Polyoxometalate Diphosphate Complexes. Folded Macrocyclic Dodecatungstates, $[(O_3PXPO_3)_4W_{12}O_{36}]^{16-}$ (X = O, CH_2)

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Received September 9, 1993
Revised Manuscript Received December 20, 1993

Interest and activity in the chemistry of polyoxometalates is largely driven by potential applications in catalysis and medicine, leading to the search for new structures with unusual combinations of properties.[1] We are currently investigating heteropolyanion complexes with diphosphate species as hetero groups in order to understand the reactivity of polytungstates and polymolybdates with biological oligophosphates and esters[2] and also to explore the structural constraints on polyoxoanion architecture following incorporation of dinuclear "tetrahedral" hetero groups. Of the several new diphosphate complexes that we have identified in aqueous solution, many are subject to slow molybdate-[3] and tungstate-promoted diphosphate hydrolysis (ultimately yielding well-known molybdo- and tungsto*mono*phosphates). Seeking to avoid this complication, we have also investigated complexes of the hydrolytically-stable diphosphate analog, methylenediphosphonate, $[O_3PCH_2PO_3]^{4-}$. Both of the title complexes (**I**, X = O; **II**, X = CH_2) are formed rapidly and in high yield in neutral or weakly acidic aqueous solution.

The *open* cyclic structure of **I** and **II** is an unusual new polyoxometalate conformation with *external* hetero groups;[4] most of the scores of structural types of polyoxoanions now recognized are based on *compact* close-packed oxide assemblies. The new complexes also are the first structurally-characterized polyanions to contain simple ditetrahedral hetero groups.[5,6]

The new anions are formed rapidly at room temperature in aqueous solution by addition of 50 mL of 0.5 M sodium diphosphate or methylenediphosphonic acid to 150 mL of 0.5 M sodium tungstate, followed by adjustment of pH to 4 (**I**) or 6 (**II**) with 12 M HCl. The characteristic NMR spectra of the new heteropolyanions are observed immediately, and these remain unchanged if the solution is stored for 1 year at room temperature (**I**, **II**) or heated to 150 °C in a bomb for 24 h (**II**). Between pH 8 and 13, the anions are gradually degraded into their components, monotungstate and diphosph(on)ate. Sodium salts of **I** and **II** were precipitated by addition of dimethyl sulfoxide (yields 26% and 92%, respectively). Single crystals of a cesium–sodium salt of **I** were isolated by addition of some DMSO to an aqueous solution and then layering with a solution of CsCl. Single crystals of the sodium salt of **II** were obtained after 3 months by layering DMSO onto an aqueous solution.

Single crystal X-ray analysis[7] reveals the structure illustrated in Figure 1, and NMR spectra are fully consistent with the same structure in solution.[8] Elemental analysis is satisfactory.[9] In accordance with the earlier suggestions of Klemperer regarding smaller molybdate oligomers,[10] the new anions may be viewed as rings of 12 corner-linked WO_4 *tetrahedra* pinned into the D_{2d} conformation of the seam of a tennis ball by the addition of four diphosph(on)ate anions. Relatively weak bonds (2.124–2.346 Å) from phosphate oxygens to the tungstens result in a distorted *octahedral* coordination environment for the latter. The structure has two saddle-shaped cavities, which incorporate either Cs^+ (**I**) or Na^+ (**II**) cations. Phosphorus-31, sodium-23, and tungsten-183 NMR spectroscopy demonstrates that cation exchange is rapid in solution for both **I** and **II**.

The approximately spherical anions, with a "diameter" of 15 Å, are significantly larger than the well-known Keggin dodecatungstates (12 Å) and have an unusually high charge, which probably accounts for their hydrolytic stability at neutral pH. The biological activity of both anions is under investigation and will be reported elsewhere.

Acknowledgment. We thank NSF for support of this work through Grants CHE-9115394 (assistance in purchase of dif-

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(1) Recent research is summarized in the following: (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (b) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, the Netherlands, 1994.

(2) (a) Katsoulis, D. E.; Lambrianidou, A. N.; Pope, M. T. *Inorg. Chim. Acta* **1980**, *46*, L55. (b) Fleury, P. *C. R. Hebd. Seances Acad. Sci.* **1931**, *193*, 1350; *Bull. Soc. Chim. Fr.* **1932**, *51*, 657; *J. Pharm. Chim.* **1932**, *16*, 333. (c) Geraldes, C. F. G. C.; Castro, M. M. C. A. *J. Inorg. Biochem.* **1986**, *28*, 319.

(3) Weil-Malherbe, H.; Green, R. H. *Biochem. J.* **1951**, *49*, 286.

(4) Zubieta has reported a molybdosquarate anion, $[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$, which has a folded M_{12} conformation similar to that of **I**, but the squarate ligands/hetero groups occupy the *interior* sites, thereby producing a closed (compact) structure [Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 70].

(5) A yellow diphosphate–molybdate complex, $[P_2Mo_{18}O_{61}]^{4-}$, isolated from nonaqueous solution by S. Himeno, A. Saito, and T. Hori (Himeno, S.; Saito, A.; Hori, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1602) has a (compact) structure based on so-called B-type PMo_9 Keggin fragments (Kortz, U.; Pope, M. T., manuscript in preparation). The true formulas and identities of tungsto- and molybdodiphosphates reported by O. W. Gibbs (Gibbs, O. W. *Proc. Am. Acad. Arts Sci.* **1886**, *21*, 107; *Am. Chem. J.* **1885/86**, *7*, 398) and by A. Rosenheim and M. Schapiro (Rosenheim, A.; Schapiro, M. *Z. Anorg. Chem.* **1923**, *129*, 196) remain to be confirmed.

(6) The structures of several complexes of molybdenum(VI) and (1-hydroxyethylidene)diphosphonic acid (Mo:L = 1:1, 1:2, 2:2, 3:1, 6:2) have been reported recently [Krol', I. A.; Starikova, Z. A.; Sergienko, V. S.; Tolkacheva, E. O. *Russ. J. Inorg. Chem.* **1990**, *35*, 2817. Tolkacheva, E. O.; Popov, K. I.; Krol', I. A.; Starikova, Z. S. *Sov. J. Coord. Chem.* **1990**, *16*, 870. Krol', I. A.; Starikova, Z. A.; Sergienko, V. S.; Tolkacheva, E. O. *Mendeleev Commun.* **1991**, 7. Krol', I. A.; Starikova, Z. A.; Tolkacheva, E. O.; Sergienko, V. S.; Makarevich, S. S. *Russ. J. Inorg. Chem.* **1992**, *37*, 141. Tolkacheva, E. O.; Krol', I. A.; Starikova, Z. A.; Popov, K. I.; Gurevich, M. Z. *Russ. J. Inorg. Chem.* **1992**, *37*, 147. Krol', I. A.; Starikova, Z. A.; Sergienko, V. S.; Tolkacheva, E. O. *Russ. J. Inorg. Chem.* **1992**, *37*, 406. Sergienko, V. S.; Tolkacheva, E. O.; Ilyukhin, A. B.; Starikova, Z. A.; Krol', I. A. *Mendeleev Commun.* **1992**, 144]. In most cases the phosphonate ligand is fully deprotonated and binds to molybdenum through both phosphate and alkoxo oxygens.

(7) Crystallographic data for **I** $Cs_{13}Na_3[(O_3POPO_3)_4W_{12}O_{36}]\cdot 24H_2O$, orthorhombic, *Pnma*; a = 34.965(7) Å, b = 18.871(4) Å, c = 14.290(3) Å, V = 9429(3) Å^3, Z = 4; D(calcd) = 3.986 g cm^{-3}. Of 14 725 reflections collected (Siemens P4/RA diffractometer, Mo Kα, 295 K), 12 557 were independent and 6659 were observed ($4\sigma(F_o)$). With all tungsten and cesium atoms refined anisotropically, R = 8.60%. Crystallographic data for, **II**: $Na_{16}[(O_3PCH_2PO_3)_4W_{12}O_{36}]\cdot 16H_2O$, monoclinic, $P2_1/m$; a = 11.817(2) Å, b = 26.738(5) Å, c = 13.350(3) Å, β = 115.6°, V = 3804.1(13) Å^3, Z = 2; D(calcd) = 3.567 g cm^{-3}. Of 11 406 reflections collected (Siemens P4/RA diffractometer, Mo Kα, 295 K), 9597 were independent and 5764 were observed ($4\sigma(F_o)$). With all non-tungsten atoms refined isotropically (no hydrogens included), R = 8.78%. Three of the sodium cations were refined with occupancy factors of 50% (see figure caption), and all 16 cations could be accounted for. Mirror symmetry is crystallographically imposed on both anions.

(8) All NMR measurements were made on a Bruker AM 300WB instrument. **I**: ^{31}P NMR δ −3.8 (d, 1P), −8.1 (d, 1P) $^2J_{PP}$ = 11 Hz); ^{183}W NMR δ −222.7 (t, 2W, $^2J_{PW}$ = 1.7 Hz), −270.7 (t, 1W, $^2J_{PW}$ = 1.2 Hz), $^2J_{WW}$ = 33.5 Hz. **II**: ^{31}P NMR δ 19.6 (d of t, 1P), 23.5 (d of t, 1P), $^2J_{PH}$ = 20 Hz, $^2J_{PP}$ = 11 Hz; ^{183}W NMR δ −226.1 (t, 2W, $^2J_{PW}$ = 1.7 Hz), −257.7 (t, 1W, $^2J_{PW}$ = 2.2 Hz), $^2J_{WW}$ = 32.5 Hz; $^{13}C\{H\}$ NMR δ 25.5 (t, 1C), $^1J_{CP}$ = 116.7 Hz; ^1H NMR δ 2.75 (t, 2H), $^2J_{HP}$ = 20 Hz. By means of $^{183}W\{P\}$ spectroscopy, the P resonance at 23.5 ppm could be assigned to the "external" phosphorus atom, which is coupled only to the −226-ppm W resonance. Solutions of the DMSO-precipitated complex occasionally showed about 5% of an impurity according to ^{31}P NMR, δ 20.4 (t). Uncomplexed diphosphonate at the same pH has δ 16.6.

(9) Elemental analyses were done by E+R Microanalytical Laboratory, Corona, NY. **I**: Anal. Calcd (Found) for $Na_{16}[(O_3PCH_2PO_3)_4W_{12}O_{36}]\cdot 44H_2O$: Na, 7.94 (7.38); P, 5.35 (5.21); W, 47.64 (47.73); H_2O, 17.12 (16.00). The crystal selected for structure analysis appeared to be of a lower hydrate; only 24 water molecules could be identified with certainty. However, it is not uncommon for many hydrate water molecules in heteropolyanion structures to be zeolytic in nature and to be undetectable by X-ray structure analysis. **II**: Anal. Calcd (Found) for $Cs_{13}Na_3[(P_2O_7)_4W_{12}O_{36}]\cdot 16H_2O$: Cs, 31.06 (31.43); Na, 1.24 (1.49). IR spectral data for **I**: 1180 (sh), 1150 (s), 1090 (s), 1030 (m), 980 (w), 925 (s), 900 (s), 860 (s), 760 (s,b), 640 (s,b), 550 (m), 530 (s). IR spectral data for **II**: 1360 (w), 1180 (m), 1130 (s), 1070 (sh), 1050 (s), 1020 (s), 925 (s), 870 (s), 760 (s,b), 640 (s,b), 550 (s), 500 (s,b) [w, weak; m, medium; s, strong; sh, shoulder; b, broad].

(10) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952.

0002-7863/94/1516-2659$04.50/0

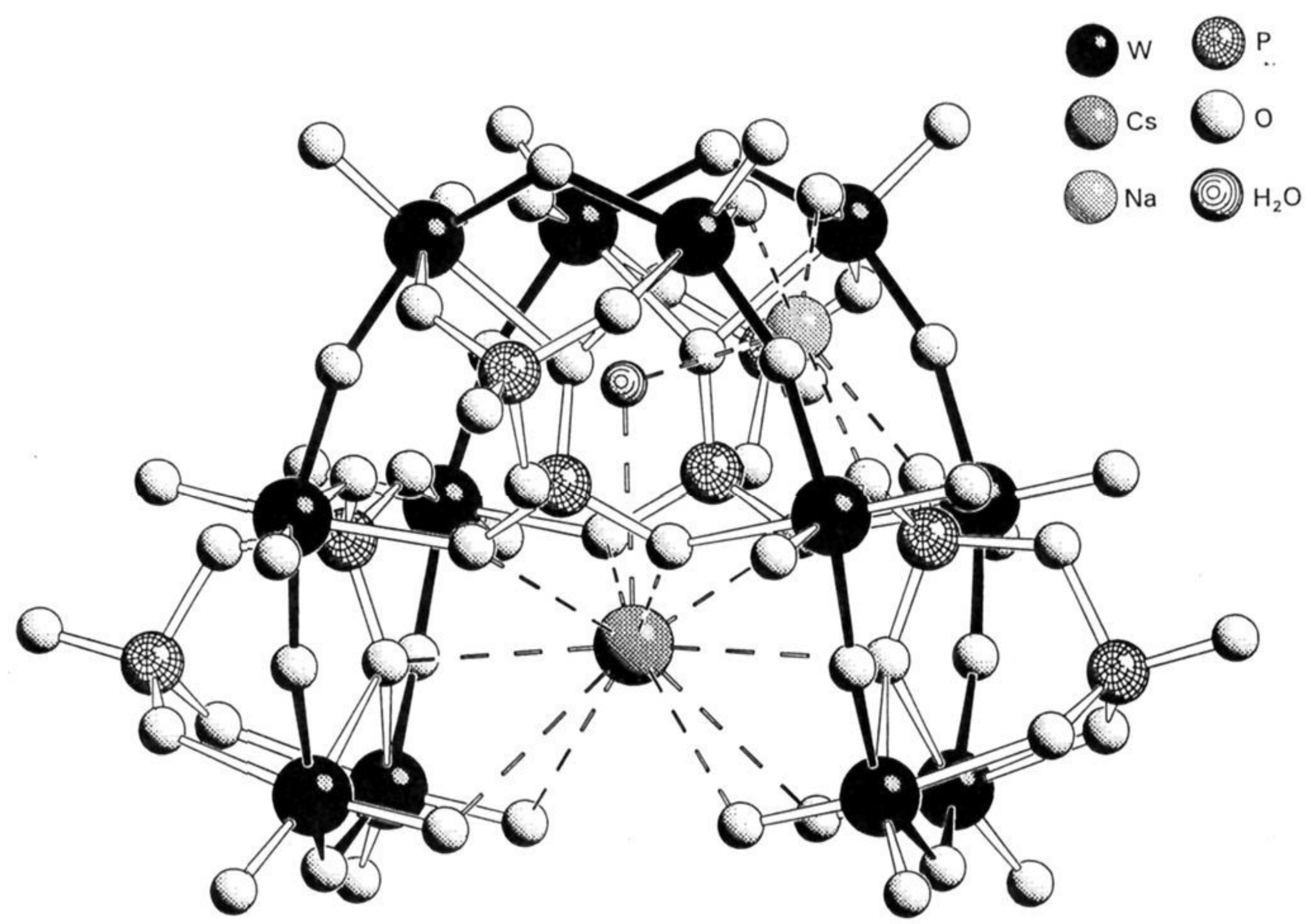

Figure 1. Structure of anion I. The bonds defining the dodecatungstate ring are emphasized. The two counterions (Cs, Na) which are associated directly with the anion and bridged by H_2O are shown. Bond length ranges (Å): W—O(terminal trans to triply-bridging O), 1.698–1.750; W—O(terminal trans to doubly-bridging O), 1.732–1.762; W—O(W), 1.852–1.970; W—O(P), 2.172–2.332; P—O(W), 1.479–1.568; P—O(terminal), 1.471–1.540; Cs—O, 3.114–3.479; Na—O, 2.350–2.499; Cs—μH_2O, 3.160; Na—μH_2O, 2.294. The other cations (2 Na, 12 Cs) occupy "external" sites. The structure of anion II is virtually identical, with similar bond lengths. In this structure, three sodium cations (two with occupancy factors of 50%) occupy the saddle cavities. One of the remaining 13 cations is also disordered over two mirror-related sites.

fractometer) and CHE-9215228. Figure 1 was generated by SCHAKAL 92 (copyright Egbert Keller, University of Freiburg).

Supplementary Material Available: Summary of data collection and refinement, atomic coordinates, anisotropic thermal parameters, and complete interatomic distances and angles (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Tables of structure factor amplitudes are available from the authors at the given address.