our data show that once oxidation takes place the resulting cation resides on only one macrocycle in P700$^+$ and on two macrocycles in P865$^+$.

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(13) Philipson, K. D.; Sauer, K. *Biochemistry* **1973**, *12*, 535.

Heteropolypentatungstobisphosphonates. Cyclopentane-Like Pseudorotation of an Oxometalate Structure

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Heteropoly- and isopolyoxometalate complexes have frequently been described as fragments of close-packed metal oxide lattices, an image which draws attention to their potential catalytic activity but which perhaps overemphasizes the electrostatic contribution to the metal-oxygen bond in these complexes and carries with it a connotation of structural rigidity. That structures of certain polyanions might be fluxional in solution has been suggested only relatively recently.[1] We report here a new series of complexes that are the first heteropolyanions unambiguously to exhibit intramolecular exchange behavior.

The complexes are the tungstate analogues of the pentamolybdobisphosphonates, $(RPO_3)_2Mo_5O_{15}^{4-}$, that have been described earlier.[2] The new tungstates have limited stability in aqueous solution in marked contrast to the molybdates,[3,4] but addition of tri-*n*-butylammonium acetate to an equimolar solution of phenylphosphonic acid and sodium tungstate yields a precipitate of $[(C_4H_9)_3NH]_4[(C_6H_5PO_3)_2W_5O_{15}]$ (I)[5] which may be recrystallized from acetone-benzene (1:1). Potassium, cesium, and guanidinium salts are easily prepared by addition of methanolic solutions of appropriate salts and acetic acid to a solution of I in acetonitrile. A zwitterionic species $Na_2[(H_3{}^+\text{-}NCH_2CH_2PO_3)_2W_5O_{15}]\cdot 5H_2O$ has also been prepared and is recrystallizable from hot water.[6] There is no doubt that the molybdates and tungstates are isostructural: IR spectra in the range 1150-600 cm^{-1} (P-O and Mo, W-O vibrations) are very similar for all $(RPO_3)_2M_5O_{15}$ complexes, and the tri-*n*-butylammonium salts of $(C_6H_5PO_3)_2Mo_5O_{15}^{4-}$ and $(C_6H_5PO_3)_2W_5O_{15}^{4-}$ are isomorphous by X-ray powder diffraction. The anion structure deduced from numerous[7] X-ray investigations of molybdo-

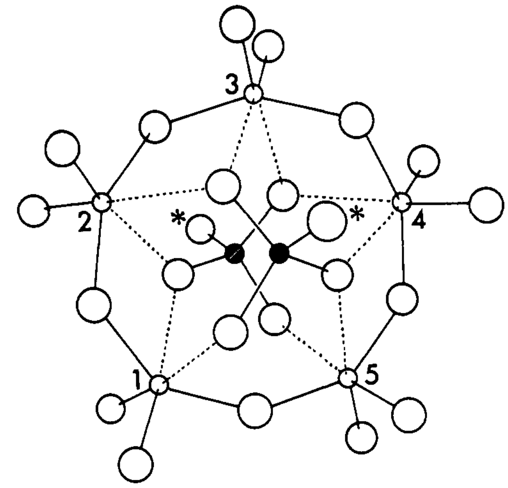

Figure 1. Oxometalate portion (C_2 symmetrized) of the structure of $(RPO_3)_2M_5O_{15}^{4-}$ (M = Mo, W) heteropolyanions. Small numbered circles, metal atoms; small dark circles, phosphorus atoms; large open circles, oxygen atoms. The alkyl, aryl, or oxo-R groups are represented by the starred atoms. Bonds are drawn to emphasize the pseudooctahedral coordination of the M atoms, but as discussed in the text, the M-O(P) bonds, shown as broken lines, are particularly long (typically 2.3 Å) and of low formal bond order.

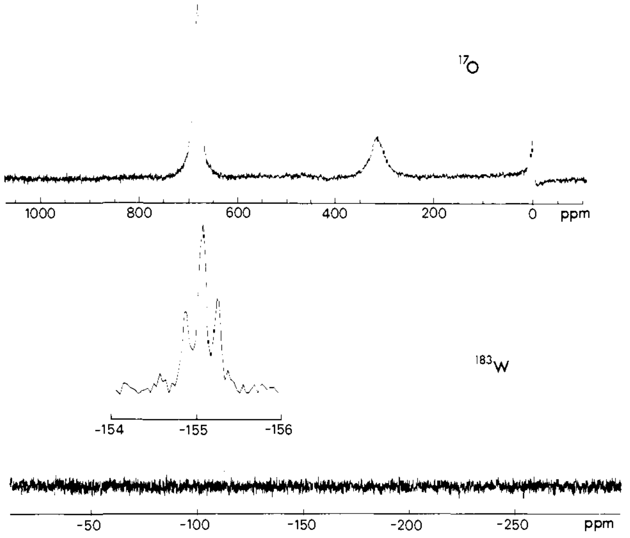

Figure 2. Top: 27.12-MHz ^{17}O NMR spectrum of I (11 atom % enriched), 0.09 M in wet acetonitrile at 299 K. Chemical shifts vs. pure D_2O [line widths, Hz]: δ +677 [780] (terminal oxygens), +311 [390] (tungsten-bridging oxygens), -6 [310] (D_2O). Phosphonate oxygens are not observed due to lack of enrichment. Bottom: 10.42-MHz ^{183}W NMR spectra of I, 0.1 M in CD_3CN at 306 K.[11b] Wide sweep spectrum, 14 000 scans; narrow sweep spectrum, 30 000 scans.

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(1) The isomerization and exchange behavior of α-$Mo_8O_{26}^{4-}$ (Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291. Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Ibid.* **1977**, *99*, 952) appears to be incompletely defined, mechanistically (Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866). Structural rearrangements are also involved in water exchange of $[(RAsO_3)_2M_6O_{18}(OH_2)]^{4-}$ (M = Mo, W) anions. (Wasfi, S. H.; Kwak, W.; Pope, M. T.; Barkigia, K. M.; Butcher, R. J.; Quicksall, C. O. *J. Am. Chem. Soc.* **1978**, *100*, 7786).

(2) Kwak, W.; Pope, M. T.; Scully, T. F. *J. Am. Chem. Soc.* **1975**, *97*, 5735.

(3) An aqueous solution (0.04 M, pH 3.6) of $K_4[(C_6H_5PO_3)_2W_5O_{15}]$ is ca. 15% dissociated into $C_6H_5PO_3{}^{2-}$ and isopolytungstate(s) [^{31}P NMR: δ +21.2 (complex), +14.1 (free phosphonate)]. The corresponding molybdate is undissociated at 0.01 M.

(4) The "inorganic" analogue, $(OPO_3)_2W_5O_{15}^{6-}$, has recently been reported as a cesium salt, unstable in solution above 60 °C (Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1865). No other salts of this tungstate are known. The corresponding molybdates, on the other hand, are a major component of weakly acidified molybdate-phosphate solutions (Pettersson, L. *Chem. Scr.* **1975**, *7*, 145) and numerous salts have been characterized.

(5) Anal. Calcd for $C_{60}H_{122}N_4P_2W_5O_{21}$: C, 32.50; H, 5.51; N, 2.53; P, 2.80; W, 41.50. Found: C, 31.83, H, 5.66; N, 2.44; P, 2.65; W, 41.78.

(6) Anal. Calcd for $C_4H_{24}N_2Na_2P_2W_5O_{26}$: C, 3.11; H, 1.56; N, 1.81; W, 59.57. Found: C, 3.46; H, 1.80; N, 2.07; W, 59.70. Details of syntheses and spectral characteristics of the new complexes will be reported in a subsequent paper.

(7) (a) Strandberg, R. *Acta Chem. Scand.* **1973**, *27*, 1004; (b) Hedman, B. *Ibid.* **1973**, *27*, 3335. (c) Fischer, J.; Ricard, L.; Toledano, P. *J. Chem. Soc., Dalton Trans.* **1974**, 941. (d) Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 1577. (e) Hedman, B. *Acta Crystallogr.* **1977**, *B33*, 3083. (f) Hedman, B.; Strandberg, R. *Ibid.* **1979**, *B35*, 278.

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phosph(on)ates and a recent report of $Cs_6[(OPO_3)_2W_5O_{15}]\cdot 7.5H_2O$[4] is shown in Figure 1.

The IR spectrum of I is unchanged when it is dissolved in acetonitrile, and ultracentrifugation measurements[8] of such solutions (0.13–0.45 mM) indicate a molecular weight of 1900 ± 200[9] ("bare" anion formula weight, 1470). Proton and phosphorus-31 NMR spectra are consistent with the C_2 structure of Figure 1,[10] but the 27.12-MHz ^{17}O NMR and 10.42-MHz ^{183}W NMR[11] spectra shown in Figure 2 point to fluxional behavior. The ^{183}W spectrum consists of a single line (δ_{306}–155.9 from 1.0 M Na_2WO_4 in D_2O) split into a 1:2:1 triplet by two equivalent ^{31}P nuclei (J = 1.95 Hz) and is consistent only with an intramolecular exchange process.[12] The nature of the molecular rearrangement can be described as follows. It has been pointed out by Day and Klemperer[13] that the P_2M_5 structure of Figure 1 incorporates weak M–O(P) bonds and that if the structure is dissected at these bonds, the oxometalate portion can be viewed as a ring of five corner-shared MO_4 tetrahedra. We note that, if the five bridging oxygens are ignored, such a ring is a topological analogue of cyclopentane and, further, that the metal atom positions fall very close to those describing an "envelope" conformer (four coplanar atoms and one atom out of the plane).[14] The five possible envelope forms of cyclopentane are readily interconverted by a ring pseudorotation, and we propose an analogous mechanism for the tungstophosphonate.[15] In the course of this process the RPO_3 groups must undergo a concerted oscillation (or rotation) about the R–P axes in order to interchange the positions of the phosphonate oxygens with respect to the metal atoms. Although each of these oxygens formally changes from doubly to triply bridging during the pseudorotation of the ring, we view this as a continuous change with no abrupt bond breaking or formation.

Further variable temperature and labeling experiments involving these complexes and related molybdates in aqueous and nonaqueous solution are in progress.

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[8] Sedimentation equilibrium method using a Beckmann Model E ultracentrifuge with UV optics and photoelectric scanner and operating at 20 000 rpm.

[9] Ultracentrifugation of aqueous solutions of the potassium salt (0.1 M formate buffer, pH 3.5) gave concentration-dependent results which indicated that dissociation of the heteropolyanion upon dilution[5] yielded an isopolytungstate with a molecular weight of ca. 3500.

[10] (a) ^1H NMR (90 MHz): δ 8.36–8.10 (m, 2, *o*-phenyl protons), 7.49–7.43 (m, 3, *m*- and *p*-phenyl protons); $(C_4H_9)_3NH^+$ multiplets at ca. δ 0.83–0.99, 1.19–1.76, 2.90–3.11. The spectrum of $C_6H_5PO_3H_2$ in CD_3CN shows all protons as an unresolved multiplet at δ 7.93–7.49. (b) $^{31}P\{^1H\}$ NMR (36.44 MHz): δ +16.4.

[11] (a) The first application of ^{183}W NMR spectroscopy to heteropolytungstates was reported by: Acerete, R.; Hammer C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267. (b) Bruker WM250. Recording conditions: 15-mm tube, multinuclear probe head, deuterium lock; pulse angle 50 μs (ca. 60°), 1–S delay, temperature 235–306 K.

[12] The structure of Figure 1 should give three ^{183}W resonances (2:2:1) with complex ^{183}W–^{31}P coupling. No coupling would be observed if the exchange were intermolecular. Although the ^{17}O spectrum shown in Figure 2 indicates the presence of water, we have also recorded identical ^{17}O and ^{183}W spectra in anhydrous CD_2Cl_2. A water exchange process similar to that observed in the hexametalloarsonates[1] is thus ruled out.

[13] Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952.

[14] On the basis of the dimensions of six independent molecules,[9b,d–f] four of the metal atoms in P_2M_5 structures lie within 0.06 ± 0.02 Å of a least-squares plane and the fifth metal atom lies 0.63 ± 0.11 Å out of the plane. Because of the effective C_2 symmetry of the anion there are two ways of choosing the "coplanar" atoms; in Figure 1 these are 1, 2, 3, and 4 *or* 2, 3, 4 and 5. The metal–metal distances around the ring are 3.37 Å except between atoms 1 and 5 (3.68 Å). The nonplanar structure for cyclopentane is normally attributed to the effects of repulsions between hydrogens. In the case of the metallophosphonates the structure is imposed by the dimensions of the RPO_3 group.

[15] Pseudorotation of cyclopentane (Kilpatrick, J. E.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2483. Pitzer, K. S.; Donath, W. E., *Ibid.* **1959**, *81*, 3213) is unhindered and can be viewed as a molecular vibration (Anet, F. A. L.; Anet, R. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York 1975; p 543). Pseudorotation of the polytungstate on the other hand should not be activationless. The ^{183}W NMR spectrum of I in acetonitrile is unchanged at 235 K (temperature limited by solvent) which indicates that $\Delta G^\ddagger$ < 14 kcal mol^{-1}. Further delineation of the exchange by measurements in other solvents and at lower temperatures is planned.

Substituent Control of the Poly(C)-Directed Oligomerization of Guanosine 5′-Phosphoroimidazolide

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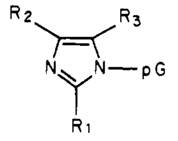
The efficiency of the oligomerization of guanosine 5′-phosphorimidazolide (**1**) in aqueous solution is greatly increased in the presence of poly(C) under conditions that permit the formation of organized helical structures. However, it is only in the presence of Zn^{2+} or Pb^{2+} that we could detect long oligomeric products.[1–3] We now report that, even in the absence of Zn^{2+} or Pb^{2+}, the poly(C)-directed oligomerization of a closely related phosphorimidazolide **2** at pH 7 and 0 °C gives long, predominantly 3′,5′-linked oligomers in good yield.



1, $R_1 = R_2 = R_3 = H$
2, $R_1 = Me; R_2 = R_3 = H$
3, $R_1 = R_3 = H; R_2 = Me$ (or $R_1 = R_2 = H; R_3 = Me$)
4, $R_1 = Et; R_2 = R_3 = H$

The ^{14}C-labeled imidazolides **1–4** were prepared by procedures described previously.[4] The oligomerization reactions were allowed to proceed in 2,6-lutidine–nitric acid buffers (pH 7.0 at room temperature, 0.4 M) at 0 °C for 14 days. In all cases the reaction mixtures remained homogeneous. The products of the reaction were separated by descending paper chromatography on Whatman 3MM paper using *n*-propanol, concentrated ammonia, and water (55:10:15) as eluant. Yields of products were determined by running the chromatograms through a radiochromatogram scanner with integrator.

The results of these experiments are summarized in Table I. The phosphorimidazolide **2** condenses far more efficiently than the closely related derivates **1**, **3**, and **4**. This efficient condensation is dependent on the presence of a poly(C) template. The efficiency increases with the concentration of reactants, presumably because the stability of the helix increases at higher concentrations of reagents.

The mean chain length of the oligomers remaining at the origin of the chromatograms was determined as described previously.[2,3] In the most concentrated solution (Table I, row 3) the imidazolide **2** yielded oligomers with mean chain length 14. The mean chain lengths of the oligomers derived from **1**, **3**, or **4** were 4, 6, 6, respectively.

The details of the product distributions were examined by HPLC on RPC5 as previously described.[2,3] Samples were degraded exhaustively with pancreatic ribonuclease before application

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[1] R. Lohrmann, P. K. Bridson, and L. E. Orgel, *Science (Washington, D.C)*, **208**, 1464 (1980).

[2] P. K. Bridson and L. E. Orgel, *J. Mol. Biol.*, **144**, 567 (1980).

[3] R. Lohrmann and L. E. Orgel, *J. Mol. Biol.*, **142**, 555 (1980).

[4] (a) T. Mukaiyama and M. Hashimoto, *Bull. Chem. Soc. Jpn.*, **44**, 2284 (1971). (b) R. Lohrmann and L. E. Orgel, *Tetrahedron*, **34**, 853 (1978); **35**, 566 (1979) (errata).

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