magnitude greater then $K_{py}^{2,2}$. For Ru(III)–Co(III), we found log $K_{py}^{3,3}$ = 12.4, which is about seven orders of magnitude greater than $K_{py}^{3,2}$. In the case of CoTPP in CH$_2$Cl$_2$ solution,[12] log K_1 for pyridine binding increase from 2.90 for Co^{II}TPP to 12.7 for Co^{III}TPP. Thus for pyridine binding the oxidation of Ru(II) has a large effect on the Lewis acidity of Co(II) and has little effect on Co(III), at least when compared to Co^{III}TPP. For 1-MeIm binding at Co(III), on the other hand, conversion of Ru(II) to Ru(III) allows the formation of the bis 1-MeIm adduct. We strongly suspect that the effects manifested by the Co(II) center upon oxidation of Ru(II) are electrostatic in origin, probably mediated by the bridging chloride. The Ru–Cl bond distance is not expected to shorten drastically upon oxidation (<0.1 Å).[18,19] Also, if the Ru^{III}Cl$_2$(nic)$_4^+$ moiety's effect were due to factors other than electrostatic, the Ru(II) should exert a greater influence on the Co(II) center than that observed, since the Co–Cl distance would be shorter in the Ru(II) form than in the Ru(III) form. However, unambiguous answers to questions about the origin and types of interactions between the Co and Ru ions must await further studies such as EPR, magnetic susceptibility, X-ray structural determination, and EXAFS, which are planned or in progress.

Irrespective of the origins of the interactive effects, this complex and the others in this series represent a unique class of porphyrin compounds having (1) a fixed, cationic axial ligand (2) with a charge which can be turned on and off and (3) without any significant geometric rearrangement. On the basis of a recent X-ray crystal structure obtained for **3**, the Ru–Co distance has been established to be 5.24 Å.[20] If there were any direct, non-electrostatic interactions such as spin coupling, these interactions would have to be mediated by the bridging chloride.

The large changes in both redox potential and binding properties of the cobalt center, triggered by changing the oxidation state and charge of the ruthenium, are both interesting and important observations because they suggest ways that one might tailor the properties of a particular porphyrin system in a desired way. For example, one could envision replacing the ruthenium with a less easily reduced metal, such as osmium or chromium, and produce similar changes in the M(II/III) couples for the more easily oxidized iron and manganese porphyrins (the oxidations of which occur at potentials negative of the Ru(II/III) couple). Similarly, replacing one or both of the ruthenium-bound chlorides with a suitable dianion would produce a fixed ligand with the opposite charge. We presently have such studies in progress.

(18) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 925.

(19) Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H.; *J. Chem. Soc., Dalton Trans.* **1977**, 1121.

(20) Anderson, O. P.; Schauer, C. K., unpublished results.

The Characterization of a New Heteropolytungstoarsonate Anion, [CH$_3$AsW$_7$O$_{27}$H]$^{7-}$. Topological Relationships among Ions Related to the Lindqvist Structure

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Abstract: Guanidinium salts of the anions [RAsW$_7$O$_{27}$H]$^{7-}$, where R = CH$_3$, C$_6$H$_5$, and *p*-NH$_2$-C$_6$H$_4$, have been isolated in crystalline form from weakly basic solutions (pH 7–8.5) of RAsO$_3^{2-}$ and WO$_4^{2-}$. Crystals of the methyl derivative as (CN$_3$H$_6$)$_7$[CH$_3$AsW$_7$O$_{27}$H]·3H$_2$O are orthorhombic, space group *Pnma*, with *a* = 17.605 (3) Å, *b* = 13.179 (1) Å, and *c* = 19.869 (3) Å, *Z* = 4, d_{calcd} = 3.29 g cm^{-3}, and d_{obsd} = 3.32 (2) g cm^{-3}. Mirror symmetry is imposed upon the anion and upon several cation sites. Least-squares refinement (2184 data with $I > 3\sigma(I)$ and (sin $\theta)/\lambda < 0.5958$ Å^{-1}) converged at values for *R* and R_w of 0.044 and 0.045. The CH$_3$AsO$_3$ moiety sits above one or the other of two chemically distinct triangular O$_3$ sites in a 75:25 ratio. The W$_7$O$_{24}$ group comprises a horseshoe of four edge-shared WO$_6$ octahedra linked at four vertices to a triangle of edge-shared octahedra. This group is topologically related to the Lindqvist M$_7$O$_{24}^{6-}$ structure. Some selected metrical details for the major isomer are given with the esd of an individual bond and the esd of the average, respectively, in parentheses: 13(W=O) 1.73 (2, 3); 16(W—O$_{bridging}$) 1.93 (1, 6); 2(W—O$_{triply\ bridging}$) 1.980 (13) and 2.213 (12); 3(W—O$_{As}$) 2.201 (12)–2.47 (2) Å. The proton is almost certainly located for the major isomer on the doubly bridging oxygen atom to which the As' is attached in the minor isomer (W—O = 2.215 (12) Å) and very likely for the minor isomer on the triply bridging oxygen atom to which As is attached for the major isomer, although in this case the expected extension of the W–O separation is masked. In the solid state the ^{13}C CPMAS NMR spectrum shows the methyl resonance at 20.3 ppm with a shoulder at ca. 17 ppm attributed to the minor isomer. The heteropolyanion (^{1}H NMR, 1.98 ppm, methyl) is rapidly converted into [(CH$_3$As)$_2$W$_6$O$_{25}$H]$^{5-}$ (2.1, 2.4 ppm) and/or CH$_3$AsO$_3^{2-}$ (1.8 ppm) in aqueous solution. Plausible mechanisms connecting W$_7$O$_{24}^{6-}$ (paratungstate-A, Lindqvist structure) and RAsO$_3^{2-}$ with both isomers of the title heteropolyanion are described.

Much of the current resurgence of interest in the chemistry of heteropolymolybdate and tungstate anions[1] may be attributed to the potential of these species for catalysis, especially since the structures of polyanions model metal oxide surfaces. For this and other reasons the field of organic/organometallic derivatives of heteropolyanions has expanded greatly since 1975.[2-12] One

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(1) Pope, M. T. "Heteropoly and Isopoly Oxometalates"; Springer-Verlag: New York, 1983.
(2) (a) Kwak, W.; Pope, M. T.; Scully, T. F. *J. Am. Chem. Soc.* **1975**, *97*, 5735. (b) Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 1577.

successful strategy to incorporate organic groups into polyoxometalate structures has been the reaction of organophosphonates[2,12] and -arsonates[3-7] with aqueous molybdate[2-5,7] and tungstate[6,12] solutions. With $RAsO_3^{2-}$ the 2:6 anions $[(RAsO_3)_2Mo_6O_{19}$-$H_2]^{4-}$[4c,7] and $[(RAsO_3)_2W_6O_{19}H]^{5-}$[6] are the predominant species in weakly acid solutions (pH 2-6). Both of these anions are susceptible to NMR-detectable inter- or intramolecular exchange or fluxional behavior. We have detected a new heteropolyanion in solutions of WO_4^{2-} and $CH_3AsO_3^{2-}$ at higher pH 7-8.5), and we report here its isolation and structural characterization. The new anion $[(CH_3AsO_3)W_7O_{24}H]^{7-}$ has an unusual stoichiometry, and it appears to be an important kinetic intermediate between the "Lindqvist" isopolyheptametalate M_7O_{24} structure and the more stable 2:6 heteropolyanions.

Experimental Section

Preparation of Guanidinium Heptatungstomethylarsonate. A mixture of 19.8 g (0.06 mol) of $Na_2WO_4 \cdot 2H_2O$ and 4.1 g (0.02 mol) of Na_2C-H_3AsO_3 was dissolved in 60 mL of water and the pH of the resulting solution was adjusted to 7-8.5 (optimum 7.1) with 9 M H_2SO_4. The solution was brought to the boil and allowed to cool, and a solution of 5 g of guanidinium chloride in 40 mL of water was added dropwise with continuous stirring. After filtration to remove traces of insoluble matter, the solution was allowed to stand for a few hours (typically overnight) whereupon about 1 g of white crystals was deposited. The crystals were filtered off, washed with cold water, and air dried. Recrystallization attempts were unsuccessful. Anal. (Galbraith Laboratories, Inc., Knoxville, TN) for $(CN_3H_6)_7[CH_3AsW_7O_{27}H] \cdot 3H_2O$, observed (calculated): C, 4.20 (4.19); N, 12.72 (12.84); W, 56.33 (56.18); As, 3.19 (3.27); H, 2.23 (2.27); H_2O, 1.98 (2.35). If the reaction was carried out with stoichiometric quantities (1:7) of $CH_3AsO_3^{2-}$ and WO_4^{2-}, or the the filtrate from the above preparation was allowed to stand longer, isopolyparatungstate salts were deposited. If the pH of the reaction mixture fell below 7, the major product was $(CN_3H_6)_5[(CH_3AsO_3)_2W_6O_{19}H] \cdot 2H_2O$.[8]

The *phenyl* and *p-aminophenyl* derivatives were prepared analogously starting with $C_6H_5AsO_3H_2$ and $p-NH_2-C_6H_4AsO_3H_2$. In both cases the yields were larger (70-80% based on W) than those for the methyl derivative, but the products were microcrystalline and unsuitable for X-ray diffraction experiments. The *p*-aminophenyl derivative was always found to be contaminated with excess isopolytungstate. Anal. for (C-

(3) (a) Pioneering work with molybdoarsonates may be traced to the following: Miolati, A.; Pizzighelli, R. *J. Prakt. Chem.* **1908**, *185*, 417. Rosenheim, A.; Bilecki, A. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 539. Souchay, P. *Bull. Soc. Chim. Fr.* **1948**, *15*, 143. (b) Barkigia, K. M.; Rajkovic, L. M.; Pope, M. T.; Quicksall, C. O. *J. Am. Chem. Soc.* **1975**, *97*, 4146. (c) Barkigia, K. M.; Rajkovic-Blazer, L. M.; Pope, M. T.; Prince, E.; Quicksall, C. O. *Inorg. Chem.* **1980**, *19*, 2531.

(4) (a) Filowitz, M.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1976**, 233. (b) Kwak, W.; Rajkovic, L. M.; Stalick, J. K.; Pope, M. T.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 2778. (c) Kwak, W.; Rajkovic, L. M.; Pope, M. T.; Quicksall, C. O.; Matsumoto, K. Y.; Sasaki, Y. *J. Am. Chem. soc.* **1977**, *99*, 6463. (d) Matsumoto, K. Y. *Bull Chem. Soc. Jpn.* **1978**, *51*, 492.

(5) (a) Filowitz, M.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1977**, 201. (b) Pope, M. T.; Quicksall, C. O.; Kwak, W.; Rajkovic, L. M.; Stalick, J. K.; Barkigia, K. M.; Scully, T. F. *J. Less-Common Met.* **1977**, *54*, 129. (c) Barkigia, K. M.; Rajkovic-Blazer, L. M.; Pope, M. T.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 3318.

(6) Wasfi, S. H.; Kwak, W.; Pope, M. T.; Barkigia, K. M.; Butcher, R. J.; Quicksall, C. O. *J. Am. Chem. Soc.* **1978**, *100*, 7786.

(7) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284.

(8) (a) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 491. (b) Day, V. W.; Thompson, M. R.; Day, C. S.; Klemperer, W. G.; Liu, R. S. *Ibid.* **1980**, *102*, 5971.

(9) Adams, R. S.; Klemperer, W. G.; Liu, R. S. *J. Chem. Soc., Chem. Commun.* **1979**, 256.

(10) (a) Ho, R. K.; Klemperer, W. G. *J. Am. Chem. Soc.* **100**, 6722. (b) Klemperer, W. G.; Shum, W. *J. Chem. Soc., Chem. Commun.* **1979**, 60. (c) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759. (d) Knoth, W. H. *Ibid.* **1979**, *101*, 2211. (e) Zonnevijlle, F.; Pope, M. T. *Ibid.* **1979**, *101*, 2731. (f) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R. S.; Shum, W. *Ibid.* **1981**, *103*, 3597. (g) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.

(11) (a) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (b) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *Ibid.* **1982**, *104*, 6158. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Ibid.* **1984**, *106*, 4125. (d) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *Ibid.* **1984**, *106*, 5750. (e) Finke, R. G.; Droege, M. W. *Ibid.* **1984**, *106*, 7274.

(12) Sethuraman, P. R.; Leparulo, M. A.; Pope, M. T.; Zonnevijlle, F.; Brévard, C.; Lemerle, J. *J. Am. Chem. Soc.* **1981**, *103*, 7665.

$N_3H_6)_7[C_6H_5AsW_7O_{27}H] \cdot 6H_2O$, observed (calculated): C, 6.34 (6.50); N, 11.73 (12.25); As, 3.06 (3.12); W, 54.03 (53.62); H_2O, 4.07 (4.50). Anal. for $(CN_3H_6)_7[p-NH_2C_6H_4AsW_7O_{27}H] \cdot 5H_2O$, observed (calculated): C, 6.44 (6.50); N, 12.18 (12.84); H, 2.36 (2.46); As, 3.06 (3.12); W, 58.81 (53.69).

Infrared Spectra. The IR spectra, in KBr disks, of the three derivatives are essentially identical in the range 1000 to 200 cm^{-1}. Major absorptions are at 860, 790, 600-700 (broad unsplit), 380, 320 cm^{-1}. These may be compared to those of $(CN_3H_6)_5[(C_6H_5As)_2W_6O_{25}H] \cdot 2H_2O$: 890, 820, 690, 655, 350 cm^{-1}.

NMR Spectra. The ^1H NMR spectrum of the methyl derivative dissolved in D_2O showed resonances for $CH_3AsO_3^{2-}$ (1.79 ppm) and $[(CH_3AsO_3)_2W_6O_{19}H]^{5-}$ (equal singlets at 2.14 and 2.49 ppm). In a synthetic reaction mixture (1:3 As-W, pH 8.3) a resonance was detected at 1.98 ppm in addition to weak lines at 2.1 and 2.4 ppm and a major line at 1.78 ppm. The 1.98-ppm resonance is tentatively attributed to $[CH_3AsW_7O_{27}H]^{7-}$. In the crystalline state the ^{13}C CPMAS NMR shows lines at ca. 160 ppm (cation) and 20.3 ppm (methyl carbon). Although the latter line is broadened ($\Delta\nu_{1/2} \sim 5$ ppm) by the adjacent As atom, a shoulder of approximately one-fourth the total intensity at ca. 17 ppm may indicate the minor isomer discovered in the structure analysis (see below).

Crystal Structure Analysis of $[CH_3AsW_7O_{27}H][CN_3H_6]_7 \cdot 3H_2O$. Symmetry and systematic absences consistent with the orthorhombic space groups *Pnma* and *Pna2$_1$* were observed with precession photography. A very small needle $0.20 \times 0.02 \times 0.02$ mm was selected for data collection upon a Picker FACS-I diffractometer with use of the NRC-Canada software incorporating in-line profile analysis. Unit cell parameters and crystal orientation were determined by least-squares refinement of the setting angles of 14 reflections and their Friedel pairs in the range 0.342 $< (\sin \theta)/\lambda < 0.384$ Å^{-1}, using graphite-monochromated Mo Kα radiation. A total of 3538 unique reflections in the range $0.0307 < (\sin \theta)/\lambda < 0.5958$ Å^{-1} were measured by using $\theta-2\theta$ scans. Three standard reflections, monitored regularly, showed no significant change during data collection. The structure was solved with use of MULTAN 11/80 and developed with use of the Enraf-Nonius SDP. At convergence, values for R and R_w (on F) for the 2184 reflections with $I > 3\sigma(I)$ used in refinements were 0.044 and 0.045. The weighting scheme employed was $w = 1/\sigma^2$ where $\sigma^2 = \sigma^2(\text{counting}) + (0.03F^2)^2$ and the extinction parameter was 5.1 (6) $\times 10^{-9}$. The $AsCH_3$ moiety had been assigned occupancy parameters of 0.375 for the O1, O1', O9 site and 0.125 for the O1, O1', O4 site, based upon earlier (As isotropic) refinements leading to values of 0.373 (4) and 0.100 (5). As a consequence one cation site is disordered and two of the three water molecules that analytical results suggest are present could not be located, and there is a generally high noise level in F maps of the cation cage of the crystal structure. The anion, nonetheless, is well determined. Although the linear absorption coefficient is large (185.9 cm^{-1}), trial calculations indicated that few reflections were affected by more than 5% (on F^2) by absorption. Tables of anisotropic thermal parameters for W and As atoms, $10|F_c|$ vs. $10|F_o|$, and bond angles and distances have been deposited as Supplementary Material. Atomic coordinates and isotropic thermal parameters are provided in Table I.

Results and Discussion

Description of the Structure. The anion $[CH_3AsW_7O_{27}H]^{7-}$ is illustrated in Figure 1, together with atom labeling and selected interatomic separations. Mirror symmetry is crystallographically imposed. A horseshoe of four edge-shared tungsten octahedra are linked at four vertices to a triangle of three edge-shared octahedra. Because the crystal structure comprises two chemically distinct species, the W-O(As/As') and O-As/As' bond lengths may be slightly inaccurate, especially for the minor isomer, involving As'. However, the parameters are biased 3:1 in favor of the major isomer, which is probably the more stable since in this case the arsonate links the otherwise loosely nailed horseshoe to the hoof. For the *whole* cation the 13 W=O separations average 1.73 (2) Å; the 16 doubly bridging oxygen atoms, O4 excluded, have an average W-O separation of 1.93 (6) or 1.93 (2) Å if the unsymmetrically placed O13 atoms are excluded (see later). The two triply bridging oxygen atoms have separations in the range 1.980 (13) to 2.213 (12) Å. The other oxygen atom triply bridging W atoms (O9) is involved in an As-O bond of 1.74 (2) Å, and as a result the W-O separations are long (2.289 (13) and 2.47 (2) Å). The other As-O (O4) separation of the major isomer is 1.696 (13) Å. The As-O separations of the minor isomer are somewhat longer (and not true values) at 1.764 (15) (O1) and 1.88 (2) (O4) Å.

Table I. Positional Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	B(A2)	Atom	x	y	z	B(A2)
W1	0.86628(5)	0.12413(9)	0.17285(5)	3.35(2)	O20	0.543(2)	-0.109(3)	0.363(2)	7(1)*
W2	0.91115(7)	0.250	0.31864(6)	2.48(3)	O20'	0.506(2)	-0.191(3)	0.361(2)	8(1)*
W3	0.82292(5)	0.12674(8)	0.46971(4)	2.34(2)	N1	0.121(1)	0.250	0.576(1)	2.6(5)*
W4	0.78069(5)	0.01985(8)	0.32794(4)	2.51(2)	N2	0.055(1)	0.338(2)	0.497(1)	4.6(5)*
AS1	0.7148(2)	0.250	0.2606(2)	1.89(8)	N3	0.298(1)	0.334(2)	0.522(1)	4.4(5)*
AS1'	0.6875(8)	0.250	0.3626(7)	3.4(3)	N4	0.296(1)	0.250	0.625(1)	3.1(6)*
O1	0.7010(8)	0.145(1)	0.3087(7)	2.8(3)*	N5	0.358(2)	0.750	0.243(1)	3.4(6)*
O2	0.8983(8)	0.045(1)	0.4806(7)	3.1(3)*	N6	0.308(1)	0.664(2)	0.335(1)	5.3(5)*
O3	0.7765(8)	0.120(1)	0.5480(7)	2.9(3)*	N7	0.027(1)	0.514(2)	0.374(1)	3.7(4)*
O4	0.742(1)	0.250	0.444(1)	2.4(4)*	N8	0.064(1)	0.469(2)	0.264(1)	5.4(6)*
O5	0.8453(7)	0.146(1)	0.3609(7)	2.5(3)*	N9	0.153(1)	0.522(2)	0.341(1)	5.9(6)*
O6	0.8105(8)	0.044(1)	0.2369(7)	3.1(3)*	N10	0.519(2)	0.628(3)	0.505(2)	10(1)*
O7	0.879(1)	0.250	0.479(1)	2.5(4)*	N11'	0.585(3)	0.090(4)	0.414(2)	4(1)*
O8	0.7918(8)	0.127(1)	0.1163(8)	3.5(3)*	N11	0.433(2)	0.660(3)	0.599(2)	7(1)*
O9	0.809(1)	0.250	0.234(1)	2.9(5)*	N12	0.386(2)	0.599(3)	0.483(2)	14(1)*
O10	0.7524(7)	0.042(1)	0.4217(7)	2.5(3)*	C1	0.074(2)	0.250	0.528(2)	4.5(9)*
O11	0.7002(9)	-0.058(1)	0.3120(8)	4.0(4)*	C2	0.291(2)	0.250	0.556(2)	3.1(7)*
O12	0.8520(8)	-0.066(1)	0.3447(8)	3.5(4)*	C3	0.322(2)	0.750	0.303(2)	4.6(9)*
O13	0.9338(8)	0.152(1)	0.2558(8)	2.9(3)*	C4	0.078(2)	0.505(2)	0.328(1)	5.1(7)*
O14	0.913(1)	0.250	0.140(1)	3.1(5)*	C5	0.438(3)	0.613(4)	0.524(3)	14(2)*
O15	0.990(1)	0.250	0.369(1)	3.1(5)*	C10	0.661(3)	0.250	0.177(2)	4(1)*
O16	0.929(1)	0.038(2)	0.1383(9)	5.2(4)*	C10'	0.590(6)	0.250	0.380(5)	1(2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2 + B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

The hydrogen atoms were not located in F maps. However, for the major isomer, oxygen atoms O4 (trans to an oxo group) and O5 (triply bridging) are possibilities—the latter is not only inaccessible but would imply disorder about the mirror plane for which there is no evidence (see Table I and Figure 1). Moreover, the W3–O4 separation of 2.215 (12) Å is consistent with protonation observed in several related structures.[6,13] For the minor isomer the proton very likely resides on the triply coordinated atom O9.

W–W separations lie in the range 3.236 (1) (W3···W4) to 3.340 (1) Å for edge-shared octahedra and 3.695 (1) to 3.809 (1) Å (W2···W4) for corner-shared octahedra; the extremes are rather shorter and longer than usually observed.[1]

The crystal structure is also compact. All terminal oxo moieties are hydrogen bonded to guanidinium cations or to the water molecule O20. The O···N separations are typically 2.82 Å. Of the bridging oxygen atoms only O13, which is a pseudo-oxo group, indulges in contacts less than 3.00 Å; this probably reflects accessibility rather than intrinsic basicity.

Formation of the Anion. According to ¹H NMR the tungstoarsonate complex rapidly decomposes in aqueous solution to give, depending on pH, varying amounts of $CH_3AsO_3^{2-}$, $[(CH_3As)_2W_6O_{25}H]^{5-}$, and, presumably, paratungstate-A anion $W_7O_{24}^{6-}$. The solutions eventually deposit crystalline paratungstate salts. For both isomers of $[CH_3AsW_7O_{27}H]^{7-}$ fairly clear and plausible pathways exist to and from the well-known Lindqvist structure[14] for $W_7O_{24}^{6-}$ and are illustrated in Figure 2. In essence the Lindqvist structure may be generated from the lacunary minor isomer (holes at O1, O1 , and O4) by rotation of the W1 W2 W1'

(13) Barrows, J. N.; Jameson, G. B.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 1771.

(14) (a) Lindqvist, I. *Ark. Kemi* **1950**, *2*, 325. (b) Shimao, E. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1609. (c) Evans, H. T., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3275. (d) Sjobom, K.; Hedman, B. *Acta Chem. Scand.* **1973**, *A27*, 3673. (e) Evans, H. T., Jr.; Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1975**, 505. (f) Burtseva, K. G.; Chernaya, T. S.; Sirota, M. I. *sov. Phys. Dokl.* (*Engl. Transl.*) **1978**, *23*, 784.
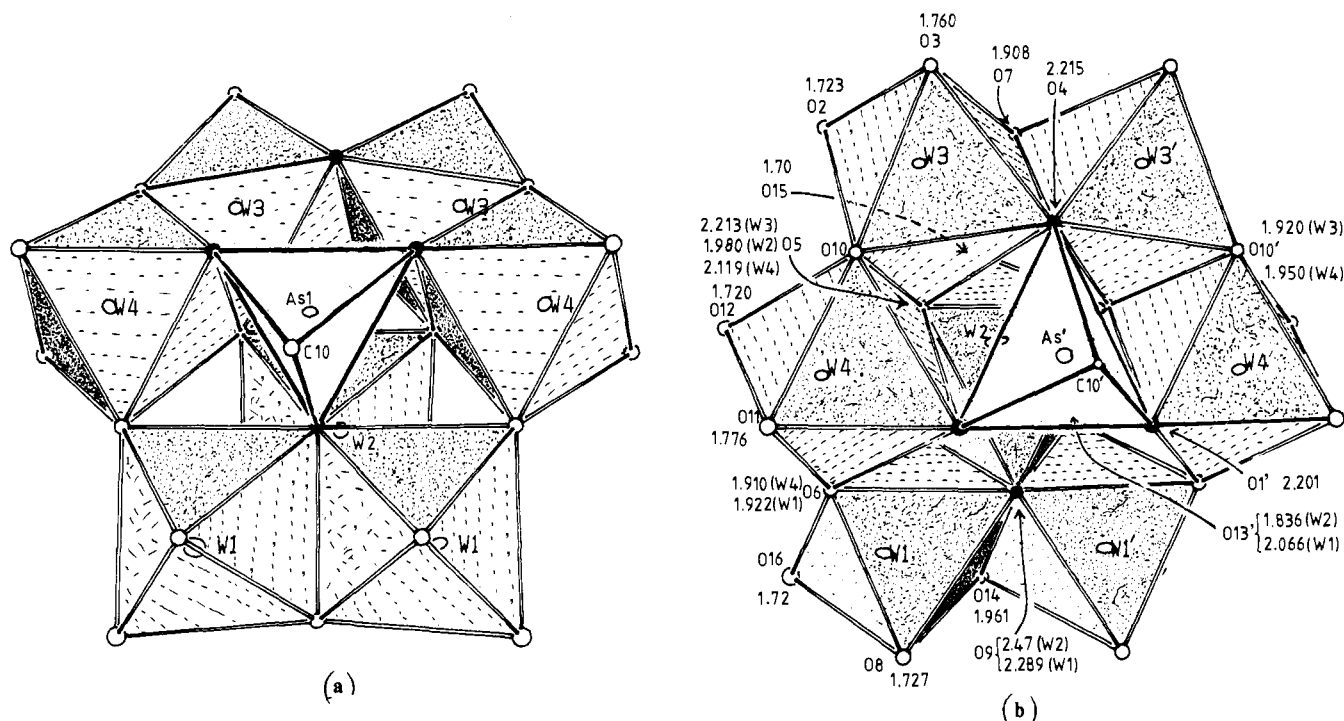
Figure 1. ORTEP diagram of the $CH_3AsW_7O_{27}^{7-}$ anion for (a) the major isomer and (b) the minor isomer. With the exception of the CH_3AsO_3 tetrahedra, faces that are approximately parallel are shaded similarly. Oxygen atoms that belong to the CH_3AsO_3 tetrahedra and/or are protonated (depending on isomer) are blacked out. W–O separations are given in angstroms and the estimated standard deviations lie in the range 0.009 to 0.02 Å.
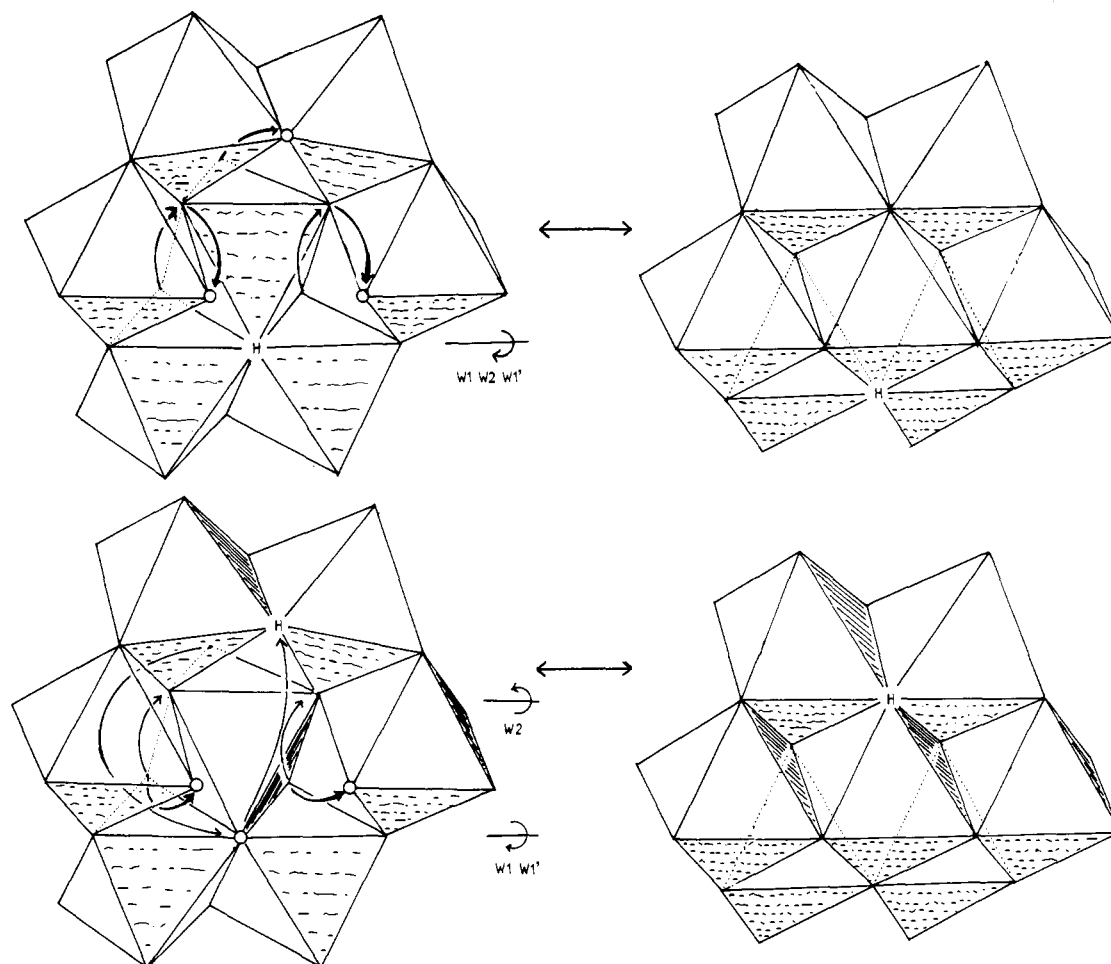
Figure 2. Diagram showing the interconversion between the lacunary $W_7O_{24}H$ ions and the Lindqvist $W_7O_{24}H^{-2}$ ion. Shading is selectively used to highlight the relationships between the two structures. Circles denote vacancies.

triad about the O6···O6′ edge: O15 of the W2 octahedron moves into the O4 hole, the O5 oxygen atoms on W2 move into the O1 holes, and the O13 atoms slide into the just created O5 holes. Note that octahedron W2 is loosely linked to octahedra W3 and W4
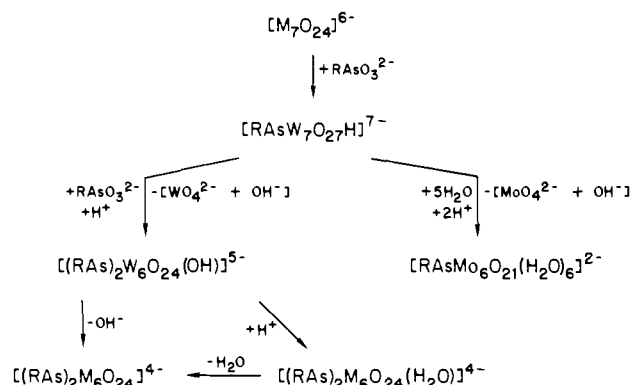
at atoms O5. And from the lacunary form of the major isomer (holes at O1, O1′, and O9) the Lindqvist structure may be derived as follows: The W2 octahedron alone rotates in an opposite direction to before so that the triad hole at O9 moves to position

O4, the O13 atoms of W2 move to the O1 holes, and atom O15 moves into the O9 hole of octahedra W1 and W1′; the W3 octahedra rotate in the opposite direction to W2, bringing the just created O13 holes to positions O5. Note also that octahedron W2 is loosely connected to octahedra W1 and W1′ at positions O13 and that the W2–O13 separations are unusually short (i.e., W2–O13 is a pseudo-oxo bond). Note also that protonation of the Lindqvist anion occurs as expected at the exposed oxygen atom(s) of the edge-shared triangle(s). In further support of this mechanism, it is observed in the Lindqvist structure anions $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$ that the central metal atoms make anomalously short bonds with the two doubly bridging oxygen atoms.[14d-f]

In the presence of organoarsonates, the chemistry of the heptatungstate $W_7O_{24}^{6-}$ with the Lindqvist structure is at first glance distinctly different from that of the analogous molybdenum species. The structure of an $AsMo_7$ species was recently determined by NMR methods,[15] but this proves to have a different overall stoichiometry and is prepared by a different route in nonaqueous solution. The $[C_6H_5AsMo_7O_{25}]^{4-}$ ion features a belt of six edge-shared octahedra capped by $C_6H_5AsO_3$ and MoO_4 tetrahedra, and thus it is structurally similar to the symmetrically capped species $[(CH_3As)_2Mo_6O_{24}]^{4-}$ and α-$[Mo_8O_{26}]^{4-}$, which have been characterized through X-ray diffraction.[4b,16] However, the minor ion of $[CH_3AsW_7O_{27}H]^{7-}$ bears a close topological relationship to the well-characterized $[(C_6H_5As)_2Mo_6O_{24}(H_2O)]^{4-}$ and $[(C_6H_5As)_2W_6O_{24}(OH)]^{5-}$ anions.[4c,6,7] The loosely held W2 octahedron, departing under acidic conditions as WO_5^{4-} (or more probably as WO_4^{2-} and OH^-), may be replaced by the arsonate ion $C_6H_5AsO_3^{2-}$ on the underside (with reference to Figure 1)—the arsonate oxygen atoms moving in at holes O5, O5′, and O13 (or O13′)—with concomitant collapse of the O13 O13′ positions to give a face-shared configuration for the W1 W1′ octahedra. The protonated atom O9 acquires a second proton for the Mo species. This unsymmetrical biarsonate complex is related to the symmetrical species, structurally characterized as the methyl derivative. $[(CH_3As)_2Mo_6O_{24}]^{4-}$.[4b] Keeping the numbering system of the title compound, the H_2O at O9 is lost and the W1 W1′ octahedra rotate about the O6···O6′ vector, yielding a ring of six

edge-shared octahedra, symmetrically capped by two tetrahedral arsonates.

Finally the $[CH_3AsW_7O_{27}H]^{7-}$ anion is also related to the highly protonated species $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$.[7] The relationships among all these species are shown below, where M means that both the Mo and W analogues are known.

$$[M_7O_{24}]^{6-}$$
$$\downarrow +RAsO_3^{2-}$$
$$[RAsW_7O_{27}H]^{7-}$$

$$+RAsO_3^{2-}\Big|\ -[WO_4^{2-}\ +\ OH^-] \qquad\qquad +5H_2O\Big|\ -[MoO_4^{2-}\ +\ OH^-]$$
$$+H^+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad +2H^+$$

$$[(RAs)_2W_6O_{24}(OH)]^{5-} \qquad\qquad\qquad [RAsMo_6O_{21}(H_2O)_6]^{2-}$$

$$\Big|\ -OH^- \qquad\qquad +H^+\searrow$$

$$[(RAs)_2M_6O_{24}]^{4-} \xleftarrow{-H_2O} [(RAs)_2M_6O_{24}(H_2O)]^{4-}$$

While these and any other mechanisms are essentially unprovable, they are entirely consistent with the chemical and, particularly, the distinctive structural data of the title complex and also the Lindqvist structure. The complex appears to be an important intermediate from the isopolyanions to the organic arsonate heteropoly species. Given the parallel chemistry of Mo species, it is reasonable to hypothesize the existence of a similar intermediate, $[CH_3AsMo_7O_{27}H]^{7-}$.

(15) Besecker, C. J.; Klemperer, W. G.; Schwartz, C.; Wright, D. A. NSF/CNRS Workshop on Polyoxoanions, St. Lambert-des-Bois, France, 1983. Besecker, C. J.; Klemperer, W. G.; Schwartz, C.; Wright, D. A. *J. Am. Chem. Soc.*, submitted for publication.

(16) (a) Fuchs, J.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 375. (b) Day, V. W.; Fredrich, M. K.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952.