

- (5) R. G. Montemayer, D. T. Sauer, S. Fleming, D. W. Bennett, M. G. Thomas, and R. W. Parry, *J. Am. Chem. Soc.*, **100**, 2231 (1978).
- (6) The synthesis and characterization of $(i\text{-Pr}_2\text{N})_2\text{P}(\text{Cl})$, $(i\text{-Pr}_2\text{N})(\text{Me}_2\text{N})\text{P}(\text{Cl})$, and other N-P compounds will be described in a subsequent publication.
- (7) In separate experiments we have established that $(i\text{-Pr}_2\text{N})_2\text{P}(\text{Cl})$ reacts with SO_2 in the absence of AlCl_3 at ambient temperature to afford $(i\text{-Pr}_2\text{N})_2\text{-P}(\text{O})\text{Cl}$.
- (8) Program MULTAN: M. M. Woolfson, J. P. Declercq, and G. Germain.
- (9) For a compilation of N-P bond distances, see, e.g., J. C. Clardy, R. L. Kolpa, and J. G. Verkade, *Phosphorus*, **4**, 133 (1974).
- (10) $\angle\text{P-N(1)-C(2)} = 132.9$ (3) $^\circ$; $\angle\text{P-N(2)-C(3)} = 132.1$ (3) $^\circ$.
- (11) A. H. Cowley and M. McKee, unpublished work.

Alan H. Cowley,* Mike C. Cushner, John S. Szobota

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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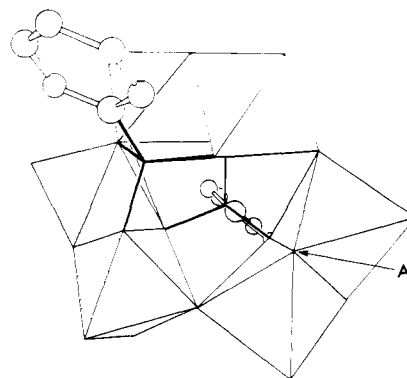


Figure 1. The structure of $[(\text{PhAs})_2\text{W}_6\text{O}_{25}\text{H}]^{5-}$ and $[(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2]^{4-}$ as a ring of six MO_6 octahedra linked by shared edges (three), corners (two), and faces (one) and capped on either side by PhAsO_3 groups. The vertex labeled A represents OH^- in the tungstate and H_2O in the molybdate.

Protonation-Induced Dynamic Stereochemistry of Hexatungstobis(organoarsonate) Anions

Sir:

The formation of heteropoly and isopoly complexes from monomeric oxo anions must involve sequences of protonation and water elimination steps which have so far eluded direct observation. We report here a heteropoly tungstate structure, protonation of which leads to fluxional behavior involving exchange of coordinated water.

Aqueous solutions of tungstate and organoarsenate anions, RAsO_3^{2-} , react at pH 5-7 to form the heteropoly anions $(\text{RAs})_2\text{W}_6\text{O}_{25}\text{H}^{5-}$, which can be isolated as guanidinium salts.¹ The salt $(\text{CN}_3\text{H}_6)_5[(\text{C}_6\text{H}_5\text{As})_2\text{W}_6\text{O}_{25}\text{H}]\cdot 2\text{H}_2\text{O}$, crystallizes as well-formed parallelepipeds in space group $Pbca$ with $a = 22.050$ (5), $b = 21.614$ (4), $c = 19.680$ (4) Å; $Z = 8$; $\rho(\text{calcd}) = 3.04$, $\rho(\text{obsd}) = 3.04$ (1) g cm^{-3} . Its crystal structure was determined by direct methods from 4238 independent nonzero diffraction intensities measured with a Picker FACS-I diffractometer using Zr-filtered Mo $K\alpha$ radiation. The structure was refined by full-matrix least squares to final consistency indices of $R = 0.065$ and $R_w = 0.077$. Complete crystallographic and structural details will appear later, but the important features of the anion are shown in Figure 1. The anion is isostructural with $[(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{25}\text{H}_2]^{4-}$,^{2,3} and is the first example of a structure involving face-shared WO_6 octahedra. We have argued previously, on the basis of metal-oxygen bond lengths, that the two nonaromatic protons in the molybdate structure formed a bridging water molecule at one of the vertices of the shared octahedral face (see Figure 1). Analogous arguments place the single proton (required by the cation stoichiometry) on the corresponding vertex of the tungstate structure. The W-O(H) bond lengths are 2.14 (2) and 2.16 (2) Å compared with 2.39 (2) and 2.48 (2) Å for Mo-O(H_2).⁴

Although the two organic groups on either side of the anion are not structurally equivalent, only a single ^1H NMR signal is seen for solutions of the molybdates in water or "wet" organic solvents.² It was suggested that equalization of the organic groups resulted from rapid exchange of the anion's bridging water molecule with the solvent. Such an exchange was postulated to involve an "anhydrous" intermediate of D_{3d} symmetry in which all six MoO_6 octahedra are linked by shared edges.⁵ In contrast to the molybdates, NMR spectra of the new tungstate complexes show two signals which coalesce as the pH is lowered. Spectra of the phenyl derivative are shown in Figure 2. Above pH 3.6 the ortho proton resonances appear as a pair of multiplets at ~ 8.1 and 8.4 ppm, whereas the meta and para protons of both phenyl groups form an unresolved multiplet in the same region (~ 7.7 ppm) as the five protons of uncomplexed phenylarsonate. When the pH is lowered the

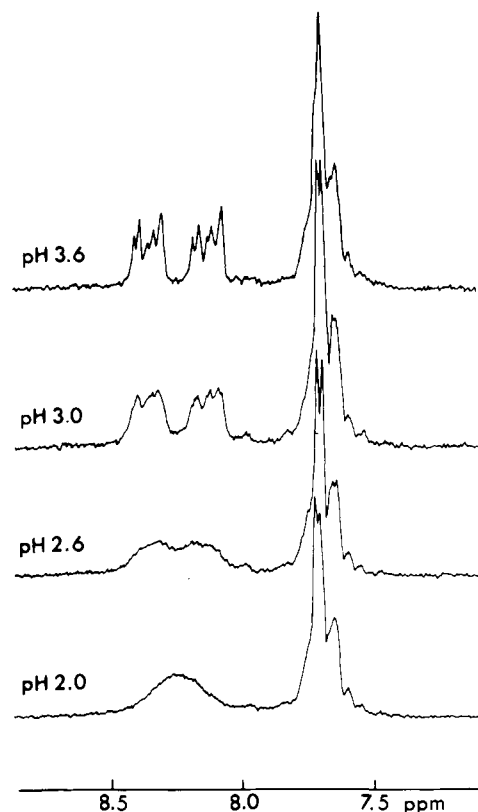


Figure 2. 90-MHz ^1H FT-NMR spectra of 0.017 M $(\text{C}_6\text{H}_5\text{As})_2\text{W}_6\text{O}_{25}\text{H}^{5-}$ prepared by mixing stoichiometric quantities of D_2O solutions of Na_2WO_4 and $\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$ and adjusting the pH with DCl (temperature, 26 $^\circ\text{C}$). The spectrum of an analyzed sample of the sparingly soluble guanidinium salt of pH 7 was identical with the top spectrum shown.

ortho resonances broaden and coalesce, but the ratio of intensities, ortho:(meta + para), remains unchanged, showing that there has been no net decomposition of the complex. The spectra support a process that involves protonation of the bridging hydroxo oxygen and subsequent water exchange as for the molybdate. Preliminary line-shape analysis of the NMR spectrum of $(\text{CH}_3\text{As})_2\text{W}_6\text{O}_{25}\text{H}^{5-}$ at pH 4.2 and 26-90 $^\circ\text{C}$ gave apparent activation parameters, $\Delta H^\ddagger \sim 12$ kJ mol^{-1} and $\Delta S^\ddagger \sim -170$ $\text{J K}^{-1} \text{mol}^{-1}$. Such parameters are not inconsistent with a mechanism involving a protonation pre-equilibrium followed by water exchange, although further investigation of this system is required and is planned. The difference in lability between the molybdate and tungstate anions may only reflect differences in basicity. Since exchange-averaged NMR spectra were observed for the molybdates over the complete pH range of stability, the pK for

$[(\text{RAS})_2\text{Mo}_6\text{O}_{24}(\text{OH}_2)]^{4-} \rightarrow [(\text{RAS})_2\text{Mo}_6\text{O}_{24}(\text{OH})]^{5-} + \text{H}^+$
must be greater than ~ 6 .²

Acknowledgments. We thank Professor J. E. Earley for helpful discussion and S.-B. Chen for assistance with the NMR measurements. This research has been supported by the National Institutes of Health through Grant No. GM23263 and, in part, by the Office of Naval Research.

References and Notes

- (1) Good elemental analyses (C, H, N, As, and W) were obtained for the derivatives where R = CH₃, C₆H₅, and *p*-C₆H₄NH₂.
- (2) W. Kwak, L. M. Rajković, M. T. Pope, C. O. Quicksall, K. Y. Matsumoto, and Y. Sasaki, *J. Am. Chem. Soc.*, **99**, 6463 (1977).
- (3) K. Y. Matsumoto, *Bull. Chem. Soc. Jpn.*, **51**, 492 (1978).

- (4) Bond lengths to the other doubly bonding oxygen in the shared face are 1.95, 1.91 (Mo),³ and 1.93, 1.94 Å (W).
- (5) In spite of an equilibrium that strongly favors the hydrated molybdate structure in aqueous solution,² salts of the D_{3d} anion, (RAS)₂Mo₆O₂₄⁴⁻, have been isolated and structurally characterized:²⁴ W. Kwak, L. M. Rajković, J. K. Stalick, M. T. Pope, and C. O. Quicksall, *Inorg. Chem.*, **15**, 2778 (1976).
- (6) At 26 °C the spectrum consists of a pair of narrow lines (~ 2 Hz) at 2.15 and 2.48 ppm. These broaden and coalesce as the temperature is raised to 90 °C. No shifts indicating exchange with uncomplexed CH₃AsO₃²⁻ (δ 1.7 ppm) were observed at any temperature.

S. H. Wasfi, W. Kwak, M. T. Pope,* K. M. Barkigia
R. J. Butcher, C. O. Quicksall

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

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Book Reviews*

Nuclei and Particles: An Introduction to Nuclear and Subnuclear Physics. 2nd Edition. By EMILIO SEGRÈ (University of California, Berkeley). W. A. Benjamin, Inc., Reading, Mass. 1977. xx + 966 pp. \$29.50.

The popular text by Nobel laureate Segrè, has been extensively revised and updated. It is suitable for graduate students and advanced undergraduates with introductory knowledge of nuclear physics and quantum mechanics. Some 20 chapters are organized into three parts: I. Tools; II. The Nucleus; III. Particles. Included is a discussion of the more recent developments in elementary particle theory, such as unitary symmetry and quark models.

Tables of Standard Electrode Potentials. By G. MILAZZO and S. CAROLI (Istituto Superiore di Sanita, Rome). Wiley-Interscience, New York. 1978. xvi + 421 pp. \$39.95.

This book is the result of a project sponsored by the IUPAC Electrochemistry Commission. It consists of a compilation of electrochemical data referenced in *Chemical Abstracts*, 1945–1973, plus an addendum covering 1973–1975.

Structure and Collisions of Ions and Atoms (Topics in Current Physics. Volume 5). Edited by I. A. SELLIN (Oak Ridge National Laboratory). Springer-Verlag, Heidelberg. 1978. x + 350 pp. DM 72.00 (\sim \$33.20).

Volume 5 in this series is a collection of eight chapters by ten authors. Theoretical and experimental aspects of atomic and molecular physics as investigated by charged particle accelerators are discussed.

Solution of Differential Equation Models by Polynomial Approximation (International Series in the Physical and Chemical Engineering Sciences). By J. VILLADSEN and M. L. MICHELSEN (Institutet for Kemiteknik, Denmark). Prentice-Hall, Englewood Cliffs, N.J. 1978. \$24.95.

This book describes how to set up models and obtain numerical solutions for phenomena described by differential equations. Applications in chemical engineering are given.

BOOKS RECEIVED

Anglo-American and German Abbreviations in Science and Technology. Volume 2. By PETER WENNICH. Bowker, New York. 1977. pp 841–1448. \$29.95.

Volume 2 of a three-volume dictionary containing some 150,000 abbreviations used in science and technology.

Treatise on Analytical Chemistry. Part I. Volume 12. Edited by I. M. KOLTHOFF (University of Minnesota) and P. J. ELVING (University

of Michigan). John Wiley, New York. 1976. xviii + pp 7235–7428. \$22.50.

Cumulative index to Volumes 1–11.

Laboratory Manual of Physical Chemistry. Second Edition. By H. D. CROCKFORD, J. W. NOWELL, H. W. BAIRD, and F. W. GETZEN. John Wiley, New York. 1976. vi + 352 pp. \$9.95.

Basic Chemical Thermodynamics. Second Edition. Oxford Chemistry Series. No. 28. By E. BRIAN SMITH (Oxford University). Oxford University Press, New York. 1977. xii + 130 pp. \$11.50 cloth; \$4.95 paper.

Annual Review of Physical Chemistry. Volume 28. Edited by B. S. RABINOVITCH (University of Washington), J. M. SCHURR (University of Washington), and H. L. STRAUSS (University of California, Berkeley). Annual Reviews Inc., Palo Alto, Calif. 1977. ix + 570 pp. \$17.00.

Includes an autobiographical essay for Henry Eyring, who edited this Annual Review for 20 years.

Modern Three-Hadron Physics (Topics in Current Physics. Volume 2). Edited by A. W. THOMAS (University of British Columbia). Springer-Verlag, Berlin. 1977. x + 250 pp. \$30.40.

Six chapters, by seven contributors, on aspects of three-body scattering theory.

Organic Chemistry. Second Edition. By N. L. ALLINGER (University of Georgia), M. P. CAVA (University of Pennsylvania), D. C. DEJONGH (University of Montreal), C. R. JOHNSON, N. A. LEBEL, and C. L. STEVENS (Wayne State University). Worth Publishers, Inc., New York. 1976. xxi + 1024 pp. \$19.95.

Weak Interactions (Graduate Student Series in Physics). By DAVID BAILIN (University of Sussex). Crane, Russak & Co., New York. 1977. ix + 406 pp. \$18.95.

A quite lucid account of the theory of weak interactions intermediate in level between textbooks such as Bjorken and Drell and the current research literature.

Modular Representations of Finite Groups (Pure and Applied Mathematics Series). By B. M. PUTTASWAMIAH and J. D. DIXON (Carleton University, Ottawa). Academic Press, New York. 1977. xv + 242 pp. \$23.50.

INTRODUCTORY TEXTS RECEIVED

Foundations of College Chemistry. Second Edition. By D. B. MURPHY (City University of New York) and V. ROUSSEAU (Iona College). Ronald Press, New York. 1975. xiii + 747 pp. \$14.95.

Frantz/Malm's Chemical Principles in the Laboratory. Second Edition. By J. L. ROBERTS, JR., and J. B. IFFT (University of Redlands). W. H. Freeman and Co., San Francisco. 1977. xiii + 483 pp. \$8.50.

* Unsigned book reviews are by the Book Review Editor.