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New Chemistry for Heteropolyanions in Anhydrous Nonpolar Solvents. Coordinative Unsaturation of Surface Atoms. Polyanion Oxygen Carriers

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In recent years the heteropolyanions of molybdenum and tungsten[1] have attracted increased attention, particularly with respect to their potential for catalysis.[2] It has generally been held that the structures of polyanions resemble fragments of metal oxide lattices[3] and that studies of these complexes could lead to further understanding of catalyst–substrate interactions.[4] Several heteropolyanions contain surface-coordinated water molecules, e.g., the substituted Keggin anion α-$[SiW_{11}Co(H_2O)O_{39}]^{6-}$ (I), and Baker and others have shown that such water molecules can be replaced by other ligands (NH_3, pyridines, etc.).[5,6] The equilibrium constants for these reactions are not particularly favorable however, and little further work has been published.

We find that heteropolyanions, including complexes like I, are easily transferred into a variety of nonpolar solvents by using phase-transfer agents in the manner first described by Corigliano and DiPasquale.[7,8] The resulting solutions, which can have concentrations approaching 0.1 M in heteropolyanion, form the basis of an unexpectedly rich and exciting chemistry which we are currently exploring. A major feature of the new chemistry is the facile loss of the coordinated water molecule(s) which leads to coordinatively unsaturated sites on the surface of the polyanion, e.g.

$$\underset{\text{I}}{[SiW_{11}Co(H_2O)O_{39}]^{6-}} \rightleftharpoons \underset{\text{Ia}}{[SiW_{11}CoO_{39}]^{6-}} + H_2O$$

For a metal ion like Co(II) the process is readily detected spectroscopically: I (and similar anions) are pink or red; Ia and its analogues are green (Figure 1). The absorption spectra of the green species match in all important respects the spectrum of the authentic square-pyramidal Co(II) complex, $[Co(ClO_4)(OAsMePh_2)_4]ClO_4$.[9] The ease of dehydration varies; when $[BW_{11}Co(H_2O)O_{39}]^{7-}$ is transferred to toluene with tetra-*n*-heptylammonium bromide (THpAB); the solution becomes green immediately.[10] In other cases it is necessary to remove the water with a molecular sieve, by passage of dry N_2 through the solution, or by storage in a vacuum desiccator. The solutions are also reversibly thermochromic, with the green form favored at high temperatures. Analogous procedures also lead to complete dehydration of anions such as $[P_2Co_4(H_2O)_2W_{18}O_{68}]^{10-}$ (II)[11] and α-$[SiW_9Co_3(H_2O)_3O_{37}]^{10-}$ (III).[12]

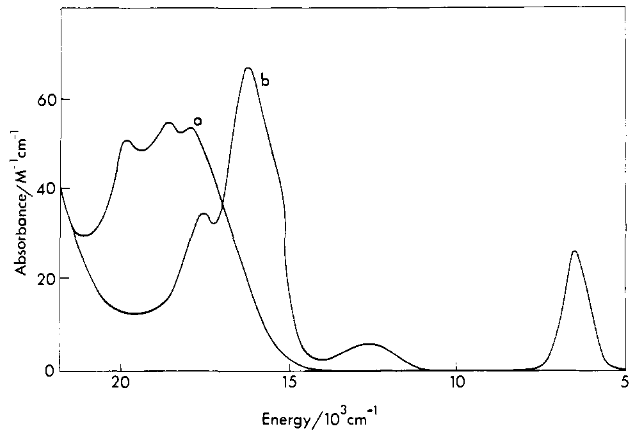

Figure 1. Absorption spectra of (a) $[SiW_{11}Co(H_2O)O_{39}]^{6-}$ and (b) $[SiW_{11}CoO_{39}]^{6-}$ in toluene/THpAB.

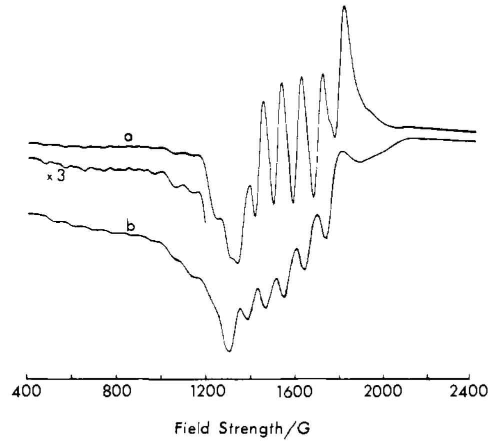

Figure 2. X-band ESR spectra of $[GeW_{11}MnO_{39}]^{6-}$ in toluene/THpAB at 77 K (a) before and (b) after oxygenation at −15 °C. Spectrum b was recorded at a gain of 6 times that of (a). Spectrum a is restored after N_2 is bubbled through the oxygenated solution at −15 °C for 10 min.

The anhydrous heteropolyanions react with a variety of donors. Alcohols, acetone, acetonitrile, pyridine, chloride ion,[13] sulfur dioxide, etc. convert the green five-coordinate Co(II) species to red or orange products. Most of these adducts are not formed in aqueous solution,[14] and extraction of the heteropolyanions back into water yields the aquopolyanion complexes quantitatively. Equilibrium constants vary widely, and ligand substitution reactions may be carried out. Some of the SO_2 adducts are formed irreversibly, e.g., reaction of SO_2 with Ia in toluene to give an orange solution (λ_{max} 505, 545 nm; ν(S–O) 1255 cm^{-1}). On the other hand, the corresponding rapid reaction of SO_2 with the anhydrous form of II is reversed by bubbling N_2 through the solution for a few minutes.

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(8) The possibilities are legion; we have used, for example, benzene, toluene, cyclohexane, carbon tetrachloride, and carbon disulfide with THpAB, Adogen 464, Aliquat 336, etc.

(9) Ciampolini, M.; Berlini, I. *J. Chem. Soc. A* **1968**, 2241.

(10) Similarly, $[SiW_{11}Cu(H_2O)O_{39}]^{6-}$ is dehydrated upon extraction into toluene.

(11) Weakley, T. J. R.; Evans, H. T., Jr.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139. Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansom, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587.

(12) Prepared by reaction of α-$Na_9HSiW_9O_{34}$ (aq) with cobalt(II) acetate. Anal. Calcd (Found) for $(Me_4N)_{10}[SiW_9Co_3O_{40}H_6]\cdot 10H_2O$; C, 14.01 (13.77); H, 3.97 (4.33); N, 4.18 (3.95); Co, 5.16 (5.14); W, 48.30 (48.30); Si 0.82 (0.86). (Sethuraman, P. R.; Pope, M. T., in preparation). Other trisubstituted Keggin anions are prepared analogously (Tēzē, A.; Leyrie, M., private communication, 1979. Ortēga, F. Ph.D. Thesis, Georgetown University, 1982).

(13) Adding as a ca. 1.5 × 10^{-2} M solution of KCl in benzene, using dibenzo-18-crown-6. When alkylammonium *chlorides* are used as phase transfer agents, the green species cannot be produced.

(14) Only derivatives of monosubstituted Keggin anions have been observed in aqueous solutions.[5,6]

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Of particular interest is the interaction of dioxygen with some manganese derivatives. When O_2 is bubbled through an anhydrous toluene solution of yellow $[SiW_{11}Mn^{II}O_{39}]^{6-}$ (IV) it is instantaneously oxidized to red $[SiW_{11}Mn^{III}O_{39}]^{5-}$.[15,16] Since no oxidation occurs in the presence of water or pyridine, an inner-sphere electron-transfer process is suggested. Oxygenation of IV at −50 to −70 °C leads to a purple-red solution, but the color change is reversed by passage of N_2 for a few seconds. The cycle can be repeated at least 20 times. When $[GeW_{11}MnO_{39}]^{6-}$ is used instead of IV, the reversible color changes occur at higher temperatures. The oxygenated solutions are purple below −15 °C and green above that temperature. Both types of solution are converted to the original yellow Mn(II) solution by passage of N_2 for about 30 s, but at room temperature the green solution is slowly (h) irreversibly oxidized to red $[GeW_{11}MnO_{39}]^{5-}$.[17] The anhydrous yellow Mn(II) and purple oxygenated species have ESR spectra with hyperfine structure characteristic of mononuclear complexes (*a*(yellow), 86.3 G; *a*(purple), 88.5 G; see Figure 2). The ESR spectra are totally reproducible when oxygenation–deoxygenation is carried out at −15 °C. The major feature in both spectra occurs at $g \sim 4.3$, as expected for rhombic high-spin Mn(II) complexes,[18] but the ESR behavior is reminiscent of the Mn-porphyrin-O_2 adduct which was eventually interpreted to be a Mn(IV)–peroxo species.[19] Whether or not the heteropolyanion system is strictly analogous remains to be determined. In any case these complexes are the first examples of oxygen carriers that contain no organic ligands.

It is clear that the possibility of generating solutions of heteropolyanions in strictly anhydrous nonpolar solvents has opened up enormous new areas of chemistry and applications for these versatile substances. Besides the obvious implications for catalysis and molecular activation, we forsee the development of novel high-temperature chemistry, new methods of synthesis, and new polyanions and derivatives.

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[15] Since it is not possible to distinguish spectroscopically between five- and six-coordinate high-spin Mn(II) complexes, IV may contain coordinated Br^- (from the THpAB). We do not think this is likely in view of the behavior of I in toluene. Coordination of Br^- to the Mn(III) species is more probable; Knoth has reported $[PW_{11}O_{39}AlCl]^{5-}$ with Cl^- bound to Al(III) (Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198).

[16] The product, extracted back into water, gave an identical absorption spectrum with that reported for $[SiW_{11}Mn(H_2O)O_{39}]^{5-}$. (Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875). An authentic sample of the latter anion, extracted into toluene and dehydrated with a stream of dry N_2, produced a solution with the same spectrum as the product of O_2 oxidation of IV.

[17] The reduction potential [Mn(III/II)] of the Ge-centered anion is 160 mV more positive than that of IV[16] and may account for the slower oxidation.

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Kinetic Lactonization of 4,6-Dimethyl- and 2,4,6,8-Tetramethyl-5-hydroxyazelaic Acids: Ground-State Conformational Control

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The potential of symmetrical dilactones **1** and their derived keto diacids **2** for control of acyclic stereorelationships has been demonstrated.[2] It is clear that additional versatility would arise from processes that efficiently desymmetrize these molecules. One such operation, exemplified by the results described here, involves the use of a functional group that resides on a symmetry element to differentiate two (or more) symmetrically equivalent functionalities elsewhere within the same molecule. The specific, two-reaction sequence designed to achieve this goal was the reduction of the C(5) ketone (which lies on the C_2 axis of symmetry) of keto diacids **2** to an alcohol followed by acid-catalyzed lactonization of the hydroxyl group to either the C(1) or C(9) carboxylic acid, which generates the monolactone **4** or **5**, respectively.

Table I. Ratio[4] of *cis*-4 to *trans*-5

	kinetic	thermodynamic
a	1:4.6	1:8.2
b	1:1.2	1:14.6
c	1:350[9]	1:4.2

Independent exposure of the *d,l*-di- and tetramethylated ketones **2a–c** to excess lithium in ammonia presumably generated the salts **3**.[3] Acidification to pH ~3 and rapid extraction did not allow isolation of the conjugate acids of **3** but instead led to kinetic ratios (see Table I) of the diastereomeric *cis*- and *trans*-5,6-disubstituted valerolactones **4** and **5**. If instead the salts **3** were acidified to pH ~1 or if the kinetically generated mixtures of **4** and **5** were reexposed to this stronger acid, a thermodynamic ratio (see Table I) of the isomers resulted. Similar thermodynamic ratios were obtained for the methyl esters corresponding to **4** and **5** (CH_2N_2) by their equilibration in absolute methanol catalyzed by Dowex acid resin.

The degree of kinetic stereoselectivity for each lactonization can be nicely explained on the basis of ground-state conformational control. Consider the four, reactive, chairlike,[5] preclosure conformations **6–9** under the assumption that the product-determining step is attack of the hydroxyl group on a protonated carboxylic acid.[6] Conformers **6** and **7** are related by a "ring-flip" and lead to the *cis*-5,6-disubstituted lactones **4**. The similarly related **8** and **9** lead to the trans lactones **5**.

In the case of **3a** (→**5a**:**4a** in 4.6:1), the conformation **6a** is not a viable reactant because of the 1,7-H_{Me},H_{Me} interaction.[7a,8] Conformer **9a**, which contains four 1,6-H,H interactions[7b] [H·

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[1] Procter and Gamble Fellow, 1982–1983. University of Minnesota Graduate School Dissertation Fellow, 1980–1981.

[2] Hoye, T. R.; Peck, D. R.; Trumper, P. K. *J. Am. Chem. Soc.* **1981**, *103*, 5618.

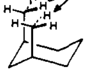
[3] Note that reduction of ketones **2a–c**, each of which possesses C_2 symmetry, can only generate a single alcohol (i.e., C(5) in **3** is achiral).

[4] This ratio was determined by integration of a capillary gas chromatogram of the methyl esters (CH_2N_2).

[5] It is unreasonable to consider boatlike reactant conformations since all involved atoms except the carboxyl carbon are sp^3 hybridized.

[6] The alternative possibility is that dehydration of the protonated tetrahedral intermediates corresponding to **6–9** is rate limiting. The subsequent analysis would still hold.

[7] (a) It is useful to identify the steric relationship that greatly destabilizes the diaxial form of *cis*-1,3-dimethylcyclohexane (i: Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 2145) or the g$^+$g$^-$ form of *n*-pentane (ii: Abe, A.; Jernigan, R. L.; Flory, P. J. *Ibid.* **1966**, *88*, 631. Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *44*, 3054. Sykora, S. *Coll. Czech. Chem. Commun.* **1968**, *33*, 3514) as a 1,7-interaction. Molecular arrangements incorporating 1,7-interactions over a set of nominally sp^3-hybridized atoms are necessarily attended by angle and/or torsional strain in order to alleviate spatial conincidence of the 1- and 7-atoms. (b) We similarly refer to butane gauchelike relationships (iii) as 1,6-interactions.



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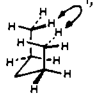

ii

iii

[8] Note that while 120° clockwise rotation about C(5)–C(6) removes the 1,7-H_{Me},H_{Me} interaction in **6**, it introduces new 1,7-interactions between the CH_2 in R″ and both the C(3)–H_{ax} and C(1)–O_{ax} atoms.