rapidly[5] with ascorbic acid to form the radical. Hydrogen atoms react only slowly with N_2O and we supposed that they should abstract a labile H atom from the ascorbic acid to form H_2. In support of this assumption, some rough measurements of the yield of H_2 gas were made from γ-ray irradiations of N_2O-saturated solutions of ascorbic acid. The results indicated hydrogen yields of 0.7–1.0, considerably greater than the yield of hydrogen coming directly from the water and hence supporting the assumption of abstraction by H. The total yield of radicals in nearly pure water is $G = 6.05$,[6] and is about 0.4 higher in nitrous oxide saturated solutions,[7] so that it was assumed here that the yield of ascorbic acid radicals was $G = 6.45$. The optical densities observed at the end of the pulse were proportional to the magnitude of the dose, and assuming this value of G we determined that the extinction coefficient ϵ is 3700 at 360 nm. Then $k = 9.5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. Yamasaki and Piette[2] found values for this constant ranging from 6.3 to $10.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$.

Transient spectra of radicals formed by OH attack on a large number of aliphatic acids and alcohols have been seen in pulse radiolysis;[8] in every case, the unpaired electron is believed to reside on carbon. In the ascorbic acid radical produced by enzyme action or autoxidation the unpaired electron is believed to reside on oxygen.[1,3] We are continuing studies designed to determine the point of radical attack on ascorbic acid and the nature and properties of the radical formed at various pH.

Acknowledgment. It is a pleasure to acknowledge the invaluable assistance of Mr. David Comstock in the experimental work. This study was supported by the U. S. Atomic Energy Commission.

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(6) B. H. J. Bielski and A. O. Allen, *Int. J. Radiat. Phys. Chem.*, 1, 153 (1969).

(7) A. Appleby and H. A. Schwarz, *J. Phys. Chem.*, 73, 1937 (1969).

(8) M. Simic, P. Neta, and E. Hayon, *ibid.*, 73, 3794, 4207, 4214 (1969).

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A New Fundamental Type of Inorganic Complex: Hybrid between Heteropoly and Conventional Coordination Complexes. Possibilities for Geometrical Isomerisms in 11-, 12-, 17-, and 18-Heteropoly Derivatives

Sir:

This paper reports establishment of a new fundamental class of complexes, of broad potential scope. Transition metal heteroatoms, M^{m+}, are polycoordinated within heteropoly complex structures, as integral parts thereof both electronically and with respect to atomic positions, while the same M^{m+} atoms are simultaneously coordinated to discrete conventional ligands such as NH_3, H_2O, pyridine, pyrazine, halide ion, etc. The existence of such complexes, which should involve a wide variety of ligands and of metals, will add a considerable new dimension to the field of heteropoly electrolytes and perhaps to the chemistry of complexes in general.

Background. In 1966 our group reported[1,2] an investigation in depth, centered on five complexes, which established unequivocally a large new general structural category of heteropoly anions, formulated

$$[H_hM^{m+}O_6X^{x+}O_4W_{11}O_{30}]^{(14-m-x-h)-}$$

It was indicated that a wide variety of metal ions might function as octahedrally coordinated M^{m+}, and a wide variety of nonmetals and transition metals, as well as $H_2{}^{2+}$, could function as X^{x+}.

The structure was shown[1,2] to be a modification of the well-known 12-tungsto "Keggin" structure.[3-7] Octahedrally coordinated M^{m+} replaces just 1 of the 12 octahedral W atoms of the conventional Keggin structure, and X^{x+} occupies the Keggin unit's central tetrahedral cavity.[8]

Subsequently, Weakley and Malik[10-12] and then the Tournés[13,14] reported preparation of a large number of 11-tungsto and 11-molybdo complexes (various M's and X's) which they formulated according to the above. Although the data they reported would be insufficient, standing alone, to establish the formulas and structures, there can be little doubt, in view of the whole body of evidence, that most and probably all of their materials do in fact belong to that new class of heteropoly complexes.[1,2]

Ripan and Puscasu,[15] also in 1968, reformulated, on the above-stated basis, three compounds which they had earlier interpreted differently.[16] They added convincing evidence to substantiate their new assignment.

The New Complexes. The work reported below unambiguously establishes that the formula for the above-described complexes can be rewritten on a still more general basis

$$[(Y^{y-})M^{m+}O_5X^{x+}O_4(\text{W or Mo})_{11}O_{30}]^{(12-m-x+y)-}$$

wherein Y^{y-} is a monodentate ligand which occupies the M's one unshared coordination position (which points toward the exterior of the heteropoly part). See Figure 1. It appears evident that for most of the many complexes heretofore reported[1,10-15] Y is a water molecule, but in some of those cases it is presumably merely an oxide ion. The present work indicates that a great variety of other ligands can also function as Y.

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(1) L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

(2) L. C. W. Baker, *et al.*, *Proc. Int. Conf. Coord. Chem., 9th, 1966*, 421 (1966).

(3) J. F. Keggin, *Proc. Roy. Soc., Ser. A*, **144**, 75 (1934).

(4) R. Signer and H. Gross, *Helv. Chim. Acta*, 17, 1076 (1934).

(5) L. C. W. Baker and V. E. Simmons, *J. Amer. Chem. Soc.*, **81**, 4744 (1959).

(6) N. F. Yannoni, Ph.D. Dissertation, Boston University, 1961.

(7) L. C. W. Baker in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 608.

(8) The derivative wherein $X = Si^{4+}$ and $M = Co^{2+}$ had been the first heteropoly anion proven to contain two different elements as heteroatoms.[1,9]

(9) V. E. Simmons and L. C. W. Baker, *Proc. Int. Conf. Coord. Chem., 7th, 1963*, 195 (1962).

(10) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

(11) S. A. Malik and T. J. R. Weakley, *Chem. Commun.*, 1094 (1967).

(12) S. A. Malik and T. J. R. Weakley, *J. Chem. Soc., A*, 2647 (1968).

(13) C. Tourné, *C. R. Acad. Sci., Ser. C*, **266**, 702 (1968).

(14) C. Tourné and G. Tourné, *ibid., Ser. C*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

(15) R. Ripan and M. Puscasu, *Z. Anorg. Allg. Chem.*, **358**, 83 (1968).

(16) R. Ripan, A. Duca, D. Stanescu, and M. Puscasu, *ibid.*, **347**, 333 (1966).

The distinctive electronic involvement of M^{m+} as an integral part of the heteropoly cage, through the five O atoms which M shares with other metal atoms of the cage and through probable overlap of orbitals between the various metal atoms, is emphasized by unusual Racah parameters,[9,17] very unusual magnetic interactions,[1] and electronic conductivity through the heteropoly structures[1,9,17–19] (*cf.* the conductivities of tungsten and molybdenum bronzes). The ability to substitute various ligands on M provides a means of modifying and of probing these effects. Conversely, the continuously modifiable structure (different X's, W or Mo, etc.) will change the ligands' attachments to given M's. From the standpoint of mechanistic studies, it may be valuable to have available a wide variety of complexes in each of which a metal ion has, in effect, only one monodentate position available, very effectively shielded from backside attacks. The potentiality for controlling solubilities in various solvents will be significant, and the role of these complexes in catalysis should be important.[20]

Evidence. Examination, in 1966, of the formulas of all ($\sim$20) of our rigorously completely analyzed salts of the original five complexes revealed strikingly that the number of H atoms contained in each complex was most usually 2 (*i.e.*, H_h in the original formula was H_2), provided the anion was presumed to contain the 40 O atoms indicated by a complete Keggin structure. That, of course, suggested that those H atoms might be present in the complex in a discrete water molecule,[24] possibly coordinated to the one unshared coordination position of M^{m+}. The X-ray structures of salts of three of the anions which contained two H atoms revealed the full complement of 40 O atoms required by the Keggin structure. Analyses later reported by others[10–14] have also indicated that most of their numerous new derivatives contain 2 H atoms per complex when formulated with 40 O atoms.

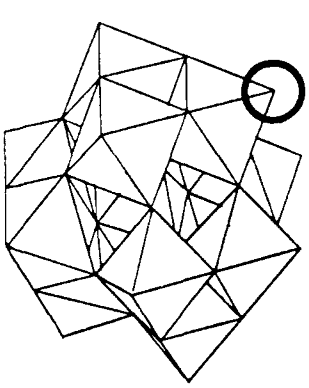

Figure 1. The modified Keggin structure. The circled vertex locates the center of that atom of the ligand Y which is coordinated to the octahedral heteroatom M^{m+}. That (upper right) octahedron contains the M^{m+}. Each of the other 11 octahedra contains W or Mo, and all the other vertices of the polyhedra locate the centers of close-packed oxygen atoms (39 in number). The X^{x+} is within the central tetrahedron. This representation shows regular polyhedra. In the actual complexes, the octahedra, which multiply share corners and edges, are all considerably distorted by movement of the metal atoms off center in the octahedra, toward the unshared vertices.[6,7]

The matter has been elucidated *via* a thorough study of a very few complexes, rather than a survey of many. Various salts were made for five closely interrelated complexes: the 11-tungsto derivatives wherein[8] X = Si^{4+}, M = Co^{2+} or Co^{3+}, and Y = H_2O, NH_3, or pyridine (except the derivative wherein M = Co^{2+} and Y = NH_3, which was not examined). The Co(III) derivatives were all free of Co(II), *e.g.*, 11-tungsto[aquocobalto(III)]silicates such as $K_5[(H_2O)Co^{3+}O_5SiO_4W_{11}O_{30}]\cdot 14H_2O$, were prepared pure for the first time.[30] The Co(II) complexes are various shades of red; the Co(III) complexes are various shades of green.

The five complexes were investigated by stringent combination of the following experimental attacks, all of which unambiguously substantiate the $[(Y^{y-})M^{m+}O_5X^{x+}O_4W_{11}O_{30}]^{(12-m-x+y)-}$ formulation: (1) analyses of recrystallized pure samples, which always revealed a Y:Co:Si:W molar ratio of 1:1:1:11; (2) electrolyses of agar-agar gel solutions,[31] during which all of the M, X, and Y moved toward the anode; (3) ion-exchange experiments, showing that none of those constituents was removed from solution by a K-cycle strong acid cation exchange resin, but all three were completely removed on a Cl-cycle strong base anion exchange resin; (4) determination of oxidation states of M *via* redox titrations; (5) determination of diamagnetism of the Co(III) derivatives, confirming the oxidation state and octahedral coordination of Co; (6) determinations of exact stoichiometries of interconversions and of preparative reactions; (7) potentiometric titrations with base,[25] establishing charges on the anions; (8) cryoscopy in fused $Na_2SO_4\cdot 10H_2O$,[27,32] to establish degree of condensation, absence of impurities in analyzed samples,[33] and thermodynamic

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(17) V. E. Simmons, Ph.D. Dissertation, Boston University, 1963.

(18) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).

(19) E. Papaconstantinou and M. T. Pope, *ibid.*, **6**, 1152 (1967).

(20) Flynn and Stucky[21] very recently proposed an interesting structure which might superficially appear to share fundamental similarities with the complexes discussed above, but which is actually basically different. Analysis of recrystallizable powders fitted the formula $Na_5[M(en)H_2O(Nb_6^{5+}O_{19})]\cdot 17H_2O$, wherein M = octahedral Cr(III) or Co(III), en = ethylenediamine, and the trivalent metals are in anions. It was presumed that in these complexes the stable isopoly 6-niobate anion,[22] $(Nb_6O_{19})^{8-}$, is coordinating intact, as a tridentate ligand, through three of its exterior O atoms, to the Cr or Co. While that arrangement fits the formal definition of a heteropoly ion, the M lacks the true involvement in the heteropoly structure outlined in the text above. Those authors had previously proven that $(Nb_6O_{19})^{8-}$ acts intact as a tridentate ligand with other metal ions.[23]

(21) C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, **8**, 178 (1969).

(22) I. Lindqvist, *Ark. Kemi*, **5**, 247 (1953).

(23) C. M. Flynn, Jr., Ph.D. Dissertation, University of Illinois, 1967.

(24) Such a postulate was far from certain, however, because (a) analytical and potentiometric procedures alone combine to leave the magnitude of *h* slightly uncertain and (b) we had shown that in other heteropoly structures those O atoms which are involved in edge sharing between MoO_6 or WO_6 octahedra and $M^{m+}O_6$ octahedra (*e.g.*, $Ni^{2+}O_6$, $Co^{3+}O_6$, or $Cr^{3+}O_6$) frequently, but not always, have *single* nontitratable H atoms attached to them.[7,25–29]

(25) U. C. Agarwala, Ph.D. Dissertation, Boston University, 1960; U. C. Agarwala and L. C. W. Baker, Abstracts of Papers Presented before the Division of Inorganic Chemistry, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

(26) K. Eriks, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallog.*, **13**, 1139 (1961).

(27) G. A. Tsigdinos, Ph.D. Dissertation, Boston University, 1961.

(28) A. Perloff, Ph.D. Dissertation, Georgetown University, 1966.

(29) H. T. Evans, Jr., and J. S. Showell, *J. Amer. Chem. Soc.*, **91**, 6881 (1969).

(30) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2940 (1967).

(31) For technique, see L. C. W. Baker and T. P. McCutcheon, *J. Amer. Chem. Soc.*, 78, 4503 (1956).

(32) O. W. Rollins and L. C. W. Baker, *Inorg. Chem.*, 8, 397 (1969).

(33) L. C. W. Baker, discussion in *Proc. Symp. Coord. Chem. 1964*, (1965).

stability; (9) studies of ligand-field spectra of solids and of solutions of analyzed samples as functions of pH, time, temperature, and concentrations of complex and of potential ligand; (10) polarography; and (11) determination of several formal redox potentials.

The ligand-field spectra confirm the distorted octahedral coordination of Co.[17] Upon replacing the coordinated H_2O by NH_3 or pyridine, the shifts in wavelengths of the bands, the changes in intensities, the changes in *Dq* (*via* rule of average environments for $Co^{III}O_5N$ coordination), and the splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band (when $Co^{III}O_6$ is replaced by lower symmetry $Co^{III}O_5N$ coordination)[34,35] all quantitatively confirm the formulations. The charge-transfer portions of the spectra correlate with the presence of Keggin-like units.

As expected, the attachment of Y to the Co(II) is reasonably labile, while its attachment to the Co(III) is much more inert.

The formal reduction potential for the

$$[(H_2O)Co^{3+}O_5SiO_4W_{11}O_{30}]^{5-} \mid [(H_2O)Co^{2+}O_5SiO_4W_{11}O_{30}]^{6-}$$

couple in 0.10 *M* Na_2SO_4 at 25° and pH 4–5 is 0.997 V *vs.* sce. At pH's above 5 the Co(III) complex oxidizes OH^- to O_2, becoming reduced itself to the Co(II) analog. That is a rare but not unique behavior.

Other Combinations. Based on the thorough study outlined above, other combinations, wherein M = Co^{2+}, Co^{3+}, and Ni^{2+} and Y = halide ion, isoquinoline, pyrazine, substituted pyridines, etc., could be surveyed with some confidence, yielding clear data to indicate formation of analogous salts. Pyrazine, in appropriate proportions, even appeared to yield some of a presumably "dumbbell-shaped" complex, wherein two heteropoly portions may be joined *via* coordination of each to one of the two N atoms of the ligand.

A Large New Class of "Heteropoly Blues." Complexes wherein M = Co^{2+} were reduced, yielding the first 11-tungsto diheteroelement "heteropoly blue" anions, another new class of complexes which has many important potentialities for future work. As with other heteropoly blue complexes,[18,19,36] the formulas are the same as for the oxidized parent complexes, but electrons have been added thereto, increasing the anionic charges and/or the extent of protonation of the complexes by titratable H^+ ions. To discuss only one example from the more extensive polarographic studies, reduction of $[(H_2O)Co^{2+}O_5SiO_4W_{11}O_{30}]^{6-}$ proceeds in two reversible two-electron steps in the pH range 4–8, yielding, successively, deep blue $(H_2[(H_2O)Co^{2+}O_5SiO_4W_{11}O_{30}])^{6-}$ and, apparently, $(H_4[(H_2O)Co^{2+}O_5SiO_4W_{11}O_{30}])^{6-}$. Above pH 9.7 the first reduction splits into two one-electron steps, and the "two-electron blue" product is apparently simply $[(H_2O)Co^{2+}O_5SiO_4W_{11}O_{30}]^{8-}$. As with other heteropoly blues,[18,19,36] the reduced complexes are stable at much higher pH's than are the oxidized parents. The two-electron blue and the four-electron blue were obtained in quantity by electrolyses at controlled potentials (ascertained from polarograms). The crystalline potassium salt of the two-electron blue was isolated, but the four-electron blue was obtained pure only in the electrolysis solution, since it apparently reduces deoxygenated water at a reasonable rate. Ion-exchange experiments under inert atmosphere show that the Co(II) is still coordinated in the anion. Oxidation immediately produces the parent "oxidized" complex quantitatively. As with the parent 11-tungsto[aquocobalto(II)]silicate and -cobaltate complexes, addition of strong acid rapidly expels simple hydrated M^{m+} from the blue tungstate matrices, presumably leaving transient 11-tungstosilicate blue species which slowly rearrange to 12-tungstosilicate blues.

17-Tungsto Species. Malik and Weakley[11,12] extended to the 18-tungstodiphosphate and 18-tungstodiarsenate heteropoly complexes the idea of replacing one octahedral W by an M^{m+}. The structure of the 18-tungsto complexes is closely related to the Keggin structure.[37] They reported 12 new 17-tungsto species, wherein M^{m+} = Mn^{2+}, Mn^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}.

Since their analyses indicate just two nontitratable H atoms in each complex, the work described in the foregoing sections makes it virtually certain (1) that these complexes should be reformulated

$$[(Y^{y-})M^{m+}O_5((P^{5+}\text{ or }As^{5+})O_4)_2(W\text{ or }Mo)_{17}O_{48}]^{(10-m+y)-}$$

(2) that many ligands will be found to function as Y, and (3) that many interesting new heteropoly blues can also be formed.

Geometrical Isomerisms for the 18-Heteropoly and for the Keggin Structure Derivatives. The parent 18-tungsto- and 18-molybdodiphosphate and -diarsenate complexes have been studied for many years,[18,19,27,38–42] but are still not completely clarified. Each has been reported to exist in "α and β" isomeric forms[39,42] (and existence of a third form has occasionally been mentioned), which should lead to interesting isomerisms for the new 17-tungsto and 17-molybdo derivatives formulated above. In the 18-heteropoly species the W (or Mo) positions are not all equivalent, as they are in the Keggin structure, and this also leads at once to obvious geometrical isomeric possibilities for the 17-tungsto and 17-molybdo derivatives.

From 1915 into the 1960's many writers[38,39] formulated the 18-heteropoly compounds as salts of 12-basic acids. In 1947 Wells[37b] proposed a structure of formula $[(P\text{ or }As)_2(W\text{ or }Mo)_{18}O_{62}]^{6-}$ and in 1952 our research group proved that formula[40] by showing that the free β isomer acids are 6-basic and the anions

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(34) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(35) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(36) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(37) (a) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, 1962, p 451; (b) ref 37a, 1st ed, 1947, p 344.

(38) Lefort, *Ann. Chim. Phys.*, **525**, 207 (1882); O. Pufahl, Dissertation, Leipzig, 1888; C. Stuhlman, *Z. Kristallogr. Mineral.*, 174 (1893); L. Duparc and F. Pierce, *ibid.*, **27**, 612 (1897); **31**, 66 (1899); A. Rosenheim and A. Traube, *Z. Anorg. Chem.*, **91**, 75 (1915); A. Rosenheim in Abegg's "Handbuch der Anorganischen Chemie," Vol. IV, Part I, ii, Leipzig, 1921, p 977; L. Pauling, *J. Amer. Chem. Soc.*, **51**, 2868 (1929); P. Souchay, *Ann. Chim. (Paris)*, [12] **2**, 203 (1947); P. Souchay and A. Tchakirian, *ibid.*, [12] **1**, 249 (1946); E. Nikitina and O. Sokolova, *Zh. Obshch. Khim.*, **24**, 1123 (1954); **24**, 1286 (1954); V. Spitsyn, *Zh. Neorg. Khim.*, **2**, 502 (1957).

(39) F. Kehrman, *Ber. Deut. Chem. Ges.*, **20**, 1805 (1887); *Z. Anorg. Chem.*, **1**, 386, 432 (1892); **4**, 138, 143 (1893); **22**, 285 (1899); O. Folin and W. Denis, *J. Biol. Chem.*, **12**, 239 (1912); H. Wu, *ibid.*, **43**, 189 (1920); E. Nikitina and N. Tsvetkov, *Russ. J. Inorg. Chem.*, **8** (1), 53 (1953); P. Souchay, R. Constant, and J. Fruchart, *C. R. Acad. Sci., Ser. C*, **264**, 976 (1967).

(40) G. A. Tsigdinos, Bachelor's Thesis, Boston University, 1952 (data presented also in ref 27).

(41) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953).

(42) E. VanDalen, Ph.D. Dissertation, Purdue University, 1962.

contain no H. Dawson[41] elucidated the X-ray crystal structure of the β isomer of $[P_2W_{18}O_{62}]^{6-}$ (Figure 2).

Removal of three WO_6 (or MoO_6) octahedra from a 12-heteropoly Keggin unit produces a 9-heteropoly "half-unit" (Figure 2). Two half-units join by sharing six O atoms to yield the 18-heteropoly structure. We have pointed out,[27] as a likely partial explanation of the α–β isomerism, that the two half-units may be joined in two ways: in one (the β isomer[41]) all of the atoms in one half-unit are eclipsed by corresponding atoms in the other half-unit (Figure 2); in the other form one half-unit is rotated 60° (around the axis through the P atoms) relative to the other, and reattached through sharing of the same O atoms, yielding a staggered arrangement for all the other atoms. This doubles the isomeric possibilities for the new 17-tungsto complexes. The data of Papaconstantinou and Pope[18,19,43] can be interpreted to show that the α isomers are 6-basic also, which negates VanDalen's suggestion[42] that the α isomer might consist of a combination of two half-units of a different sort, each formed by plucking one threefold edge-sharing tritungsto group from the Keggin structure. The latter arrangement would contain only 61 O atoms instead of 62 (because of sterically required O sharing between the central PO_4 tetrahedra) and so would be only 4-basic and not really an isomer. VanDalen's suggestion, however, may account for the third form sometimes reported.

Geometrical isomers (both 12-tungsto and 12-molybdo) of the Keggin structure also exist.[44-46] We suggest that these very possibly result from 60° rotations, about the threefold axes, of the trigonal edge-sharing W_3O_{13} (or Mo_3O_{13}) units of the Keggin structure and reattachment *via* sharing of the same O atoms. Five isomers for each formula are thus theoretically possible: the Keggin structure and the isomers wherein one, two, three, or all four of the trigonal units have been rotated.[47]

It is obvious that the geometrical isomers of the Keggin structure will probably yield numerous geometrical isomers for the new 11-heteropoly derivatives discussed in the beginning of this paper.

Further, the 18-tungsto structure (Figure 2) has, at its ends, two W_3O_{13} units, which can be rotated as we have proposed above for the 12-tungsto complexes from which the 18-tungsto anions are derived. *Each* of the (α and β) 18-tungsto isomers derived from 60° rotation of one 9-tungsto half-unit therefore also has the probability, if it is formed from the non-Keggin isomer of the 12-heteropoly derivative, of existing in up to three isomeric forms itself, yielding a total of six possible isomers for each 18-tungsto complex. Several combinations of these should be distinguishable by polarography.[49]

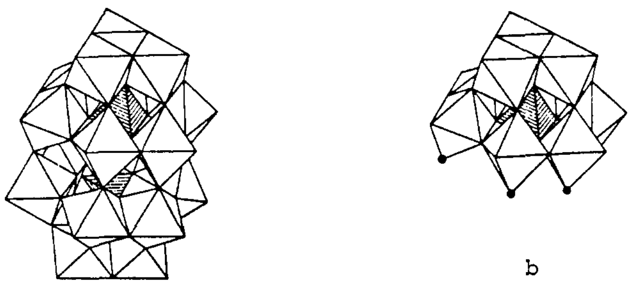

Figure 2. (a) The structure[41] of β-$[P_2W_{18}O_{62}]^{6-}$. A W atom is within each octahedron and a P atom is within each central tetrahedron. The centers of the O atoms are located by the vertices of the polyhedra. (b) The 9-tungsto (or 9-molybdo) "half-unit" (see text) formed by removal of three WO_6 (or MoO_6) octahedra from a 12-tungsto (or 12-molybdo) Keggin unit (Figure 1).

This situation also adds to the probabilities, already large as outlined above, for interesting geometrical isomerisms of the new 17-tungsto triheteroatom species. In fact it should be easier to distinguish and separate the isomers for certain of the 17-tungsto triheteroatom complexes than for the 18-tungsto anions, *via* a greater influence of the M^{m+} position on the properties.

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(43) E. Papaconstantinou, Ph.D. Dissertation, Georgetown University, 1968.

(44) W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. I, Elsevier, Amsterdam, 1950, p 183, and references therein.

(45) P. Souchay, "Polyanions et Polycations," Gauthier-Villars, Paris, 1963, p 62, and references therein.

(46) J. D. H. Strickland, *J. Amer. Chem. Soc.*, **74**, 868 (1952).

(47) The last possibility yields the structure once proposed by Kraus[48] for those 12-heteropoly ions for which Keggin[3] proved his well-known "Keggin structure."

(48) O. Kraus, *Z. Kristallogr.*, **91**, 402 (1935); **93**, 379 (1936).

(49) It is also probable that molybdo half-units can be made to combine with tungsto half-units, etc.

(50) Addressee for reprints and correspondence at Georgetown University.

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Hydrogen Scrambling in Organic Ions as a Function of Internal Energy. Extension of the Energy Range[1]

Sir:

The occurrence of H/D scrambling in organic ions in the mass spectrometer may considerably complicate the spectra of D-labeled compounds and consequently make conclusions hazardous in mechanism and/or structural studies. It would therefore be of considerable advantage to implement conditions under which such scrambling reactions are minimized. Variations in the degree of scrambling with ion lifetime (and hence with internal energy) have been observed in several cases,[2] and it is a common situation that a greater degree of scrambling is observed in metastable ions (low energy) compared with daughter ions formed in the source (higher energy) from the same reaction. This situation is a consequence of the lower appearance potential and the shallower rise of reaction rate constant, *k*, with ion internal energy, *E* (tighter activated complex), for the scrambling reaction compared with the decomposition reaction.[3,4] Therefore, in order to minimize scrambling reactions it should be desirable to develop means of investigating decompositions from higher energy molecular ions. This paper reports that secondary decompositions can provide information on molecular ions formed with a variety of internal

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(1) Metastable Ion Characteristics, XV; paper XIV: R. B. Fairweather and F. W. McLafferty, submitted for publication.

(2) See, for example, A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).

(3) F. W. McLafferty and R. B. Fairweather, *ibid.*, **90**, 5915 (1968).

(4) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).