Solution Structures of Large Group 5A and 6A Polyoxoanions by ^{17}O Nuclear Magnetic Resonance

Sir:

A barrier to rapid progress in polyoxoanion chemistry has been the extreme difficulty of structural characterization in solution and, to a lesser extent, in the solid state.[1,2] Examination of the ^{17}O NMR spectra of several representative compounds of known structure shows this to be an important new approach to the determination of solution stereochemistry in polyoxoanions. The species observed are usually enriched (~1-2 atom % ^{17}O), but in favorable cases they may be observed at natural abundance (0.037 atom % ^{17}O).

Variable temperature ^{17}O 12.20-MHz NMR spectra were recorded in the Fourier mode using a Bruker HFX-90 spectrometer with a Digilab FTS/NMR-3 data system and pulser. A 3-mm coaxial capillary containing C_6F_6 was used in the 10-mm sample tube to provide a lock. Since both spin-spin (T_2) and spin-lattice (T_1) relaxation are expected to be dominated by quadrupolar relaxation (except for oxygen nuclei where the electric field gradient is zero by symmetry), the spectra were taken utilizing a small number of data points (2048 over 12500 Hz) and pulsing rapidly to optimize signal/noise.

The isopolyanions $Mo_6O_{19}^{2-}$, $Nb_6O_{19}^{8-}$, and $Ta_6O_{19}^{8-}$ all have the octahedral metal-oxygen framework illustrated for the hexamolybdate ion in Figure 1a. The three nonequivalent sets of oxygen nuclei give three well-resolved resonances for each of these polyoxoanions (Table I). As anticipated,[3] increased metal to oxygen π bonding correlates with larger downfield shifts. Thus, in general, the more metals which the oxo ligands bridge, the further upfield their resonances lie.

Figure 1b shows a typical ^{17}O NMR spectra. Integrated intensities are not a reliable measure of the number of symmetry equivalent nuclei for the following reasons: (1) relaxation times for oxygen nuclei located at chemically nonequivalent sites are, in general, different; (2) the pulse power decreases with increasing frequency from the carrier; (3) audio frequency filtering decreases the signal intensity exponentially from left to right across the spectra; (4) the degree of isotopic enrichment may be different for each set of sites. The narrow line width for the central oxygen atom in $Mo_6O_{19}^{2-}$ is consistent with its octahedral environment (zero electric field gradient).

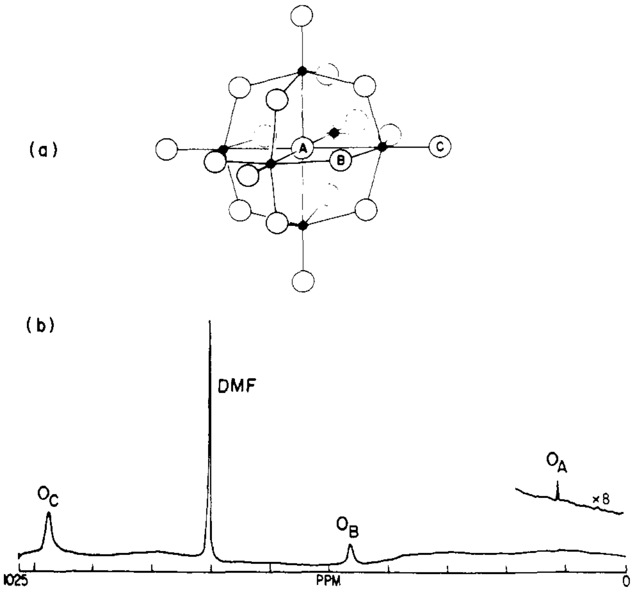

Figure 1. (A) O_h symmetrized structure of $Mo_6O_{19}^{2-}$ (see H. R. Allock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, **12**, 2963 (1973). Small filled circles represent molybdenum nuclei and large open circles represent oxygen nuclei. The unique, central oxygen atom is labeled A, one of the 12 symmetry equivalent twofold bridging oxygens is labeled B, and one of the six symmetry equivalent terminal oxygens is labeled C. (B) The ^{17}O NMR spectra of $[(C_4H_9)_4N]_2Mo_6O_{19}$ (0.9 atom % ^{17}O) in *N,N*-dimethylformamide (DMF) solution at 25°. Assignments of the $Mo_6O_{19}^{2-}$ resonances correspond to the labeling scheme given in Figure 1a. Downfield shifts lie further to the left.

Table I. ^{17}O Chemical Shifts with Respect to H_2O (Positive Chemical Shift is Upfield)

	O_A	O_B	O_C
$Mo_6O_{19}^{2-}$[a]	+27	−559	−829
$Nb_6O_{19}^{8-}$[b]	−20	−386	−594
$Ta_6O_{19}^{8-}$[b]	+41	−329	−476

	Terminal oxygens	Bridging oxygens
$PMo_{12}O_{40}^{3-}$	−936	−569
$PW_{12}O_{40}^{3-}$	−767	−428
$SiW_{12}O_{40}^{4-}$	−750	−415

[a] Chemical shifts were measured relative to the solvent, *N,N*-dimethylformamide, which has been assigned a chemical shift of −324 ppm relative to H_2O (H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn, *Helv. Chim. Acta*, 44, 865 (1961). [b] Resonances were observed in aqueous solution at natural ^{17}O abundance.

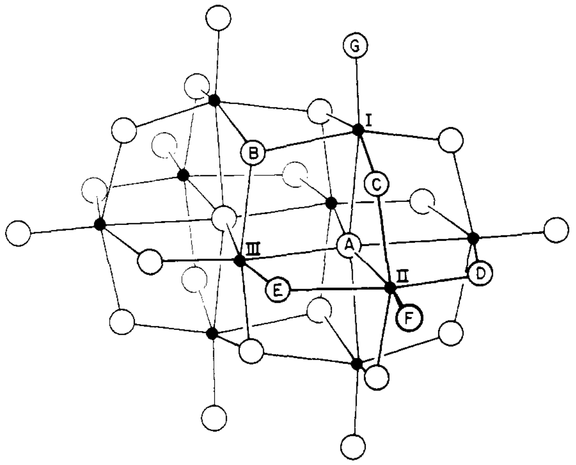

Figure 2. D_{2h} symmetrized structure of $V_{10}O_{28}^{6-}$ (see ref 1) Small filled circles represent vanadium nuclei and large open circles represent oxygen nuclei. As in Figure 1b, one member of each set of symmetry equivalent oxygen nuclei is labeled.

The heteropolyacids $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ all possess the tetrahedral Keggin structure[1] which involves 12 equivalent terminal oxygens, two nonequivalent sets of 12 doubly bridging oxygens, and four equivalent central oxygens each of which is bonded to three metal atoms as well as the central heteroatom. When dissolved in a stabilizing solvent mixture (20% dioxane-water)[4] at 25°, the ^{17}O resonances of these strong acids were too broad to observe. At 65°, the resonances were narrowed sufficiently to be detected (Table I). The spectrum of $PMo_{12}O_{40}^{3-}$ (enriched to ~2 atom % ^{17}O) has a peak at −936 ppm (terminal oxygens) and a peak at ca. −569 ppm which is assigned to two partially resolved resonances (the two sets of nonequivalent bridging oxygens). This evidence supports the empirical correlation between the number of metal atoms bonded to an oxygen atom and the upfield shift. Similar spectra were observed for the other two compounds. No resonances were detected for the four central oxygen nuclei.

$K_6V_{10}O_{28}\cdot 9H_2O$ was dissolved in water (2.2 atom % ^{17}O, pH 6.5–7) and heated to 65° to increase the isotope exchange rate. Resonances observed at −72, −400, −772, and −906 ppm are tentatively assigned to the sixfold bridging oxygens (O_A), threefold bridging oxygens (O_B), doubly bridging oxygens (O_C, O_D, O_E), and terminal oxygens (O_F, O_G), respectively, using the labeling scheme shown in Figure 2 and assuming that the more metal atoms an oxo ligand bridges, the further upfield its resonance will lie. Other features in the ^{17}O spectrum are observed which correspond to degraded species known to coexist with protonated $V_{10}O_{28}{}^{6-}$ species in the pH range 6.5–7.[2] Future experiments will be carried out to determine the structure(s) of these species.

An important qualitative correlation has been demonstrated between oxygen environment and chemical shift; as further data are gathered more detailed interpretations should be possible.

Acknowledgment. W. G. K. acknowledges the National Science Foundation, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also gratefully acknowledge Messrs. G. Watunya and F. N. Schoch for obtaining some of the NMR spectra.

References and Notes

(1) H. T. Evans, Jr., *Perspect. Struct. Chem.*, **4**, 1–59 (1971).
(2) D. L. Kepert, "Comprehensive Inorganic Chemistry", Vol. 4, J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickinson, Ed., Pergamon Press, Oxford, 1973, pp 607–672.
(3) (a) J. A. Jackson and H. Taube, *J. Phys. Chem.*, **69**, 1844 (1965); (b) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Can. J. Chem.*, **43**, 145 (1965); (c) R. G. Kidd, *Can. J. Chem.*, **45**, 605 (1967).
(4) G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, **9**, 2488 (1970).

A. D. English, J. P. Jesson
Contribution No. 2270, Central Research and Development Center, E. I. du Pont de Nemours and Company
Experimental Station
Wilmington, Delaware 19898

W. G. Klemperer,* T. Mamouneas, L. Messerle
W. Shum, A. Tramontano
Department of Chemistry, Columbia University
New York, New York 10027

Received April 21, 1975

Additions and Corrections

Stereochemistry of Dioxovanadium(V) Complexes. II. The Crystal and Molecular Structures of Ammonium (Dihydrogen ethylenediaminetetraacetato)dioxovanadate(V) Trihydrate [*J. Am. Chem. Soc.*, **93**, 3873 (1971)]. By W. ROBERT SCHEIDT, D. M. COLLINS, and J. L. HOARD,* Department of Chemistry, Cornell University, Ithaca, New York 14850.

Professor E. C. Lingafelter has called our attention to some errors in Table I. The corrected values are given below.

Table I. Atomic Coordinates in Crystalline $NH_4[VO_2AH_2]\cdot 3H_2O$

Atom	10^4x	10^4y	10^4z
O_7	2951 (3)	−267 (2)	344 (1)
O_9	−4603 (3)	−1591 (2)	1528 (1)
C_3	4142 (3)	−229 (2)	3120 (2)
C_4	5169 (3)	−840 (2)	3752 (2)

Molecular Orbital Studies of Hydrogen Bonds. V. Analysis of the Hydrogen-Bond Energy between Lower Excited States of H_2CO and H_2O [*J. Am. Chem. Soc.*, **95**, 7563 (1973)]. By SUEHIRO IWATA and KEIJI MOROKUMA,* Department of Chemistry, University of Rochester, Rochester, New York 14627.

The first term in parentheses of eq 13 should be $E_2{}^i$ instead of $E_1{}^i$. The first term of eq A-3 should have a factor $\binom{1}{0}$. The denominator of eq A-4 should be $(1 \pm S_{\alpha\mu}{}^2)$, not $(1 + S_{\alpha\mu}{}^2)^{1/2}$. In the sixth line following eq A-4, $\sqrt{2}$ should not be there. The numerical factor of the second term of eq A-6 should be 4, not $2\sqrt{2}$. All the calculations were done with correct formulas.

Stereochemistry of Low-Spin Cobalt Porphyrins. III. The Crystal Structure and Molecular Stereochemistry of Bis(piperidine)-α,β,γ,δ-tetraphenylporphinatocobalt(II) [*J. Am. Chem. Soc.*, **96**, 84 (1974)]. By W. ROBERT SCHEIDT, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

The value for the unit cell constant, α, is incorrectly reported in the abstract and the paper. The correct value is $\alpha = 104.99\ (2)°$.

Synthesis and Characterization of a 1,8-Naphthoquinodimethane [*J. Am. Chem. Soc.*, **96**, 2291 (1974)]. By RICHARD M. PAGNI* and CHARLES R. WATSON, JR., Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916.

In reference 9 of this paper the rate constant at 128.8° is reported as 1.88×10^{-5} sec^{-1}. The value should be 1.88×10^{-4} sec^{-1}.

A Deuterium Isotope Study of Electrogenerative Hydrogenation. Mechanism of Hydrogenation of Ethylene at Positive Potentials [*J. Am. Chem. Soc.*, **93**, 1092 (1971)]. By STANLEY H. LANGER,* IRAJ FEIZ, and COLIN P. QUINN, Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

Recently, it was brought to our attention that computational errors led to the reporting of incorrect predicted mass spectra of deuterated ethanes in this paper. Corrected spectra calculated on the basis of assumptions given in this report are now presented in Table I. Use of these spectra resulted in corrected labeled ethane distributions which are