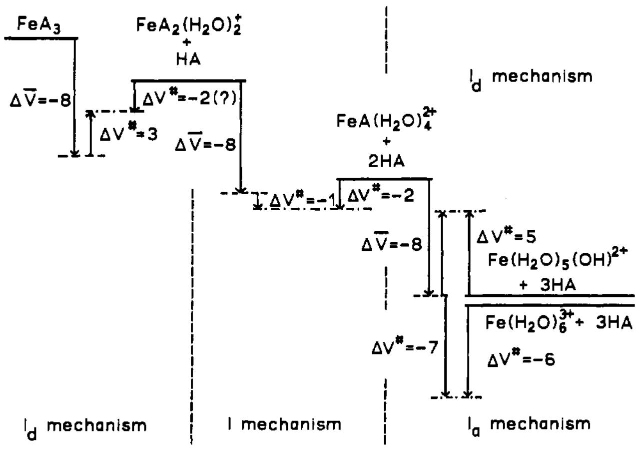

Figure 6. Overall volume profile for the stepwise aquation and formation of tris(acethydroxamato)iron(III), FeA_3: (—) reactant and product states; (- - -) ring-opened species; (-··-) transition states.

from the metal to be in direct contact with the solvent during the ring-opening process.

A similar volume collapse (ca. -8 cm^3/mol) is expected for the acid-catalyzed ring-opening reactions that occur prior to the rate-determining loss of HA during the stepwise aquation reactions. Here again protonation of coordinated A^- (ring closed) is not expected to cause a significant volume change, whereas protonation of the ring-opened species should be accompanied by a large volume increase due to the neutralization of charges. Thus in the latter case the increase in electrostriction due to the ring opening of A^- will be offset by the neutralization process and very similar volume changes are expected as for the uncatalyzed ring-opening reaction. It follows that, for all studied hydrolysis reactions, the observed ΔV^* is a composite of a reaction volume of ca. -8 cm^3/mol for the ring-opening-process and an activation volume for the subsequent rate-determining loss of the monodentate HA moiety. On the basis of these arguments it follows that ΔV^* for the loss of HA in the ring-opened $Fe(H_2O)_5AH^{3+}$ species is ca. -7 cm^3/mol (i.e. $-15.6 - (-8)$), which is in agreement with an I_a mechanism suggested on the basis of microscopic reversibility.

Similar calculations for the proton-catalyzed aquation in the first and second reaction steps result in ΔV^* values of ca. $+3$ and -1 cm^3/mol, respectively. These suggest the operation of an I_d or I mechanism, respectively, and demonstrate the labilization effect of coordinated hydroxamate. It follows that for the proton-catalyzed aquation of the complex the calculated activation volumes indicate a mechanistic changeover from I_d to I_a depending on the number of hydroxamato ligands coordinated to the metal center.

The formation of $Fe(H_2O)_2A_2^+$ from $Fe(H_2O)_4A^{2+}$ exhibits a slightly negative ΔV^* value, which suggests an I mechanism in which bond formation and breakage participate equally. The ΔV^* value for the formation of FeA_3 is subject to large error limits, since this reaction is at the limit of the resolution of the high-pressure stopped-flow instrument, and the reported standard deviation of this parameter is just a fortunate consequence of the averaging procedure on the highly scattered individual data points. An overall volume profile for the hydrolysis of tris(acethydroxamato)iron(III) is presented in Figure 6. In this profile each hydrolysis step is presented as a volume decrease of -8 cm^3/mol for the formation of the ring-opened species (see above outlined arguments), followed by an activation volume for the rate-determining loss of HA, such that the overall values represent the volumes of activation for the hydrolysis steps reported in Table I. This volume profile clearly demonstrates a gradual changeover from I_a to I_d for the complex formation reactions of $Fe(H_2O)_6^{3+}$ and a changeover from I_d to I_a for the reverse acid-catalyzed aquation reactions. Furthermore, it also includes our assumption on the basis of microscopic reversibility that, in the case of the complex formation of $Fe(H_2O)_5(OH)^{2+}$ with HA, both the forward and the reverse spontaneous aquation reactions follow an I_d mechanism.

The results presented in this work reveal that the substitution behavior of the Fe(III) complexes is controlled by the presence of OH^- or A^- in the coordination sphere. This is in an agreement with the observation[15] that the formation rate of mono(acethydroxamato)iron(III), as well as its aquation rate, gradually increases by subsequent coordination of Cl^-, possibly as a consequence of a similar mechanistic changeover from I_a to I_d.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Research Council of Croatia and a bursary to M.B. from the Commission of the European Communities.

Registry No. $Fe(H_2O)_6^{3+}$, 15377-81-8; acetohydroxamic acid, 546-88-3; desferrioxamine B, 70-51-9; tris(acetohydroxamato)iron(III), 14587-53-2; (desferrioxamine B)iron(III), 14836-73-8.

Contribution from the Chemistry Department, Tokyo Gakugei University, Koganei, Tokyo 184, Japan,
Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Interaction of Metal Cations with Heteropolytungstate Ions $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$

Akira Saito[†] and Gregory R. Choppin*[,‡]

Received April 11, 1991

The stability constants for the binding of the metal cations Ca^{2+}, Eu^{3+}, Th^{4+}, and UO_2^{2+} to two heteropolytungstates, $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$, have been determined by the solvent extraction technique. The stability constants increase with the positive charge of the cations, reflecting the ionic character of the interactions. The stability constants of UO_2^{2+} provide evidence for steric effects of the linear dioxo cation in the interaction with the binding sites on the heteropolyanions.

Introduction

Solution electrochemical and solid-state structural studies[1-3] of isopoly and heteropoly oxometalates of the transition elements (e.g., Mo and W) have shown that over certain ranges of pH these species exist in solution as stable, discrete anions of the same structure as that of the solids. These heteropolyanions can bind metal cations, but quantitative data for such binding are scarce. The susceptibility of these anions to attack by base has prevented characterization of their acidity constant values by potentiometric titration although optical spectroscopy has been employed for some systems.[4-6]

[†] Tokyo Gakugei University.

[‡] Florida State University.

(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(2) Tsigdinos, G. A. *Heteropoly Compounds of Molybdenum and Tungsten*; Topics in Current Chemistry 76; Springer-Verlag: Berlin, 1978.
(3) Weakley, T. J. R. *Some Aspects of the Heteropolymolybates and Heteropolytungstates*; Structure and Bonding 18; Springer-Verlag: Berlin, 1974.

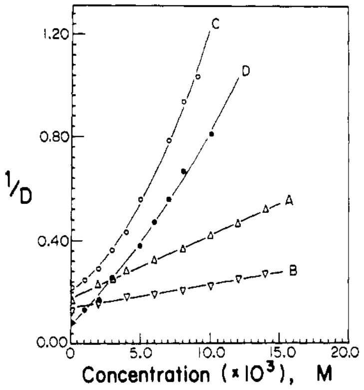

Figure 1. Plots of $1/D$ (D = distribution ratio) vs the heteropoly oxometalate concentration for solutions of pH 4.00 and ionic strength 0.1 M ($NaClO_4$) at 298 K. Ca^{2+} ([DEHP] = 0.05 M): curve A, $P_2W_{18}O_{62}^{6-}$; curve C, $SiW_{12}O_{40}^{4-}$. UO_2^{2+} ([TTA] = 0.05 M): curve B, $P_2W_{18}O_{62}^{6-}$; curve D, $SiW_{12}O_{40}^{4-}$.

Saito and Shibukawa reported the use of a solvent extraction technique to measure stability constants for the binding of metal ions by the heteropolytungstate $P_2W_{18}O_{62}^{6-}$.[7] We have studied metal complexation with both $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ at pH by this technique since these anions are stable in solutions of pH 3-6.[8] The $SiW_{12}O_{40}^{4-}$ anion has a spherical "Keggin" structure[9] of ca. 11 Å diameter with 12 peripheral oxygen atoms, each bound to a tungsten atom. $P_2W_{18}O_{62}^{6-}$ is a spheroid of ca. 20 Å (major axis) by ca. 10 Å (minor axis) with 18 peripheral oxygen atoms.[10] Although the charge transfer from $O_{p\pi}$ to $W_{d\pi}$ causes rather small partial charges on the oxygen atoms, as reflected by the low values of the pK_a's ($\lesssim 2$), a number of salts are known.[11]

Many metal oxides are present in natural waters as inorganic particulate materials and play important roles in controlling the metal ion concentrations in aquatic systems. In these systems, sorption of metals is explained by a model of surface complexation with oxygen as the coordinating atom.[12] Isopoly and heteropoly anions can be considered as small fragments of metal oxide lattices. Consequently, a purpose of the present study was to obtain a better understanding of the parameters for metal cation interaction on the surface of the oxide particles in aquatic environments. The interaction of Ca^{2+}, Eu^{3+}, and Th^{4+} with $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ has been measured as representative of +2, +3, and +4 cations. The binding of UO_2^{2+} was also studied to evaluate the effect of the linear dioxo structure.[13]

Experimental Section

Reagents. Thenoyl(trifluoroacetyl)acetone (HTTA) was purified by a double vacuum sublimation at 45 °C and dissolved in benzene. Bis(2-ethylhexyl)phosphoric acid (HDEHP) was purified by precipitation of $Cu(DEHP)_2$.[14] The purified HDEHP was dissolved in toluene and the concentration determined by titration with standard sodium hydroxide solution. All other reagents were analytical grade and used without further purification.

Tracers. The radioactive nuclides ^{45}Ca, ^{152}Eu + ^{154}Eu, ^{230}Th, and ^{233}U were used. The radiochemical purity of the latter three elements was checked by α-ray (Th, U) and γ-ray (Eu) spectral analysis with a multichannel analyzer. The ^{45}Ca purity was confirmed from the half life decay.

Table I. Distribution Ratios for Extraction of UO_2^{2+} [a]

$[P_2W_{18}O_{62}^{-6}]$, M	D_{av}	$1/D$
0	7.551 ± 0.181	0.1324
2.00×10^{-3}	6.376 ± 0.049	0.1568
4.01×10^{-3}	5.476 ± 0.067	0.1826
6.00×10^{-3}	5.208 ± 0.056	0.1920
8.00×10^{-3}	4.856 ± 0.045	0.2059
1.00×10^{-2}	4.470 ± 0.032	0.2237
1.20×10^{-2}	4.010 ± 0.075	0.2493
1.40×10^{-2}	3.719 ± 0.022	0.2689

[a] pH = 4.00, T = 298 K, I = 0.1 M ($NaClO_4$), [TTA] = 0.007 M in benzene, $\beta'_1 = (6.99 \pm 0.30) \times 10^1$.

Table II. Distribution Ratios for Extraction of Ca^{2+}

$10^3[SiW_{12}O_{40}^{4-}]$, M	D_{av}	$[(D_0/D) - 1][L]$
0	4.636 ± 0.025	
1.00	4.405 ± 0.107	146
2.00	3.421 ± 0.007	178
3.00	2.751 ± 0.015	228
4.00	2.310 ± 0.076	252
5.00	1.793 ± 0.082	317
7.00	1.274 ± 0.029	377
8.00	1.066 ± 0.032	419
9.00	0.9659 ± 0.0421	422

[a] pH = 4.00, T = 298 K, I = 0.1 M ($NaClO_4$), [HDEHP] = 0.05 M in toluene, $\beta'_1 = (1.13 \pm 0.10) \times 10^2$, and $\beta'_2 = (3.68 \pm 0.19) \times 10^4$.

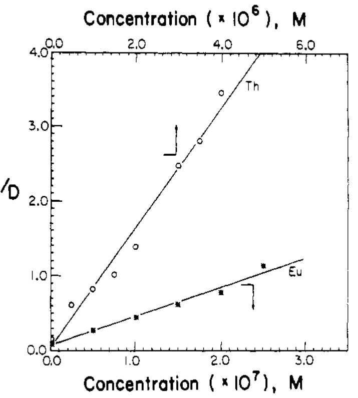

Figure 2. Plot of 1/D vs the concentration of $SiW_{12}O_{40}^{4-}$ for Eu^{3+} (using [TTA] of 0.07 M) and Th^{4+} (using [TTA] of 2.5×10^{-4} M) in solutions at 298 K of pH 4.00 and ionic strength 0.1 M ($NaClO_4$).

Syntheses of the Heteropolytungstates. $H_4[SiW_{12}O_{40}]\cdot 7H_2O$ was prepared according to the method in ref 15. To confirm the composition, the tungsten content was determined by inductively coupled plasma emission spectrometry. Anal. Calcd for $H_4[SiW_{12}O_{40}]\cdot 7H_2O$: W, 73.4. Found: W, 72.9.

$(NH_4)_6(P_2W_{18}O_{62})\cdot 14H_2O$ was prepared by the method in ref 16. The compound was analyzed gravimetrically for ammonium ion and for tungsten with tetraphenylborate[17] and oxinate.[18] Anal. Calcd for $(NH_4)_6(P_2W_{18}O_{62})\cdot 14H_2O$: NH_4^+, 2.29; W, 70.1. Found: NH_4^+, 2.25; W, 69.2.

Preparation of Solutions. Ten milliliters each from stock solutions of 0.1 M CH_3COOH and 1 M $NaClO_4$ were placed in a 100-mL beaker and aliquots of heteropolytungstate stock solution added. The final solutions were adjusted to pH 4.00 and ionic strength 0.1 M. A combination glass electrode calibrated with standard pH 4.00 and pH 7.00 buffers was used. The stock and the working solutions of each hetero-

---

(4) Tourne, C.; Tourne, G. *Bull. Soc. Chim. Fr.* **1969**, 1124.

(5) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836.

(6) Spitsyn, V. I.; Torchenkova, E. A.; Kazanskii, L. P. *Z. Chem.* **1974**, *14*, 1.

(7) Saito, A.; Shibukawa, J. *J. Radioanal. Nucl. Chem., Lett.* **1988**, *126*, 189.

(8) Kepert, D. L. In *Comprehensive Inorganic Chemistry*; Bailor, J. C., Emeleus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., Eds., Pergamon: Oxford, England, 1974; Vol. 4, Chapter 51, p 662.

(9) Keggin, J. F. *Nature* **1933**, *131*, 908.

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

(11) Tsigdinos, G. A. *Ind. Eng. Chem., Prod. Res. Dev.* **1974**, *13*, 267.

(12) Shindler, P. W.; Stumm, W. In *Aquatic Surface Chemistry*; Stumm, W., Ed., Wiley-Interscience: New York, 1987; Chapter 4.

(13) Ahrland, S. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1980; Vol. 2, Chapter 21, p 1480.

(14) McDowell, W. J.; Purdue, P. T.; Case, G. N. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2127.

(15) North, E. O. *Inorganic Syntheses*; McGraw-Hill: New York, 1939; Vol. 1, p 129.

(16) Brauer, G., Ed. *Handbuch der Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, Germany 1954; p 1271.

(17) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed., MacMillan: New York, 1969; p 666.

(18) Williams, W. J. *Handbook of Anion Determination*; Butterworths: London, 1979; p 108.

Table III. Correction for Complexations with Hydroxide and Acetate Ions

(1) Acetate Complexation[a]

metal	log $^{OAc}\beta_n$	temp, °C	I, M	$\Sigma_n{}^{OAc}\beta_n[OAc]^n$
Ca^{2+}	1.18	25	0	0.033
Eu^{3+}	2.13, 3.64, 4.24	25	0.1	0.31
Th^{4+}	4.06, 7.10, 9.12, 10.4[b]	25	0.1	97.1
UO_2^{2+}	2.6, 4.9, 6.3	20	0.1	1.25

(2) Hydroxide Complexation[c]

metal	log $^{OH}\beta_i$	temp, °C	I, M	$\Sigma_i{}^{OH}\beta_i[OH]^i$
Ca^{2+}	1.3	25	0	
Eu^{3+}	5.42	25	0.3	
Th^{4+}	10.2, 20.3	25	0.1	3.57
UO_2^{2+}	8.0	25	1.0	0.01

(3) Correction Term $A = 1 + \Sigma_n{}^{OAc}\beta_n[OAc]^n + \Sigma_i{}^{OH}\beta_i[OH]^i$

metal	$\Sigma_n{}^{OAc}\beta_n[OAc]^n$	$\Sigma_i{}^{OH}\beta_i[OH]^i$	A
Ca^{2+}	0.03		1.03
Eu^{3+}	0.31		1.31
Th^{4+}	97.1	3.57	101.7
UO_2^{2+}	1.25	0.01	2.26

[a] $[CH_3COO^-] = 2.159 \times 10^{-3}$ M (pK_a = 4.56 at 25 °C, I = 0.1 M, pH 4.00). [b] Estimated from values at I = 1.0 M. [c] $[OH] = 10^{-10}$ M.

Table IV. Stability Constants[a]

metal/HPA		$SiW_{12}O_{40}^{4-}$	$P_2W_{18}O_{62}^{6-}$
Ca^{2+}	log β_{121}	2.07 ± 0.12	2.17 ± 0.02
	log β_2	4.58 ± 0.07	
Eu^{3+}	log β_1	7.68 ± 0.13	6.71 ± 0.15[b]
Th^{4+}	log β_1	8.70 ± 0.32	11.3 ± 0.3[b]
	log β_2		17.8 ± 0.3[b]
UO_2^{2+}	log β_1	3.10 ± 0.13	2.21 ± 0.10
	log β_2	4.94 ± 0.26	

[a] 25 °C, I = 0.1 M ($NaClO_4$). [b] Reference 7 (I = 0.7 M NaCl, pH = 5.00 and room temperature).

polytungstate were prepared immediately prior to use to avoid degradation. In the Ca^{2+} and UO_2^{2+} systems the changes in ion concentration upon complexation were sufficient to change the ionic strength so addition of $NaClO_4$ was required to maintain the ionic strength at 0.1 M.

Solvent Extraction. The extractions were carried out with 5.0 mL of each of the aqueous and organic phases. To minimize sorption loss of Th^{4+} on the walls, the extraction vials were silanized by the method of ref 19. The phases were mixed for 5 h in a water bath thermostated at 25 °C. This time had been confirmed in separate experiments as sufficient for equilibrium. The extractions were performed at least in duplicate over a range of eight different ligand concentrations from 0 to 0.014 M for Ca^{2+} and UO_2^{2+} and from 0 to 2.5 × 10^{-7} M for Eu^{3+} and from 0 to 4 × 10^{-6} M for Th^{4+}. The radioactivity in the two phases was determined for aliquots of each phase by liquid scintillation (for α and β decay) and NaI(Tl) crystal scintillation (for γ decay) counting.

Results

Sample sets of distribution ratios for varying ligand concentrations are given in Tables I and II and Figures 1 and 2. Degradation of the heteropolytungstates would produce changes in the concentrations of the ligand and of the hydrogen ion. In some of the duplicate samples, particularly of the $SiW_{12}O_{40}^{4-}$ systems, poorer reproducibility probably can be attributed to some degree of degradation of the heteropolytungstate ligand even though it was reported to be stable at pH 4. The errors listed reflect the quality of the reproducibility.

The data were analyzed using the following assumptions: (1) only mononuclear complexes are formed; (2) heteropolyanions and their metal complexes are not extracted into the organic phases; (3) heteropoly anions are deprotonated completely at pH 4.00. The distribution was described by

$$1/D = (1/D_0)\{1 + \beta'_1[L] + \beta'_2[L]^2 + ...\} \tag{1}$$

where $D = \sum(M)_{org}/\sum(M)_{aq}$, $\sum(M)_{org}$ and $\sum(M)_{aq}$ are the sum of the metal concentrations in the organic and the aqueous phases, respectively, D_0 is the value of D in the absence of L, [L] is the free ligand concentration and $\beta'_i = \beta_i/A$. A is the correction term for hydroxide and acetate complexation, and is given by

$$\begin{aligned} A &= 1 + \{^{OH}\beta_1[OH] + {}^{OH}\beta_2[OH]^2 + ...\} + \\ &\qquad \{^{OAc}\beta_1[OAc] + {}^{OAc}\beta_2[OAc]^2 + ...\} \\ &= 1 + \sum_i {}^{OH}\beta_i[OH]^i + \sum_n {}^{OAc}\beta_n[OAc]^n \end{aligned} \tag{2}$$

where $^{OH}\beta_n$ and $^{OAc}\beta_n$ are stability constants for hydrolysis and acetate complexation from the literature.[20,21] These constants and the calculated values of A are listed in Table III. All stability constants are defined by

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \tag{3}$$

where brackets denote concentrations at 0.1 M ($NaClO_4$) ionic strength.

For all the systems studied, the formation of 1:1 and/or 1:2 complexes only were indicated by the data. The values of β'_1 and β'_2 were calculated by the least-squares method for the relationships

$$1/D = 1/D_0 + (\beta'_1/D_0)[L] \tag{4}$$

$$[(D_0/D)\text{-}1][L]^{-1} = \beta'_1 + \beta'_2[L] \tag{5}$$

The literature data used in the correction for acetate complexation have not all been measured under the same conditions. However, the difference in temperature for the reported stability constants of the UO_2^{2+} + acetate system and for our system is not significant since the enthalpy change for complexation indicates a very small temperature dependence.[20] By contrast, the difference in ionic strength between the literature and our study is not negligible for the Th^{4+} + acetate system. We assume that log $^{OAc}\beta_n$ values for this system are uncertain by ±0.2 when adjusted to 0.1 M ionic strength so the correction factor A is uncertain by the same factor. For Eu^{3+} and UO_2^{2+}, acetate complexation is not as significant as it is for Th^{4+}. Log $^{OAc}\beta_n$ values with errors of ±0.1 introduce final errors of ±0.02 (Eu^{3+}) and ±0.05 (UO_2^{2+}). At pH 4, hydroxide complexation is significant only for Th^{4+}.[21]

The correction terms used are listed in Table III. The correction for Th^{4+} is quite large, and the thorium values in Table IV include the estimated error based on the reported values of $^{OAc}\beta_n$ in Table III but do not reflect the possibility of absolute error in the reported values. Consequently, the corrected log β_n values for the thorium systems are considered less reliable than those for the other cations.

The corrected values of log β_1 and log β_2 are given in Table IV. The stability constants for the Eu^{3+}, Th^{4+} + $P_2W_{18}O_{62}^{6-}$ systems reported in ref 7 are also listed. The error limits of the stability constants arise from uncertainties in the ligand concentrations, the distribution ratios, and the corrections for acetate and hydroxide complexation. To calculate the ligand concentrations, we assumed that the heteropolytungstate ions are deprotonated completely at pH 4 since the pK_a values of the multibasic ligands are reported to be $\lesssim 2$.[1] The reproducibility of the distribution ratios for metal + $SiW_{12}O_{40}^{4-}$ systems are rather poor, presumably due to some slight ligand instability. Three standard deviations were used as a reasonable measure of the uncertainty in the measurements of D.

Discussion

With $SiW_{12}O_{40}^{4-}$ the data supported formation by the divalent cations Ca^{2+}, and UO_2^{2+} of 1:1 and 1:2 complexes. For the Eu^{3+} and Th^{4+} cations, the D values at higher ligand concentrations

---

(19) Caceci, M. S.; Choppin, G. R. *Radiochim. Acta* **1983**, *33*, 113.

(20) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York: (a) 1976; Vol. 4, Inorganic Complexes. (b) 1977; Vol. 3, Organic Complexes.

(21) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley and Sons: New York, 1976; p 158.

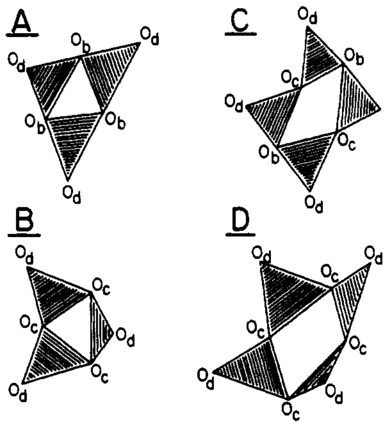

Figure 3. Possible metal binding sites of $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$. Shaded triangles are faces of WO_6 octahedra. Oxygen atoms are distinguished as follows: O_d, unshared; O_c, shared by two W atoms as a common corner; O_b, shared by two W atoms as a common edge.

show significant decreases in extraction, which is an indication of higher order complexation, but it was not possible to calculate a set of β_1, β_2 stability constants that gave satisfactory fits over the whole range of data. With $P_2W_{18}O_{62}^{6-}$, the Th^{4+} data was consistent with formation of both 1:1 and 1:2 complexes while for the other cations evidence for formation of only the 1:1 complex was obtained. The sequence of the β_1 values for both heteropolytungstates is $Th^{4+} > Eu^{3+} > UO_2^{2+} \geq Ca^{2+}$. This order is somewhat unusual as, for simple anionic ligands, UO_2^{2+} usually has a stability constant which lies between the values for Th^{4+} and Eu^{3+}.[22] The Th^{4+} and Eu^{3+} values for binding to these heteropolytungstates are similar to the values for complexation of these cations by divalent oxalate anion while the UO_2^{2+} values are closer to those for complexation by monovalent iodate and acetate anions.

The radius of the spherical $SiW_{12}O_{40}^{4-}$ was determined to be 5.6 Å both in solution[23] and in crystalline form.[24] The spheroidal $P_2W_{18}O_{62}^{6-}$ ion is estimated to have dimensions of roughly 20 × 10 Å. The $SiW_{12}O_{40}^{4-}$ anion has 12 unshared oxygen atoms at peripheral positions, while the $P_2W_{18}O_{62}^{6-}$ anion has 18 such atoms. These peripheral oxygen atoms have four types of geometrical arrangements for possible metal binding sites (Figure 3). In sites A and B, the O_d atoms are at the apices of equilateral triangles of about 5.6 and 4.7 Å, respectively. Site A has three O_b atoms in the same plane, whereas site B is formed by three O_c atoms which are separated from the triangle of the O_d atoms by about 1.9 Å. Site C has six oxygen atoms (i.e., four O_d and two O_b) which form a rectangle of about 5.6 × 4.7 Å. Site D, which exists only in the $P_2W_{18}O_{62}^{6-}$ structure, has four O_d atoms in a square of about 4.6 Å on a side with four O_c atoms in a parallelogram separated from the square of the O_d atoms by 1.4 Å.

Several systems are known for which definite coordination geometries have been determined. For example, Er^{3+} in $(NH_4)_2[UMo_{12}O_{42}(Er(H_2O)_5)_2]\cdot nH_2O$[25] and Th^{4+} in $(NH_4)_4[UMo_{12}O_{42}(Th(H_2O)_3)]\cdot 15H_2O$[26] are coordinated by three terminal oxygen atoms, which form a triangle similar to site B. In these compounds Er–O and Th–O distances are reported to be 2.4 Å. In $Ba_2[SiW_{12}O_{40}]\cdot nH_2O$,[27] Ba^{+2} is coordinated by four terminal oxygen atoms of site C with Ba–O distances of 2.7–2.8 Å. These structures indicate that the O_d atoms are the likely binding sites, which is consistent with the presence of unshared electron pairs on these oxygens. In $V_{10}O_{28}^{6-}$, and $V_2W_4O_{19}^{4-}$, ^{17}O NMR spectra have been interpreted as indicating that the O_c sites are the most basic, but this is not supported by the correlation of bond lengths and bond strengths.[28]

The values of the stability constants of Th^{4+} and Eu^{3+} suggest that these cations are probably associated with three or more oxygen donors while those of Ca^{2+} and UO_2^{2+} are consistent with binding to a smaller number of oxygens or binding at greater metal–oxygen distances. If we assume that the metal cations associate only with the planes defined by O_d atoms, the shortest distances between the cations and O_d atoms are estimated to be as follows: site A, 3.2 Å; site B, 2.6 Å; site C, 3.5 Å; site D, 3.2 Å. These values indicate preferred interaction at site B with C and D less likely. The smaller stability constant for Ca^{2+} may reflect a binding site of greater interatomic distance. The linear structure of the UO_2^{2+} cation must perturb the interaction between the binding sites and the central uranium atom so the UO_2^{2+} interacts by its net charge of +2 rather than by the "effective" charge on the U atom of +3.3.[22] This could account for the similarity in binding strength of Ca^{2+} and UO_2^{2+}.

Acknowledgment. This research was supported by a grant from the USDOE—OBES Division of Chemical Sciences.

---

(22) Choppin, G. R. *Radiochim. Acta* **1983**, *32*, 43.

(23) Baker, L. C. W.; Pope, M. T. *J. Am. Chem. Soc.* **1960**, *82*, 4176.

(24) Baker, M. C.; Lyons, P. A.; Singer, S. J. *J. Am. Chem. Soc.* **1955**, *77*, 2011.

(25) Tatyanina, I. V.; Fomicheva, E. B.; Molchanov, V. N.; Zanodnik, V. E.; Belskii, V. K.; Torchenkova, E. A. *Sov. Phys. Crystallogr.* **1982**, *27*, 142.

(26) Molchanov, V. N.; Tatyanina, I. V.; Torchenkova, E. A. *J. Chem. Soc., Chem. Commun.* **1981**, 93.

(27) Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 885.

(28) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544; **1978**, *100*, 4892.