this work).

We recently described the synthesis and structure of a series of hexamolydbisorganoarsonates, $(\text{RAs})_2\text{Mo}_6\text{O}_{24}^{4-}$ (A),^{4,5} which are isolated from aqueous acidified solutions of RASO_3^{2-} and MoO_4^{2-} (1:3 molar ratio) at pH 3-5. We now report that it is possible, reproducibly, to isolate from the same solutions salts of a second 2:6 molybdoarsonate complex (B), and that furthermore the B complexes are the predominant solute species in such solutions. The stoichiometry of the new complexes according to chemical analysis of three derivatives ($\text{R} = \text{Me}, \text{Ph}, p\text{-C}_6\text{H}_4\text{NH}_2$) is identical with that of the A complexes. Salts of the B anions can be distinguished from those of A by a consistent displacement of a strong infrared absorption band from ~ 795 (A) to ~ 825 cm^{-1} (B); see Figure 1. The corresponding Raman bands (solid samples) appear at ~ 790 and ~ 850 cm^{-1} , respectively. In aqueous or D_2O solutions at room temperature, Raman and infrared spectra show bands corresponding to the B form only, in the pH range 2.5-7.⁶

An x-ray structural investigation of the guanidinium salt of the B phenyl derivative has been carried out (K.Y.M. and Y.S.). The salt $(\text{CN}_3\text{H}_6)_4[(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2] \cdot 4\text{H}_2\text{O}$ crystallizes in space group $P2_1$ with $a = 13.754$ (8), $b = 15.752$ (7), $c = 11.900$ (5) Å; $\beta = 115.59$ (2)°; $Z = 2$. The x-ray intensities were measured up to $2\theta = 60^\circ$ on a Philips automatic four-circle diffractometer and the structure was solved by the heavy-atom method. Anisotropic temperature factors were applied to all nonhydrogen atoms and the structure was refined by the block-diagonal least-squares method. The final unweighted R value based on 4720 independent reflections was 0.066. Details of the structure determination will be published later elsewhere.⁷

The anion consists of six MoO_6 octahedra, which form a ring with one face sharing at O(13), O(14), and O(15), two corner sharings, and three edge sharings. The two tetrahedral $\text{C}_6\text{H}_5\text{AsO}_3$ groups cap the ring, one from above and the other from below, as is shown in Figure 2b.

The structure of the B anion differs from that of A (Figure 2a) by the introduction of face sharing between two of the MoO₆ octahedra. This arrangement requires 25 oxygen atoms, as opposed to 24 in the A structure, and consequently A and B are, strictly speaking, not isomers. The metal-oxygen bond lengths in the new structure fall in the expected ranges⁸ for the types of bridging or terminal oxygen involved, *with one exception*—the bonds to O(15), one of the atoms in the shared face, are anomalously long, 2.393 (14) and 2.478 (15) Å.⁹ We therefore believe that a bridging water molecule occupies this site. If O(15) is removed from the structure, only a slight rotation of the previously face-shared dimolydate group is necessary to produce the A structure. Conversely, A could be transformed to B if a water molecule is introduced adjacent to any two of the oxygen atoms of a PhAsO₃ group.¹⁰

Although the B ("hydrated") structure is the predominant solute species in aqueous solution, the equilibrium, B ⇌ A + H₂O, can be displaced to the right by rigorous removal of water from an acetonitrile solution. The pure B salt (Bu₄N)₄[(PhAs)₂Mo₆O₂₅H₂] can be obtained by precipitation from aqueous solution and drying at 110 °C. Recrystallization of this salt from MeCN yields mixtures of A and B anions according to IR spectra. The 90-MHz ¹H FT-NMR spectrum of a recrystallized sample (predominantly B) in CD₃CN shows two phenyl multiplets centered at 8.26 (2 H) and 7.49 (3 H) ppm,¹² and the H₂O resonance (exchange peak between anion and traces of water in solvent) at 3.38 ppm (at 26 °C).¹³ The chemical shifts of the phenyl resonances are unchanged between -20 and 90 °C, but, if the solution is kept at 90 °C (sealed tube) for several hours, the phenyl resonances then appear at 8.10 and 7.52 ppm, the H₂O peak has disappeared, and two broad peaks have developed at 5.7 and 6.3 ppm. Addition of a drop of water to the cooled solution immediately restores the original phenyl spectrum (8.22 and 7.48 ppm). Parallel treatment of a solution in MeCN, monitored by infrared spectroscopy, confirms that the above changes reflect the dehydration and subsequent rehydration



During the heating, water present in the solution from dissociation of B reacts with the solvent to produce acetamide. The acetamide accounts for the NMR peaks at 5.7 and 6.3 ppm, and also for IR bands at 3485, 3375, 1682, and 1670 cm⁻¹ that appear in the heated solutions.^{14,15} Further NMR studies of the A-B interconversion are in progress.

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References and Notes

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- (6) At the higher end of the pH range, absorption bands due to small amounts of MoO₄²⁻ and RAsO₃²⁻ are also observed.
- (7) Submitted to *Bull. Chem. Soc. Jpn.*
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- (9) The Mo-O bond lengths to O(13) are 1.952 (13) and 1.908 (14) Å and to O(14) (triple bridging) are 2.255 (16) and 2.314 (14) Å. The As-O(15) bond length is 1.707 Å.
- (10) We note that Day et al.³ have recently speculated about the lability of the RAsO₃²⁻ groups in the A structure.
- (11) The IR spectrum of this salt was unchanged after 9 h in vacuo at 125 °C.
- (12) The corresponding resonances in a solution (Bu₄N)₂PhAsO₃ in CD₃CN appear at 7.87 and 7.61 ppm, respectively.
- (13) The chemical shift of this resonance is strongly temperature dependent and varies from 4.34 (-20 °C) to 2.43 ppm (85 °C).
- (14) All the NMR and IR features that develop in the heated solutions could be reproduced by dissolving acetamide in a fresh solution of the B anion.
- (15) Filowitz and Klemperer⁵ deduced the A structure from the ¹⁷O NMR spectrum of the Bu₄N⁺ salt in MeCN. The spectrum was accumulated at 80 °C, i.e., under conditions where B is dehydrated by the process described here.

Wonsuk Kwak, Ljudmila M. Rajković
Michael T. Pope,* Carl O. Quicksall

Department of Chemistry, Georgetown University
Washington, D.C. 20057

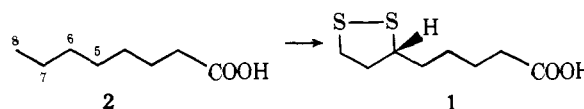
Kazuko Y. Matsumoto, Yukiyoshi Sasaki*

Department of Chemistry, University of Tokyo
Bunkyo-ku, Tokyo 113
Received June 13, 1977

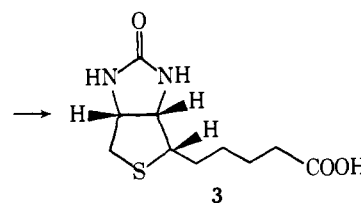
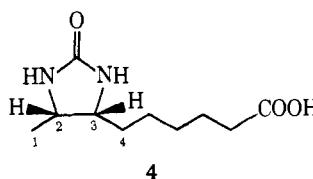
Biosynthesis of Lipoic Acid. 1. Incorporation of Specifically Tritiated Octanoic Acid into Lipoic Acid

Sir:

α-(+)-Lipoic (6,8-thioctic) acid (1) is an essential coenzyme for all systems of α-keto acid dehydrogenase complexes that have been investigated.¹ Although considerable information is available concerning the mechanism of action of lipoic acid, little is known about the biosynthesis of this important compound. In 1964, Reed reported² that octanoic acid (2) serves as a specific precursor of 1 in *Escherichia coli*. This is an in-



triguing observation since it suggests that the dithiolane ring system of 1 may be generated via the introduction of sulfur at two saturated carbon atoms. The biosynthesis of lipoic acid may therefore resemble the biosynthesis of the vitamin (+)-biotin (3) from (+)-dethiobiotin (4), a transformation that has



recently been investigated in our laboratories.³ We now report experiments that confirm Reed's unpublished observation and demonstrate that the mode of sulfur introduction in lipoate biosynthesis does indeed bear some resemblance to the mechanism of sulfur introduction in biotin biosynthesis.

The first stage of our investigation required that we verify the observation that [1-¹⁴C]octanoic acid is specifically incorporated into lipoic acid. Accordingly, sodium [1-¹⁴C]octanoate was administered to shake cultures of *E. coli* (Crookes strain, ATCC 8739) and the cells harvested by centrifugation after 16 h at 32-34 °C. The cells were sonicated, radioactive lipoic acid was added as carrier, and the mixture was then