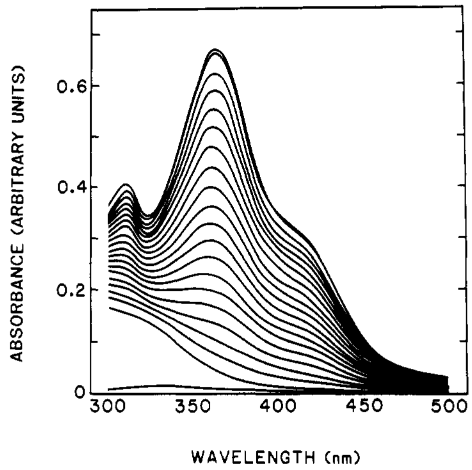

Figure 7. Optical titration of $[n\text{-}Bu_4N][TcOCl_4]$ with 3,4-toluenedithiol (in MeOH).

Inspection of a molecular model of the compound shows that the extra methylene groups effectively block access to the otherwise vacant sixth coordination sites of the Tc atoms and explains the lack of reactivity of this substance even in the presence of excess dithiol. The discovery of this dimer has ramifications for radiopharmaceutical chemistry. The compound dihydrothioctic acid $[HSCH_2CH_2CH(SH)(CH_2)_4COOH]$ is used[20] as a ligand for the preparation of a ^{99m}Tc hepatobiliary agent. Marzilli et al. have shown[21] that the product of the stannous ion reduction of no-carrier-added $^{99m}TcO_4^-$ in the presence of dihydrothioctic acid is the bis(ligand) *monomer*, not the dimer. This observation demonstrates the importance of reaction conditions in the synthesis of 1,3-dithiolato complexes of technetium.

This study was extended to aromatic dithiols, and it was discovered that titration (Figure 7) of $[TcOCl_4]^-$ in MeOH with 3,4-toluenedithiol led directly to the bis(dithiolato) monomer $[TcO(S_2C_6H_3(CH_3))_2]^-$ without formation of an intermediate. The reasons for this behavior are not clear but could involve factors that destabilize the (hypothetical) intermediate or stabilize the final monomer.

The results of this series of experiments with dithiols and $[TcOCl_4]^-$ demonstrate how the mechanism and the final product of their reaction depend sensitively on the detailed structure of the dithiol species. It is this type of information that will be useful in designing highly selective reactions for ^{99m}Tc-radiopharmaceutical syntheses.

Acknowledgment. This work was supported by USPHS Grant No. GM23270 and DOE Contract No. AC02-76EV04115.

Registry No. $[(TcO)_2(SCH_2CH_2S)_3]$, 86119-88-2; $[n\text{-}Bu_4N][TcOCl_4]$, 71341-65-6; $[(TcO)_2(SCH_2CH_2CH_2S)_3]$, 86119-89-3; $Na[TcO(OCH_2CH_2O)_2]$, 86119-90-6; $[n\text{-}Bu_4N][TcO(O_2C_6H_4)_2]$, 86119-92-8; $[Ph_4As][TcO(SCH_2CH_2O)_2]$, 86119-94-0; $[Ph_4As][TcO(SCH_2CH_2S)_2]$, 70177-06-9; $[TcO(SCH_2CH_2O)(SCH_2CH_2S)]^-$, 86119-95-1; $[TcO(O_2C_6H_4)(SCH_2CH_2S)]^-$, 86119-96-2.

---

(20) Tonkin, A. K.; DeLand, F. H. *J. Nucl. Med.* **1974**, *15*, 539.

(21) Marzilli, L. G.; Worley, P.; Burns, H. D. *J. Nucl. Med.* **1979**, *20*, 871.

Contribution from the Department of Chemistry,
Portland State University, Portland, Oregon 97207

Hydrolysis of Cations. Formation Constants and Standard Free Energies of Formation of Hydroxy Complexes

DENNIS W. BARNUM

Received October 4, 1982

The formation constants and standard free energies of formation of both mononuclear and polynuclear hydroxy complexes of metal ions throughout the periodic table have been examined. Some empirical correlations are presented that make it possible to predict rough values for these constants. For mononuclear complexes the equation is $\Delta G_f^\circ\{M(OH)_y\} = \Delta G_f^\circ\{M\} + By + Cy^2 + D/y$, where B, C, and D are empirical parameters and y is the number of coordinated hydroxide ions. These parameters are subject to constraints that limit acceptable values. For example, B, C, and electronegativity are interrelated. This equation can be rearranged to define a new function, U, that is linearly related to y. This allows the interpolation of unmeasured free energies and hence formation constants. For mononuclear complexes predicted values of $\log K_{1y}$ have an uncertainty of about ±0.5. For polynuclear hydroxy complexes a relation previously proposed by Baes and Mesmer has been slightly modified and used to predict unknown formation constants with an uncertainty in $\log K_{xy}$ of about $\pm 0.5y$. Mercury(II) and silver(I), which form especially stable "linear" complexes, do not follow the above correlations because of the structure change that occurs upon going from the $M(OH)_2$ to the $M(OH)_3$ species. The tetrahedrally coordinated $Be^{2+}(aq)$ ion is more acidic than expected when compared with octahedrally coordinated aquo ions of divalent metals. Each hydrogen must carry a somewhat greater portion of the positive charge than it would in an octahedral complex, and this makes the removal of a proton easier. Aqueous Sn^{2+} is also unusually acidic, and it is suggested that it too has fewer water molecules in the primary coordination sphere than one would expect for a "normal" octahedrally coordinated metal ion. A reason is suggested for the experimental difficulty previous investigators have encountered in determining the formation constants for polynuclear hydroxy complexes of certain metal ions such as bismuth(III), cerium(IV), and zirconium(IV).

Metal ions in aqueous solution generally hydrolyze to form a series of mononuclear and polynuclear hydroxy complexes. The general equation is

$$xM^{n+} + yH_2O \overset{K_{xy}}{\rightleftharpoons} M_x(OH)_y^{n-y} + yH^+ \qquad (1)$$

Iron(III), for example, forms $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3(aq)$, $Fe(OH)_4^-$, $Fe_2(OH)_2^{4+}$, and probably other polynuclear species. In the last four decades much effort has gone into the identification of the species present in aqueous solutions and the measurement of their formation constants. The work up to 1974 has been critically reviewed and summarized by Baes and Mesmer.[1] Despite the large number of equilibrium constants that have been measured, there are still a number of cases in which data are conflicting or absent. In some of these the formation constants are experimentally difficult to determine because equilibrium is reached very

---

(1) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

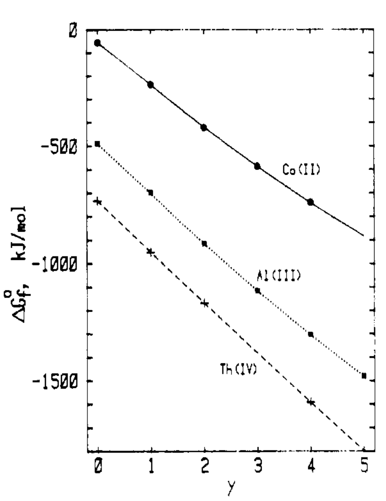

Figure 1. Standard free energy of formation of aqueous mononuclear hydroxy complexes plotted against the number of coordinated hydroxide ions.

slowly or because the metal ion is in an unstable oxidation state. It would be desirable to have a method to predict unknown formation constants and to sort out conflicting data.

This paper describes some empirical relations among formation constants and standard free energies of formation of hydroxide complexes that are applicable to most of the metals in the periodic table and are sufficiently good to make rough estimates of many unknown data. The uncertainty in estimated values of log K_{xy} is about $\pm 0.5y$ for both mononuclear and polynuclear complexes. There are a few cases in which metal ions do not fit the proposed correlations, but in most instances, these can be traced to variations in structure.

Notation and Methods of Calculation

All hydrolysis constants used in this work are based on eq 1 unless explicitly stated otherwise. For example, K_{34} is the formation constant for the complex $M_3(OH)_4$ (ionic charge not shown) with $x = 3$ and $y = 4$.

Standard free energies of formation and equilibrium constants are for 25 °C and zero ionic strength unless otherwise noted. The calculation of free energies from equilibrium constants utilized[2] $\Delta G_f^\circ\{H_2O(l)\} = -237.19\ (\pm 0.025)$ kJ/mol and $\Delta G_f^\circ\{OH^-\} = -157.34\ (\pm 0.05)$ kJ/mol.

Literature values of ΔG_f° of complexes are often based on a different value of $\Delta G_f^\circ\{M\}$ than used in this work. Corrections have been applied in these cases in order to obtain an internally consistent set of free energies.

The uncertainties shown are standard deviations, σ, which tend to be optimistic. The reproducibility of data obtained in different laboratories tends to be about 2 or 3 times σ. Uncertainties were taken from the literature wherever available. Otherwise, a guess was made on the basis of comparable data and the agreement generally found between data from different workers. No attempt has been made to document all of the sources and calculations of standard deviations.

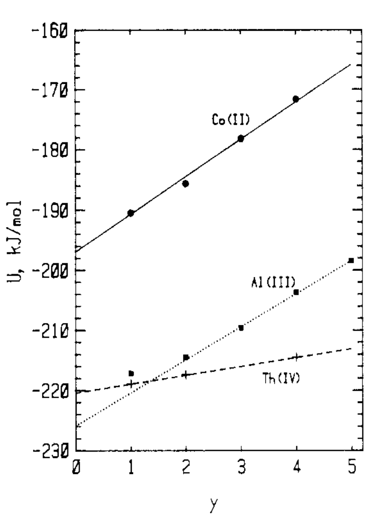

Figure 2. Linear plots of U (defined by eq 4 or 5) against the number of coordinated hydroxide ions. These are the same three metal ions shown in Figure 1.

An Empirical Correlation between $\Delta G_f^\circ\{M(OH)_y\}$ and y for Mononuclear Complexes

For most metal ions a graph of the standard free energy of formation of its mononuclear hydroxy complexes against the number of coordinated hydroxide ions is a smooth curve such as those shown in Figure 1. These curves suggest that the free energies can be fit to an empirical quadratic equation. Indeed this is the case, but a still better fit is obtained if a term D/y is added. The equation is therefore

$$\Delta G_f^\circ\{M(OH)_y\} = \Delta G_f^\circ\{M\} + By + Cy^2 + D/y \qquad (2)$$

where B, C, and D are empirical constants to be fit to the experimental data and y is the number of coordinated OH^- ions. (If $y = 0$, then D/y is taken to be 0.) It was found that for all divalent and trivalent metal ions $D = 8.37$ kJ/mol and for tetravalent metal ions $D = 0$. There are insufficient data to evaluate D for monovalent ions or for oxycations. The parameter B is related to Δ, the difference in the standard free energies of formation of the 1:1 hydroxy complex and the uncomplexed metal ion:

$$\Delta = \Delta G_f^\circ\{MOH\} - \Delta G_f^\circ\{M\} \qquad (3)$$

As shown below, there is also a correlation between B and the electronegativity of the metal ion. The C term determines the curvature of the plot, and there is a good correlation between B and C that depends only on the oxidation number of the central metal. Therefore, although the parameters are empirical, there are constraints that limit the range of acceptable values.

A Linear Relation for Successive Hydrolysis Steps. Rearranging eq 2 gives

$$[\Delta G_f^\circ\{M(OH)_y\} - \Delta G_f^\circ\{M\} - D/y]/y = B + Cy = U\{M(OH)_y\} \qquad (4)$$

The quantity $U\{M(OH)_y\}$ can be readily calculated from known free energies of formation and the knowledge that $D = 8.37$ kJ/mol for divalent and trivalent metal ions and 0 for tetravalent metal ions. It can also be calculated directly from log K_{1y} by combining eq 4 with ΔG° for eq 1; i.e., $\Delta G^\circ = -RT \ln K_{1y} = \Delta G_f^\circ\{M(OH)_y\} - \Delta G_f^\circ\{M\} - y\Delta G_f^\circ\{H_2O\}$, from which one obtains

$$U\{M(OH)_y\} = \Delta G_f^\circ\{H_2O\} - D/y^2 - (2.303RT \log K_{1y})/y \qquad (5)$$

It will be seen in eq 4 that a graph of U vs. y will be a straight line with slope = C and y intercept = B. Most of the values of B and C used in this work were determined in this manner. Examples of this type of plot are shown in Figure 2.

Besides determining B and C, the graph of U vs. y allows the prediction of unknown formation constants. For example, there is no experimental value for log K_{13} for $Th(OH)_3^+$, and the point for this species is missing in Figure 2. It can be predicted, however, either from the B and C values or from the value of $U\{Th(OH)_3^+\}$ interpolated from the graph. One might also extrapolate to predict log K_{15} and ΔG_f° for $Th(OH)_5^-$.

Still another advantage of plotting U vs. y is that disparate data are readily detected. Whether the disparity is due to poor experimental data, a failure of the empirical equations, or to something unusual about the structure or stability of the comlex can then be the object of further study.

For certain metal ions the formation constant for only one hydroxy complex is known. For example, for titanium(III), cerium(III), and

---

(2) The Committee on Data for Science and Technology recommended key values for thermodynamics: *CODATA Bull.* **1977**, *No. 28*; *J. Chem. Thermodyn.* **1972**, *4*, 331–336; **1975**, *7*, 1–3; **1976**, *8*, 603–605; **1977**, *9*, 705–706.

(3) Latimer, W. M. "Oxidation Potentials"; Prentice-Hall: Englewood Cliffs, NJ, 1952.

(4) Robie, R. A.; Waldbaum, D. R. *Geol. Surv. Bull. (U.S.)* **1968**, *No. 1259*.

(5) Hemingway, B. S.; Robie, R. A.; Kittrick, J. A. *Geochim. Cosmochim. Acta* **1978**, *42*, 1533–1543.

(6) Lindsay, W. L. "Chemical Equilibria in Soils"; Wiley-Interscience: New York, 1979; pp 385–422.

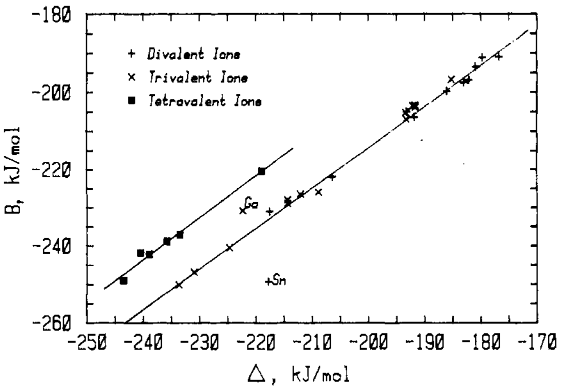

Figure 3. Correlation between the slope parameter, B, and the difference between the standard free energy of formation of the 1:1 metal hydroxide complex and that of the metal aquo ion (eq 3 defines Δ).

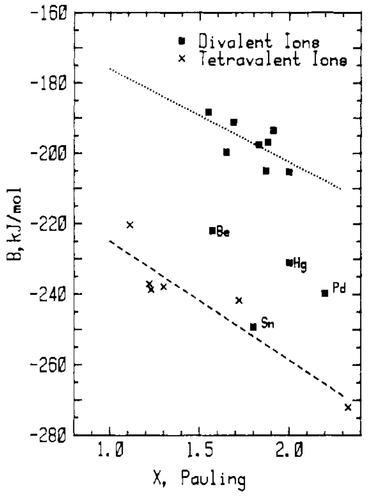

Figure 4. Correlation between the slope parameter, B, and Pauling's electronegativity for divalent and tetravalent metal ions. Deviations by Be(II), Pd(II), Hg(II), and Sn(II) are explained in the text.

some of the lanthanoids, only log K_{11} has been measured. This gives only a single point on the graph of U vs. y, but it can be combined with approximate values of B and C estimated from electronegativity in order to predict the remaining unknown formation constants and free energies.

Table I compares experimental and calculated values of formation constants and standard free energies of formation for a selected group of metal ions. It gives an idea of the kind of agreement one can expect to obtain. Table II gives the values of B and C for all metal ions for which there are sufficient data to make an accurate determination. These values of B and C can be inserted into eq 2 to obtain the calculated free energies and hence formation constants.

Correlation between B and Δ. Because B is the initial slope in the graph of $\Delta G_f°$ vs. y, one might expect a correlation with Δ (defined by eq 3). Indeed, a good correlation exists, as shown in Figure 3. Only Sn(II) and Ga(III) deviate substantially. Why gallium deviates is unknown. The case of tin(II) is discussed below.

Least-squares treatments of the data in Figure 3 gave the following expressions[26] (B and Δ in kJ/mol): for divalent and trivalent metals $B = 1.057\Delta - 2.936$ (±1.5; 0.9980; 23); for tetravalent metals $B = 1.099\Delta - 20.13$ (±1.3; 0.9912; 6). These equations are useful for estimating B in cases where K_{11} is the only known hydrolysis constant.

Correlation between B and Electronegativity. It is well-known that the acidity of metal aquo ions depends strongly on the electronegativity, χ, of the metal. It is therefore not surprising to find the correlations shown in Figures 4 and 5. Among the divalent metal ions, the points for Hg(II), Be(II), Pd(II), and Sn(II) lie well away from the others but for good reasons discussed below. Of the trivalent metal ions, the point for scandium lies outside the expected range, and the reason is unknown.

Part of the scatter in Figures 4 and 5 may be due to uncertainty in the electronegativities. The electronegativity scales of Sanderson and of Allred and Rochow were also tried, but they gave even greater scatter than those obtained by Pauling's method.

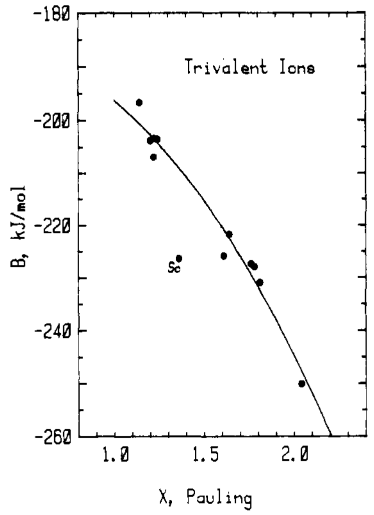

Figure 5. Correlation between the slope parameter, B, and Pauling's electronegativity for trivalent metal ions only. The reason scandium(III) deviates is unknown.

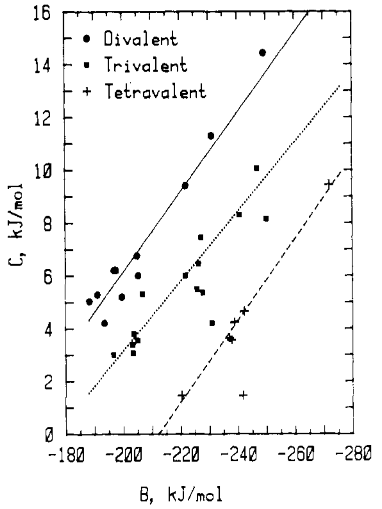

Figure 6. Correlation between the slope parameter, B, and the curvature parameter, C.

Least-squares treatments of the data in Figures 4 and 5 gave the following:[26] for divalent metal ions $B = -149.77 - 26.38\chi$ (±4.6; 0.655; 8); for trivalent metal ions $B = -189.63 + 14.21\chi - 20.89\chi^2$ (±2.5; 0.986; 11); for tetravalent metal ions $B = -191.42 - 33.61\chi$ (±6.1; 0.928; 6).

Correlation between B and C. As shown in Figure 6, there is a good correlation between the curvature parameter, C, and the slope parameter, B. Only points for Sn(IV), Ga(III), and Tl(III) deviate markedly. The reasons for these deviations are unknown.

Linear regression treatments of these data give the following equations: for divalent metal ions $C = -0.1509B - 24.04$ (±0.7; 0.950; 11); for trivalent metal ions $C = -0.1318B - 23.21$ (±0.8; 0.932; 14); for tetravalent metal ions $C = -0.1550B - 32.90$ (±0.2; 0.997; 6).

Mononuclear Hydroxy Complexes of Lanthanum(III). As an example of how the above correlations can be used, consider aqueous lanthanum(III). Baes and Mesmer[1] give log $K_{11} = -8.5$ (±0.1). Taking $\Delta G_f°\{\text{La}^{3+}\} = -683.7$ kJ/mol,[7] one calculates $\Delta G_f°\{\text{LaOH}^{2+}\} = -872.4$ kJ/mol, and therefore from either eq 4 or eq 5 $U\{\text{LaOH}^{2+}\} = -197.1$ (±0.6) kJ/mol. The electronegativity of lanthanum[27] is

---

[7] *NBS Tech. Note (U.S.)* **1968**, *No. 270–3*; **1969**, *No. 270–4*; **1971**, *No. 270–5*; **1971**, *No. 270–6*; **1973**, *No. 270–7*.

[8] This species has not been detected experimentally.

[9] Fedorov, V. A.; Kalosh, T. N.; Mironov, V. E. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1971**, *16*, 1596.

[10] Vasil'ev, V. P.; Grechina, N. K. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1967**, *12*, 315.

Table I. Formation Constants and Standard Free Energies of Formation of Hydroxy Complexes[a]

	$\Delta G_f°$, kJ/mol			log K_{xy}			
species	calcd	exptl	±σ	calcd	exptl	±σ	ref
Al^{3+}		−489.5	1.3				5
$AlOH^{2+}$	−698.4	−698.3	1.3	−5.0	−4.97	0.02	1, 6
$Al(OH)_2^+$	−911.5	−914.2	2.1	−9.2	−8.70	0.3	1, 5, 6
$Al(OH)_3(aq)$	−1113.4	−1115.5	2.2	−15.4	−15.0	0.3	1
$Al(OH)_4^-$	−1306.1	−1302.1	2.2	−23.1	−23.85	0.3	1, 5, 7
$Al(OH)_5^{2-}$	−1490.2	−1480.0	3.1	−32.5	−34.24	0.5	6
Be^{2+}		−379.7	0.8				7
$BeOH^+$	−583.9	−586.1	1.0	−5.8	−5.40	0.1	1
$Be(OH)_2(aq)$	−781.8	−776.2	1.0	−12.7	−13.65	0.1	1
$Be(OH)_3^-$	−958.1	−958.6	0.8	−23.3	−23.25	0.04	1
$Be(OH)_4^{2-}$	−1114.8	−1114.9	1.4	−37.4	−37.41	0.2	1, 7
Bi^{3+}		92.34	0.08				9–11
$BiOH^{2+}$	−138.0	−138.6	0.19	−1.2	−1.09	0.03	1, 12
$Bi(OH)_2^+$	−361.3	(−359.2)		−3.6	(−4)		1, 7
$Bi(OH)_3(aq)$	−562.2	−568.7	0.6	−10.0	−8.86	0.1	1
$Bi(OH)_4^-$	−742.8	−732.0	0.6	−19.9	−21.8	0.1	1
Cd^{2+}		−77.66	0.35				2
$CdOH^+$	−258.3	−257.3	0.7	−9.9	−10.08	0.1	1, 13, 14
$Cd(OH)_2(aq)$	−438.7	−435.9	1.2	−19.9	−20.35	0.2	1, 13, 14
$Cd(OH)_3^-$	−603.7	−597.3		−32.5	−33.62		1, 13, 14
$Cd(OH)_4^{2-}$	−755.3	−756.1	0.7	−47.5	−47.35	0.1	1, 13, 14
$Cd(OH)_5^{3-}$	−894.0	−908.5		−64.8	−62.22		13, 14
$Cd(OH)_6^{4-}$	−1019.8	−1060.7		−84.3	−77.10		13, 14
Co^{2+}		−54.39	0.8				7
$CoOH^+$	−236.8	−236.5	0.9	−9.6	−9.65	0.05	1
$Co(OH)_2(aq)$	−419.2	−421.5	1.0	−19.2	−18.8	0.1	1
$Co(OH)_3^-$	−586.5	−586.2	1.0	−31.4	−31.5	0.1	1, 15
$Co(OH)_4^{2-}$	−740.7	−738.9	1.0	−46.0	−46.3	0.1	1
Cu^{2+}		65.59	0.4				2
$CuOH^+$	−125.3	−126.2	1.2	−8.1	−7.96	0.2	6, 16
$Cu(OH)_2(aq)$	−316.7	−316.0	0.7	−16.1	−16.26	0.1	6, 16, 17
$Cu(OH)_3^-$	−493.3	−493.3		−26.7	−26.7		3, 6
$Cu(OH)_4^{2-}$	−657.1	−657.1	1.2	−39.6	−39.6	0.2	1, 3, 6
Er^{3+}		−669.0	0.8				7
$ErOH^{2+}$	−861.1	−861.1		−7.9	−7.9		1
$Er(OH)_2^+$	−1059.4	(−1052.6)		−14.7	(−15.9)		1
$Er(OH)_3(aq)$	−1248.9	(−1242.4)		−23.0	(−24.2)		1
$Er(OH)_4^-$	−1431.8	−1431.7		−32.6	−32.6		1
Hf^{4+}		−656.1	0.8				12
$HfOH^{3+}$	−890.6	−891.8	1.9	−0.46	−0.25	0.3	1
$Hf(OH)_2^{2+}$	−1116.7	(−1116.7)		−2.4	(−2.4)		1
$Hf(OH)_3^+$	−1334.4	(−1333.3)		−5.8	(−6.0)		1
$Hf(OH)_4(aq)$	−1543.7	−1543.7	6	−10.7	−10.7	1	1
$Hf(OH)_5^-$	−1744.2	−1743.8		−17.1	−17.2		1
Fe^{3+}		−4.47	0.4				7
$FeOH^{2+}$	−228.3	−229.2	0.4	−2.3	−2.19		1, 3, 18
$Fe(OH)_2^+$	−448.1	−446.5	0.7	−5.4	−5.67	0.1	1, 19
$Fe(OH)_3(aq)$	−648.4	(−641.3)		−11.9	(−13.1)		1, 6, 7, 20
$Fe(OH)_4^-$	−831.5	−829.9	1.2	−21.3	−21.6	0.2	1
Pb^{2+}		−23.97	0.2				2
$PbOH^+$	−212.7	−217.2	0.6	−8.5	−7.71	0.1	1, 21
$Pb(OH)_2(aq)$	−401.6	−400.6	0.6	−17.0	−17.12	0.1	1, 6
$Pb(OH)_3^-$	−575.3	−575.4	0.4	−28.1	−28.06	0.05	1
$Pb(OH)_4^{2-}$	−735.9	(−748.6)		−41.5	(−39.3)		22, 23
Mn^{2+}		−230.6	0.08				6
$MnOH^+$	−407.4	−407.3	0.24	−10.6	−10.59	0.04	1, 6
$Mn(OH)_2(aq)$	−585.2	(−578.3)		−21.0	(−22.2)		1
$Mn(OH)_3^-$	−748.8	−748.1		−33.9	−33.5		1, 6
$Mn(OH)_4^{2-}$	−900.1	−903.7	0.6	−48.9	−48.3	0.1	1
Ni^{2+}		−46.44	0.1				4
$NiOH^+$	−227.3	−227.3	0.2	−9.9	−9.86	0.03	1
$Ni(OH)_2(aq)$	−412.4	(−412.4)		−19.0	(−19)		1
$Ni(OH)_3^-$	−586.2	−586.8	0.3	−30.1	−30.0	0.05	1
$Ni(OH)_4^{2-}$	−750.9	>−744.1		−42.8	<−44		1
Pu^{4+}		−494.5	0.8				3, 24
$PuOH^{3+}$	−728.8	−728.8	1.0	−0.5	−0.5	0.1	1
$Pu(OH)_2^{2+}$	−956.0	(−955.8)		−2.2	(−2.3)		1
$Pu(OH)_3^+$	−1176.1	(−1175.8)		−5.2	(−5.3)		1
$Pu(OH)_4(aq)$	−1389.1	−1389.0	1.4	−9.5	−9.5	0.2	1
$Pu(OH)_5^-$	−1594.9	(−1594.8)		−15.0	(−15.0)		1
$Pu(OH)_6^{2-}$	−1793.6			−21.7			

Table I (*Continued*)

species	$\Delta G_f°$, kJ/mol calcd	$\Delta G_f°$, kJ/mol exptl	±σ	log K_{xy} calcd	log K_{xy} exptl	±σ	ref
Tl^{3+}		214.64	0.8				7
$TlOH^{2+}$	−18.95	−19.00	1	−0.6	−0.62	0.1	1
$Tl(OH)_2^+$	−248.8	−250.7	1	−1.9	−1.57	0.1	1
$Tl(OH)_3(aq)$	−459.5	−478.1	3	−6.6	−3.3	0.5	1
$Tl(OH)_4^-$	−653.2	−648.5	2	−14.2	−15.0	0.3	1
Th^{4+}		−733.0					3
$ThOH^{3+}$	−951.9	−951.9		−3.2	−3.2	0.2	1
$Th(OH)_2^{2+}$	−1167.9	−1167.8		−6.9	−6.93	0.2	1
$Th(OH)_3^+$	−1381.0	⩾−1377.8		−11.1	⩽−11.7		1
$Th(OH)_4(aq)$	−1591.1	−1591.0		−15.9	−15.9	0.3	1
$Th(OH)_5^-$	−1798.3			−21.1			
U^{4+}		−579.1					3
UOH^{3+}	−812.5	−812.5		−0.65	−0.65	0.04	1, 3
$U(OH)_2^{2+}$	−1038.7	(−1038.5)		−2.6	(−2.6)		1
$U(OH)_3^+$	−1257.7	(−1257.7)		−5.8	(−5.8)		1
$U(OH)_4(aq)$	−1469.3	(−1469.0)		−10.3	(10.3)		1
$U(OH)_5^-$	−1673.6	−1673.6		−16.0	−16.0	0.1	1
$U(OH)_6^{2-}$	−1870.7			−23.0			
Zn^{2+}			0.15				2
$ZnOH^+$	−333.3	−333.2	0.3	−8.9	−8.96	0.05	1
$Zn(OH)_2(aq)$	−521.6	−525.1		−17.5	−16.9		1
$Zn(OH)_3^-$	−696.6	−696.7	1.2	−28.4	−28.4	0.2	1
$Zn(OH)_4^{2-}$	−860.5		0.6	−41.2	−41.2	0.1	1
Zr^{4+}		−589.9	0.8				3
$ZrOH^{3+}$	−827.5	−828.8	0.85	0.06	0.3	0.05	1
$Zr(OH)_2^{2+}$	−1055.7	(−1054.6)		−1.5	(−1.7)		1
$Zr(OH)_3^+$	−1274.6	(−1272.4)		−4.7	(−5.1)		1
$Zr(OH)_4(aq)$	−1484.2	−1483.3	6	−9.6	−9.7	~1	1
$Zr(OH)_5^-$	−1684.5			−16.0	−16.0		1
$Zr(OH)_6^{2-}$	−1875.5			−24.1			

[a] Comparison of experimental and calculated values. All free energies are in kJ/mol and refer to 25 °C and $I = 0$ unless noted otherwise. Values enclosed in parentheses are questionable or unreliable. Calculated values were obtained from the B and C values in Table II and eq 2.

Table II. B and C Parameters Determined by Plotting $U\{M(OH)_y\}$ vs. y

cation	B,[a] kJ/mol	C,[a] kJ/mol	Δ,[a] kJ/mol	χ[a]	cation	B,[a] kJ/mol	C,[a] kJ/mol	Δ,[a] kJ/mol	χ[a]
Ag^+	−183.4[b]	12.30[b]		1.93	Mn^{3+}	(−222)	(6.02)		(1.65)
Ag^+	−183.4[b]	6.289[b]			Fe^{3+}	−240.5	8.305	−223.6	1.96
Tl^+	(−173.6)		−161.8	1.62	Co^{3+}	(−245)	(9.04)		1.98
Be^{2+}	−222.0	9.414	−206.4	1.57	Bi^{3+}	−248.5	9.80	−231.0	2.02
Mg^{2+}	(−182.8)	(3.56)	−171.9	1.31	U^{3+}	(−211.3)	(4.636)		1.7
Ca^{2+}	(−176.4)	(2.573)	−163.8	1.00	La^{3+}	(−200.3)	(3.15)	−188.7	1.10
Sr^{2+}	(−171.1)	(1.787)	−161.4	0.95	Ce^{3+}	(−201.8)	(3.376)	−189.8	1.12
Ba^{2+}	(−171.1)	(1.786)	−160.3	0.89	Pr^{3+}			−190.0	1.13
Cr^{2+}	(−192)	(5.00)		1.66	Nd^{3+}	−196.7	3.004	−194.2	1.14
Mn^{2+}	−188.3	5.042	−176.7	1.55	Sm^{3+}			−192.1	1.17
Fe^{2+}	−197.6	6.213	−182.9	1.83	Eu^{3+}			−192.5	
Co^{2+}	−196.9	6.213	−182.1	1.88	Gd^{3+}	−203.8	3.807	−191.6	1.20
Ni^{2+}	−193.5	4.217	−180.9	1.91	Tb^{3+}			−192.1	
Cu^{2+}	−205.3	6.017	−191.8	2.0	Dy^{3+}	−203.4	3.381	−191.5	1.22
Zn^{2+}	−199.7	5.213	−186.0	1.65	Ho^{3+}			−191.5	1.23
Cd^{2+}	−191.2	5.293	−179.6	1.69	Er^{3+}	−203.5	3.067	−192.1	1.24
Hg^{2+}	−231.0[b]	11.30[b]		2.00	Tm^{3+}			−193.2	1.25
Hg^{2+}	−230.6[b]	4.531[b]			Yb^{3+}	−205.2	3.556	−193.2	
Sn^{2+}	−249.3	14.43	−217.7	1.80	Lu^{3+}			−193.8	1.27
Pb^{2+}	−205.0	6.765	−193.2	1.87	Ti^{4+}	−233.5	1.65	(−231.8)	
Al^{3+}	−221.5	4.205	−208.8	1.61	Ce^{4+}	(−247.5)	(5.460)	(−243.5)	1.08
Sc^{3+}	−226.4	6.456	−212.0	1.36	Zr^{4+}	−242.2	4.653	−238.9	
Y^{3+}	−206.9	5.314	−193.2	1.22	Hf^{4+}	−238.8	4.238	−235.7	1.23
Ga^{3+}	−230.9	4.205	−222.3	1.81	U^{4+}	−237.1	3.640	−233.4	1.22
In^{3+}	−227.9	5.356	−214.4	1.78	Th^{4+}	−220.4	1.464	−218.9	1.11
Tl^{3+}	−250.1	8.159	−233.6	2.04	Sn^{4+}	−241.8	1.464	−240.5	1.72
Ti^{3+}	−221.8	6.012	(−224.6)	(1.64)	Pb^{4+}	−270.7	9.367		2.33
Cr^{3+}	−227.3	7.448	−214.3	(1.76)					

[a] For divalent and trivalent metal ions $D = 8.37$ kJ/mol. For tetravalent cations $D = 0$. Electronegativities, χ, are those determined by Pauling's method. Values in parentheses are estimated from limited data and are somewhat uncertain. [b] See text.

1.10, and its correlation with B predicts $B \approx -199$ kJ/mol. On the other hand, the correlation between B and Δ predicts $B \approx -202$ kJ/mol. Using an average value of B from the two estimates and the correlation between B and C gives $C = 3.15$ kJ/mol. If a straight line with slope 3.15 is drawn through the point for $LaOH^{2+}$ on a graph of U vs. y, the y intercept gives $B = -200.3$ kJ/mol (±0.6). Therefore, using $B = -200.3$ kJ/mol, $C = 3.15$ kJ/mol, and $D = 8.37$ kJ/mol, one calculates the following: $\Delta G_f°\{La(OH)_2^+\} = -1067.5$ (±3.4) kJ/mol, log $K_{12} = -15.9$ (±0.6); $\Delta G_f°\{La(OH)_3\} = -1253.5$ (±7.3) kJ/mol, log $K_{13} = -24.8$ (±1.3); $\Delta G_f°\{La(OH)_4^-\} = -1432$ (±12) kJ/mol, log

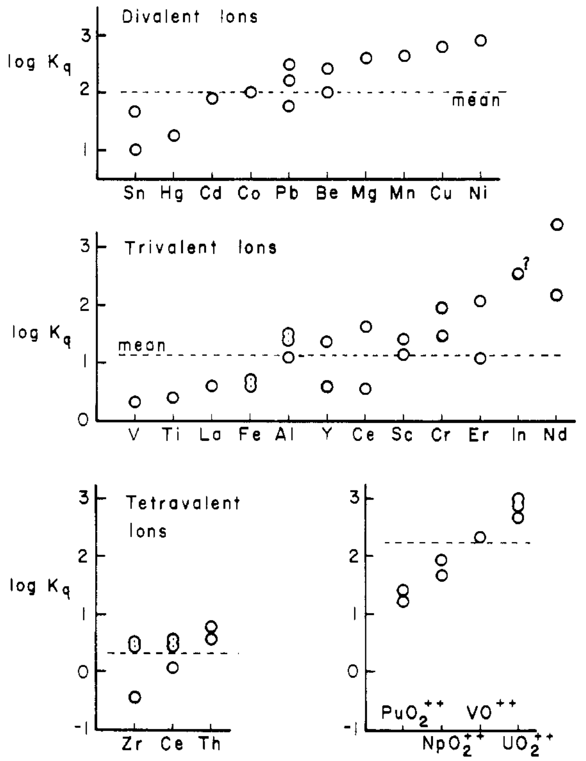

Figure 7. log K_q values (defined by eq 6) for polynuclear hydroxy complexes.

$K_{14} = -35.0$ (±2.3). The uncertainties are based on ±0.1 for log K_{11}, ±0.6 for B, and ±0.8 for C.

Correlations with log K_{11} and $\Delta G_f°\{MOH\}$. To a large extent the formation constants for complexes with two, three or four hydroxide ions per metal ion, as well as those for polynuclear hydroxy complexes, are a reflection of the first ionization constant of the aquometal ion. That is, all subsequent hydrolysis constants are related to K_{11}. Thus, Baes and Mesmer[1] found that for polynuclear complexes the value of log K_q for the following equilibrium is approximately constant for many different metal ions:

$$MOH \overset{K_q}{\rightleftharpoons} (1/y)M_x(OH)_y + [(y-x)/y]M \qquad (6)$$

This equation can be derived by combining the general case of eq 1 for $M_x(OH)_y$ with the specific case for MOH. Likewise, by combining the equilibrium constants, one obtains

$$\log K_{xy} = y(\log K_q + \log K_{11}) \qquad (7)$$

By converting K_{xy} and K_{11} (but not K_q) to the mole fraction scale, Baes and Mesmer obtained

$$\log K_{xy} = y[\log K_q + \log K_{11} + (1 - x) \log 55.5] \qquad (8)$$

In this equation K_{xy} and K_{11} are still on the molar concentration scale, and the log 55.5 term converts to the mole fraction scale. It was found that the average value of log K_q for eq 8 is about 2.8 for polynuclear complexes. Using this average value, one can make use of a known value of log K_{11} for a particular metal ion to predict the formation constants for other polynuclear hydroxy complexes of the same metal ion.

This approach was examined further in the present work. It was found that there is no particular advantage in converting K_{11} and K_{xy} to the mole fraction scale. In fact, if K_q is also converted, the log 55.5 term drops out. Therefore, eq 7 was used.

Values of log K_q for known polynuclear hydroxy complexes (excluding M_2OH complexes) are tabulated in Table III and shown graphically in Figure 7. In Figure 7 there is no significance to the order of the metal ions along the x axis other than to arrange them in order of generally increasing values of log K_q. No correlation could be found between K_q and other parameters such as B, C, x, y, $\Delta G_f°\{M\}$, or electronegativity. It will be seen that, within a given group of metals with the same oxidation number, K_q can range over 2 or 3 orders of magnitude. It can only be considered constant when compared with K_{xy}, which generally ranges over 30 or more orders of magnitude.

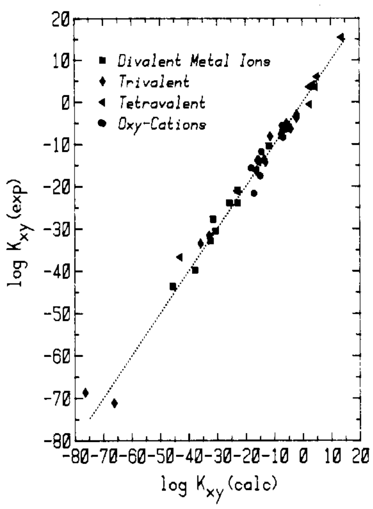

Figure 8. Comparison of experimental and calculated values of log K_{xy} for polynuclear hydroxy complexes.

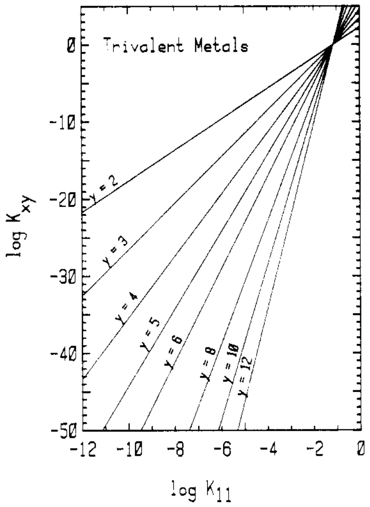

Figure 9. Correlation between log K_{xy} for polynuclear hydroxy complexes, log K_{11}, and y as given by eq 7. The value of log K_q used for this graph is the average of all known polynuclear hydroxy complexes of trivalent metal ions. Similar graphs are obtained for divalent and tetravalent metal ions and oxycations.

In spite of the variability of K_q, Figure 7 shows that one can still make sufficiently accurate guesses at its value that it can be used in eq 7 along with log K_{11} to predict approximate values of log K_{xy}. Recommended values of log K_q are given in Table IV. For polynuclear complexes, the best approach is to use an average value of log K_q from other complexes of the same metal ion (excluding that of the M_2OH complex). For example, the only reported polynuclear complex of cadmium is $Cd_4(OH)_4^{4+}$, for which log $K_q = 1.87$. According to Figure 7 other polynuclear complexes of cadmium should also have log $K_q \approx 1.9$. Combining this with log $K_{11} = -10.08$ for $CdOH^+$, one obtains from eq 7 log $K_{22} = -16.4$ for $Cd_2(OH)_2^{2+}$, log $K_{33} = -24.5$, log $K_{35} = -40.9$, etc. In the absence of any log K_q values for a particular metal ion, one can still use the overall averages given in Table IV provided K_{11} is known.

For an indication of the reliability of eq 7 for predicting log K_{xy}, Table III compares experimentally observed formation constants with those calculated from the recommended log K_q values in Table IV. These data are also compared graphically in Figure 8.

Equation 7 can also be applied to mononuclear complexes by using the appropriate log K_q values in Table IV, but the linear graph of U vs. y combined with correlations between B, C, Δ, and electronegativity are more reliable.

To the extent that log K_q is constant for metal ions of the same oxidation state, eq 7 shows that there is a simple linear relationship between log K_{xy} and log K_{11} that depends only on the number of coordinated hydroxide ions. This is shown in Figure 9 for trivalent

Table III. Comparison of Experimental and Predicted Values of log K_{xy} for Polynuclear Complexes[a]

species	log K_{11} exptl	log K_q exptl	log K_{xy} exptl	log K_{xy} calcd
$Sn_2(OH)_2^{2+}$	−3.40	1.01	−4.77	−2.8[b]
$Cu_2(OH)_2^{2+}$	−7.96	2.78	−10.36	−11.9
$Mn_2(OH)_3^{+}$	−10.59	2.62	−23.9	−25.7
$Be_3(OH)_3^{3+}$	−5.40	2.42	−8.92	−10.2[b]
$Hg_3(OH)_3^{3+}$	−3.40	1.26	−6.42	−4.2[b]
$Sn_3(OH)_4^{2+}$	−3.40	1.68	−6.88	−5.6[b]
$Pb_3(OH)_4^{2+}$	−7.71	1.74	−23.88	−22.8
$Cd_4(OH)_4^{4+}$	−10.08	1.87	−32.85	−32.3
$Co_4(OH)_4^{4+}$	−9.65	2.02	−30.53	−30.6
$Ni_4(OH)_4^{4+}$	−9.86	2.92	−27.74	−31.4
$Mg_4(OH)_4^{4+}$	−11.44	2.62	−39.71	−37.7
$Pb_4(OH)_4^{4+}$	−7.71	2.49	−20.88	−22.8
$Be_6(OH)_8^{4+}$	−5.40	2.00	−27.2	−27.1[b]
$Pb_6(OH)_8^{4+}$	−7.71	2.26	−43.61	−45.6
$V_2(OH)_2^{4+}$	−2.26	0.36	−3.8	−2.2
$Ti_2(OH)_2^{4+}$	−2.2	0.40	−3.6	−2.1
$Ce_2(OH)_2^{4+}$	−8.3	(0.55)	<−15.5	−14.3
$Al_2(OH)_2^{4+}$	−4.97	1.12	−7.7	−7.2
$Y_2(OH)_2^{4+}$	−7.7	0.59	−14.23	−13.1
$Fe_2(OH)_2^{4+}$	−2.19	0.72	−2.95	−2.1
$Er_2(OH)_2^{4+}$	−7.9	1.08	−13.65	−13.5
$Sc_2(OH)_2^{4+}$	−4.40	1.40	−6.0	−6.5
$Cr_2(OH)_2^{4+}$	−8.3	1.47	−5.06	−5.7
$Nd_2(OH)_2^{4+}$	−9.1	2.17	−13.86	−15.9
$Al_3(OH)_4^{5+}$	−4.97	1.49	−13.9	−14.5
$Fe_3(OH)_4^{5+}$	−2.19	0.62	−6.3	−4.2
$Cr_3(OH)_4^{5+}$	−4.0	1.96	−8.15	−11.4
$In_3(OH)_4^{5+}$	−4.0	2.55	−5.82[c]	−11.4
$Ce_3(OH)_5^{4+}$	−8.3	1.60	−33.5	−35.8
$Y_3(OH)_5^{4+}$	−7.7	1.38	−31.6	−32.8
$Er_3(OH)_5^{4+}$	−7.9	(2.04)	<−29.3	−33.8
$Sc_3(OH)_5^{4+}$	−4.40	1.13	−16.34	−16.3
$Nd_3(OH)_5^{4+}$	−9.1	(3.4)	<−28.5	−39.8
$La_5(OH)_9^{6+}$	−8.5	0.59	−71.2	−66.2
$Al_8(OH)_{20}^{4+}$	−4.97	1.54	−68.7	−72
$Ce_2(OH)_2^{6+}$	(0.8)	(0.7)	(3.6)	2.3
$Th_2(OH)_2^{6+}$	−3.2	0.13	−6.14	−5.7
$Ce_2(OH)_3^{5+}$	(0.8)	0.57	(4.1)	3.4
$Ce_2(OH)_4^{4+}$	(0.8)	0.08	(3.5)	4.5
$Zr_3(OH)_4^{8+}$	0.3	−0.45	−0.6	2.5
$Zr_3(OH)_5^{7+}$	0.3	0.44	3.70	3.2
$Zr_4(OH)_8^{8+}$	0.3	0.45	6.0	5.0
$Th_4(OH)_8^{8+}$	−3.2	0.56	−21.1	−23.0
$Ce_6(OH)_{12}^{12+}$	(0.8)	0.48	(15.4)	13.6
$Th_6(OH)_{15}^{9+}$	−3.2	0.75	−36.76	−43.1
$(PuO_2)_2(OH)_2^{2+}$	−5.6	1.42	−8.36	−6.8
$(NpO_2)_2(OH)_2^{2+}$	−5.15	1.96	−6.39	−5.9
$(UO_2)_2(OH)_2^{2+}$	−5.8	2.99	−5.62	−7.2
$(VO)_2(OH)_2^{2+}$	−5.67	2.33	−6.67	−7.0
$(UO_2)_3(OH)_4^{2+}$	−5.8	(2.86)	(−11.75)	−14.5
$(PuO_2)_3(OH)_5^{+}$	−5.6	1.27	−21.65	−17.1
$(NpO_2)_3(OH)_5^{+}$	−5.15	1.65	−17.49	−14.9
$(UO_2)_3(OH)_5^{+}$	−5.8	2.67	−15.63	−18.1

[a] Values of log K_{xy} were predicted from eq 7 by using the experimental value of log K_{11} and the value of log K_q recommended in Table IV. [b] The low coordination numbers of Sn^{2+}(aq) and Be^{2+}(aq) and the linear structure of $HgOH^+$ cause K_{11} to be unusually large, and eq 7 is not expected to apply in these cases. [c] Baes and Mesmer[1] have a footnote beside their entry for $In_3(OH)_4^{5+}$ noting that the composition of this species is not well established.

Table IV. Recommended Average Values of log K_q To Be Used in Eq 7

Mononuclear Complexes

	log K_q	±σ	N[a]
$M^{II}(OH)_2$	−0.16	0.52	8
$M^{II}(OH)_3^-$	−0.71	0.33	7
$M^{II}(OH)_4^{2-}$	−1.72	0.35	8
$M^{III}(OH)_2^+$	−0.32	0.34	13
$M^{III}(OH)_3$	−0.86	0.72	13
$M^{III}(OH)_4^-$	−1.47	1.1	13
$M^{IV}(OH)_2^{2-}$	−0.65	0.33	7
$M^{IV}(OH)_3^+$	−1.33	0.59	7
$M^{IV}(OH)_4$	−1.91	0.85	7

Polynuclear Complexes

	log K_q	N[a]		log K_q	N[a]
Sn^{2+}	1.3	2	V^{3+}	0.4	1
Hg^{2+}	1.3	1	Ti^{3+}	0.4	1
Cd^{2+}	1.9	1	Ce^{3+}	1.1	2
Co^{2+}	2.0	1	La^{3+}	0.6	1
Pb^{2+}	2.2	3	Al^{3+}	1.4	3
Be^{2+}	2.2	2	Y^{3+}	1.0	2
Mg^{2+}	2.6	1	Fe^{3+}	0.7	2
Mn^{2+}	2.6	1	Er^{3+}	1.6	2
Cu^{2+}	2.8	1	Sc^{3+}	1.3	2
Ni^{2+}	2.9	1	Cr^{3+}	1.7	2
	av 2.01 (±0.54)		Nd^{3+}	2.8	2
			In^{3+}	2.6?	1
				av 1.15 (±0.65)	
PuO_2^{2+}	1.3	2	Zr^{4+}	0.15	3
NpO_2^{2+}	1.8	2	Ce^{4+}	0.4	3
UO_2^{2+}	2.8	3	Th^{4+}	0.7	2
VO^{2+}	2.3	1		av 0.33 (±0.36)	
	av 2.18 (±0.66)				

[a] N is the number of experimental data used to estimate the "best value" of log K_q.

metal ions by using log K_q = 1.15. Very similar graphs are obtained for divalent ions, tetravalent ions, and oxycations. It will be seen that there is an isosbestic point at log K_{11} = −1.15. It is interesting that for bismuth(III) log K_{11} = −1.09 and according to Figure 9 all polynuclear bismuth(III) complexes should have approximately the same formation constant (≈0) regardless of their composition. Baes and Mesmer[1] have critically reviewed the history of studies of the hydrolysis behavior of bismuth(III). They quote log $K_{6,12}$ = −0.53 (in 1 M $NaClO_4$) for $Bi_6(OH)_{12}^{6+}$, although the correct formula for the "bismuthyl ion" is[25] probably $Bi_6O_4(OH)_4^{6+}$. Other polynuclear hydroxide complexes are probably present, but their formation constants are uncertain. Similarly, among tetravalent ions the isosbestic point occurs at log K_{11} = −0.3, and one therefore expects polynuclear hydroxide species of cerium(IV) with log K_{11} = 0.8 and zirconium(IV) with log K_{11} = 0.3 to have nearly the same formation constants.

M_2OH Complexes. As mentioned above, eq 7 does not work well for complexes of the type M_2OH because log K_q varies over too large a range. These complexes have therefore been omitted from Table III and Figure 8. Their log K_q values are as follows: Be_2OH^{3+}, 1.43; Cd_2OH^{3+}, 0.69; Co_2OH^{3+}, −1.55; Pb_2OH^{3+}, 1.35; Mn_2OH^{3+}, 0.03; Hg_2OH^{3+}, 0.07; Ni_2OH^{3+}, −0.84; Zn_2OH^{3+}, −0.04. An alternative is to use a least-squares treatment to find the best linear relation between log K_{11} and log K_{21}. The result is log K_{21} = 1.166 log K_{11} + 1.51 (±0.9; 0.972; 9).

Standard Free Energies of Formation of Polynuclear Complexes. If eq 7 is expressed in terms of free energies, one obtains

$$\Delta G_f^\circ\{M_x(OH)_y\} = y\Delta G_f^\circ\{MOH\} + (x-y)\Delta G_f^\circ\{M\} - 2.303RTy \log K_q \quad (9)$$

It is seen that a direct linear relation between the free energy of formation of a complex and $\Delta G_f^\circ\{MOH\}$ is not expected except in those cases where $x = y$. However, if one defines the function

$$P = y\Delta G_f^\circ\{MOH\} + (x-y)\Delta G_f^\circ\{M\} \quad (10)$$

then it is clear that a plot of $\Delta G_f^\circ\{M_x(OH)_y\}$ vs. P will be a straight line since variations in log K_q are so small that they do not change the intercept appreciably. One can also treat this relation somewhat differently by finding the best least-squares relation between $\Delta G_f^\circ\{M_x(OH)_y\}$ and P, but the improvement between experimental and calculated values of the free energies is marginal.

Structure Changes

Mononuclear hydroxy complexes of aluminum(III), cobalt(II), and probably several other metal ions undergo a structure change from octahedral to tetrahedral as one goes from the aquo ion to higher hydroxy complexes. From the visible absorption spectrum it is clear that Co^{2+}(aq) is octa-

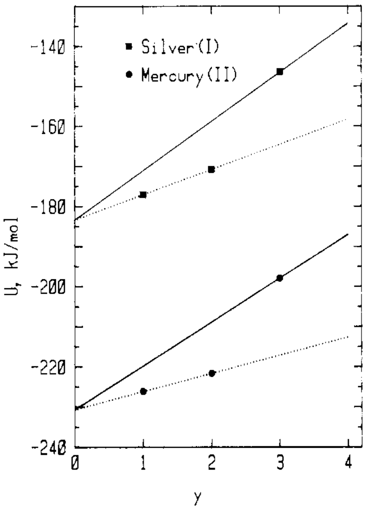

Figure 10. Plots of *U* vs. *y* for silver(I) and mercury(II) aquo and hydroxy complexes showing a discontinuity due to a structure change.

hedrally coordinated whereas in strong base the $Co(OH)_4^{2-}$ species has the intensely blue color characteristic of tetrahedral cobalt(II). Similarly, aqueous Al^{3+} is octahedrally coordinated[11,28,29] whereas $Al(OH)_4^-$ is tetrahedral.[29,30] It is therefore somewhat surprising that the graphs of free energy vs. the number of coordinated hydroxide ions in Figure 1, or still better the graphs of *U* vs. *y* in Figure 2, do not show any break or discontinuity that can be ascribed to a structure change. A possible explanation is that each species is actually present in both octahedral and tetrahedral forms that are in equilibrium with one another and the position of equilibrium simply shifts from predominantly octahedral for the aquo ions to predominantly tetrahedral for $Al(OH)_4^-$ and $Co(OH)_4^{2-}$. Presumably, the driving forces for the change in structure are (1) the increase in entropy due to the release of coordinated water molecules and (2) the increase in electrostatic repulsion between hydroxide ligands as the negative charge on the complex increases. Provided the equilibrium shifts gradually as the number of coordinated hydroxide ions increases, there will be a gradual change in the free energy rather than a discontinuity. In favor of this suggestion, Swift[31,32] has presented evidence both from NMR studies and from studies of the rate of exchange of coordinated water molecules that aqueous Co^{2+} and Zn^{2+} contain small amounts of tetrahedrally coordinated metal ions in equilibrium with the predominant octahedral species. As discussed below, there is also good evidence that $Ag^+(aq)$ is present in more than one structural form. On the other hand, the existence of $Al(OH)_5^{2-}$ is difficult to explain. Since $Al(OH)_4^-$ is tetrahedral, there must be a change in structure on going from four- to five-coordinated hydroxide ions, yet there is no obvious discontinuity in the free energies of formation. One might question the existence of $Al(OH)_5^{2-}$. Despite many studies of basic aluminum(III) solutions, this species has been proposed by only one research group.[33] In this work the temperature and ionic strength were apparently not controlled.

An obvious place to look for a structure change is between $Hg(OH)_2(aq)$ and $Hg(OH)_3^-$ or between $Ag(OH)_2^-$ and $Ag(OH)_3^{2-}$. Both of these metals are well-known for their tendency to form linear complexes. Figure 10 shows the graph of *U* vs. *y* for these two metal ions and the obvious "break" on going from two- to three-coordinated hydroxide ions. Fortunately, the structures of $Hg^{2+}(aq)$, $HgOH^+$, and $Hg(OH)_2(aq)$ have been investigated by X-ray scattering.[34-36] It was found that $Hg^{2+}(aq)$ is octahedrally coordinated by water molecules with an Hg–O bond length of 2.41 Å. There was no evidence for a linear $H_2O–Hg–OH_2^{2+}$ species. When the pH is raised to the region where first $HgOH^+$ and then $Hg(OH)_2(aq)$ predominate, "about two" Hg–O bonds are shortened to 2.0–2.1 Å and the remaining four are lengthened to 2.5 Å. No data were obtained in the $Hg(OH)_3^-$ region, but one may note that the slope of the solid line in Figure 10 is that expected for an octahedral or tetrahedral structure. That is, the slope is that predicted by the correlations between *B*, *C*, and electronegativity described above.

From the appearance of Figure 10, one would expect that silver(I) behaves in the same way as mercury(II). Information about the structure of $Ag^+(aq)$ is conflicting. Akitt[37] found the number of water molecules in the primary coordination sphere to be 0.6 on the average, but the assumptions involved in his calculations have been questioned by Brown and Symons,[38] who concluded that $Ag^+(aq)$ is probably not linear and that there are at least four water molecules in the first coordination sphere. In a later paper[39] these same workers suggested that there is a range of discrete Ag^+ solvates rather than a single preferred unit. Maeda et al.[40] studied aqueous $AgClO_4$

---

(11) Burgess, J. "Metal Ions in Solution"; Ellis Horwood Ltd. or Wiley: Chichester, England, 1978.

(12) Pourbaix, M. "Atlas of Electrochemical Equilibria in Aqueous Solution"; Franklin, J. A., Translator (Engl.); Pergamon Press: New York, 1966.

(13) Spivakovskii, V. B.; Moisa, L. *Russ. J. Inorg. Chem.* (*Engl.* Transl.) **1964**, *9*, 2287–2294.

(14) The formation constants for cadmium hydroxy complexes reported in ref 13 do not give a linear graph of *U* vs. *y*. There is a systematic curvature. However, the values recommended in ref 1 give a straight-line plot.

(15) Reference 7 gives $\Delta G_f°\{HCoO_2^-\}$ = –407.5 kJ/mol, which corresponds to $\Delta G_f°\{Co(OH)_3^-\}$ = –644.8 kJ/mol. This value must certainly be incorrect.

(16) Paulson, A. J.; Kester, D. R. *J. Solution Chem.* **1980**, *9*, 269–277.

(17) Reference 6 gives $\Delta G_f°\{Cu(OH)_2(aq)\}$ = –330.2 kJ/mol, which must be incorrect.

(18) Milburn, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 537–540.

(19) Reference 7 gives $\Delta G_f°\{Fe(OH)_2^+\}$ = –438.1 kJ/mol, which must be incorrect.

(20) According to Baes and Mesmer,[1] the value of log K_{13} for iron(III) is very uncertain. They give log $K_{13} < -12$. Other values can be calculated from measurements of the solubility of $Fe(OH)_3(s)$ or $FeO(OH)(c)$, but these measurements generally suffer from uncertainty about the exact nature of the solid phase. One can obtain values of log K_{13} from –6.9 to –13.0 depending on the free energy of formation one assumes for the solid. The most reliable value is probably the one obtained in this work from the empirical correlations.

(21) Reference 7 gives $\Delta G_f°\{PbOH^+\}$ = –226.4 kJ/mol, which must be incorrect.

(22) Aksel'rud, N. V. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 1067.

(23) Reference 22 gives $G_f°\{Pb(OH)_4^{2-}\}$ = –748.6 kJ/mol but does not state what value of $G_f°\{Pb^{2+}\}$ was used to make the calculation. It is therefore considered to be uncertain.

(24) In "dilute aqueous $HClO_4$".

(25) Sundvall, B. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 93–98.

(26) Throughout this paper equations resulting from linear regression analysis of the data are followed by three additional numbers in parentheses. They are respectively the standard deviation of the residuals, the correlation coefficient, and the number of data points included in the correlation.

(27) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; pp 162–164. Little, E. J.; Jones, M. M. *J. Chem. Educ.* **1960**, *37*, 231.

(28) Connick, R. E.; Fiat, D. N. *J. Chem. Phys.* **1963**, *39*, 1349.

(29) Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.

(30) Moolenaar, R. J.; Evans, J. C.; McKeever, L. D. *J. Phys. Chem.* **1970**, *74*, 3629.

(31) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *32*, 307.

(32) Swift, T. J. *Inorg. Chem.* **1964**, *3*, 526.

(33) Sullivan, J. H.; Singley, J. E. *J.—Am. Water Works Assoc.* **1968**, *60*, 1280–1287.

(34) Johansson, G. *Acta Chem. Scand.* **1971**, *25*, 2787.

(35) Johansson, G. *Acta Chem. Scand.* **1971**, *25*, 2799.

(36) Sandström, M.; Persson, I.; Ahrland, S. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 607.

(37) Akitt, J. W. *J. Chem. Soc., Dalton Trans.* **1974**, 175.

(38) Brown, R. D.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1976**, *426*–428.

(39) Brown, R. D.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans.* **1977**, *73*, 1490–1498.

and $AgNO_3$ solutions by X-ray scattering and, although the pertinent region of the radial distribution curve was somewhat obscured by other atom–atom distances, concluded that $Ag^+(aq)$ has two coordinated water molecules with Ag–O distances of 2.41 Å in $AgClO_4$ and 2.45 Å in $AgNO_3$ solutions. There is no information about the structures of hydrolyzed silver(I) species. As with mercury(II), the slope of the solid line in Figure 10 for silver(I) is that expected from the correlation between *B*, C, and electronegativity found for "normal" octahedral/tetrahedral complexes.

Thallium(III) might be expected to behave in the same way as mercury(II) and silver(I), but it does not. Instead, the $Tl(OH)_3(aq)$ species is reported to be much more stable than expected from the correlations found in this work, whereas $TlOH^{2+}$, $Tl(OH)_2^+$, and $Tl(OH)_4^-$ behave normally.

Tin(II), Beryllium(II), and Palladium(II)

In the correlation between *B* and electronegativity shown in Figure 4, it can be seen that beryllium(II), mercury(II), palladium(II), and tin(II) do not behave in the same fashion as other divalent metal ions.[41] All four are more acidic than one would expect on the basis of electronegativity. The reason for the high acidity of mercury(II) was shown above to be due to the unusual stability of "linear" $H_2O{-}Hg{-}OH^+$. The high acidity of beryllium(II) and palladium(II) is probably due to the small number of water molecules in the primary coordination sphere. In an octahedral complex there are twelve hydrogen atoms to help carry part of the positive charge. In tetrahedral $Be^{2+}(aq)$ and square-planar $Pd^{2+}(aq)$, however, there are only eight hydrogen atoms, so each hydrogen must carry a somewhat larger portion of the charge. The larger the relative positive charge on a hydrogen atom the more easily it ionizes.

In some of its crystalline compounds tin(II) is three-coordinated.[42a] For example, $SnCl_2(OH_2)$ and $SnCl_3^-$ have a trigonal-pyramidal structure with two unshared electrons at the apex. It is suggested that aqueous tin(II) has the same structure, and therefore, as in the cases of beryllium and palladium, the small number of hydrogen atoms available to help carry the positive charge leads to greater acidity. Johansson and Ohtaki[43] have studied the X-ray scattering of 3 M tin(II) solutions, both in acidic solution and after hydrolysis. They found that $Sn^{2+}(aq)$ has between two and three coordinated water molecules in the inner coordination sphere at 2.3 Å. There is a second peak in the radial distribution curve at 2.8 Å that may be due to a second group of more weakly bound water molecules. Upon hydrolysis, only minor changes were observed in the first hydration sphere. Also in support of the proposed structure of aqueous tin(II), note that even in the most basic solutions complexes with more than three hydroxide ions have not been detected.[44] However, discrete $Sn(OH)_6^{4-}$ ions occur[42b] in crystalline $K_4[Sn(OH)_6]$.

Conclusion

The results described above highlight two major deficiencies in the present state of knowledge about aqueous hydroxy complexes. First, it is apparent that there are still many hydroxide complexes, especially polynuclear complexes, that have not yet been detected. The correlations developed here should be of considerable help in deciding what species to look for and deciding in what pH region they might be found. Second, it appears that equilibria between different structural forms of the same species will turn out to be a rather widespread phenomenon among aqueous hydroxy complexes. For example, one would expect that the species $Al(OH)_2^+$ will be found to be present in a tetrahedral form and as octahedral cis and trans isomers. From the little evidence now available it appears that the free energy difference between the different structural forms is generally small.

---

(40) Maeda, M.; Maegawa, Y.; Yamaguchi, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2545–2550.

(41) From ref 1 log K_{11} for $PdOH^+$ = −2.3 (17 °C; 0.1 M $NaClO_4$). The correlations in this work predict log K_{11} = −7.9.

(42) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975: (a) p 937; (b) pp 524–525.

(43) Johansson, G.; Ohtaki, H. *Acta Chem. Scand.* **1973**, *27*, 643–660.

(44) Smirnova, V. A.; Kravtsov, V. I.; Illyuvieva, G. V. *Elektrokhimya* **1978**, *14*, 249–251.

Contribution from the Dipartimento di Chimica,
Università di Perugia, 06100 Perugia, Italy

Photostereochemistry of the *cis*-Dicyanotetraamminechromium(III) Ion

PIETRO RICCIERI and EDOARDO ZINATO*

Received July 16, 1982

Upon ligand field excitation in acid aqueous solution, *cis*-$Cr(NH_3)_4(CN)_2^+$ undergoes simultaneous aquation of NH_3 and CN^-, the former being predominant over the latter by 1 order of magnitude. The quantum yields and their ratios are wavelength dependent. The product of NH_3 release, $Cr(NH_3)_3(H_2O)(CN)_2^+$, was isolated by ion-exchange chromatography and demonstrated to consist of a mixture of 1,2-CN-3-H_2O and 1,2-CN-6-H_2O isomers, the proportion of which varies from ca. 2:1 to ca. 1:1 on passing from the first to the second ligand field band. The major reaction is that expected for the lowest excited quartet, ^4E in D_{4h} approximation, by various photolysis models. The product configurations are also consistent with prevalent ^4E reaction, in terms of currently proposed mechanisms, either dissociative (symmetry restricted) or associative (edge displacement). The complexity of the system does not allow a satisfactory interpretation of the wavelength dependence.

Introduction

The stereochemistry of photosubstitutions of chromium(III) acidoamines upon ligand field (LF) excitation continues to draw both experimental[1–5] and theoretical[6,7] attention. The systems studied in this regard have been mostly of the types CrN_5X^{z+} and *trans*-CrN_4XY^{z+} (N = NH_3 or amines; X, Y = anionic groups of H_2O). Despite this interest, the photochemistry of *cis*-CrN_4XY^{z+} ions has been investigated partially

---

(1) Zinato, E. in "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 4, p 143.

(2) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.

(3) Zinato, E.; Riccieri, P.; Prelati, M. *Inorg. Chem.* **1981**, *20*, 1432.

(4) Kirk, A. D.; Frederick, L. A. *Inorg. Chem.* **1981**, *20*, 60.

(5) Cimolino, M. C.; Linck, R. G. *Inorg. Chem.* **1981**, *20*, 3499.

(6) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475.

(7) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1979**, *18*, 3475.

0020-1669/83/1322-2305$01.50/0