studying manganese oxide solubility because $MnCl_2$–NaCl (830 °C) and $MnSO_4$–Na_2SO_4 (930 °C) solutions were found to be unstable. We have therefore used a potentiometric technique in which the appropriate oxide and molten salt are equilibrated, the oxide activity is measured potentiometrically, and the metal is determined from quenched melt samples by standard analytical techniques. A similar technique was used by Rapp and co-workers[8,9] to measure the solubility of Al_2O_3, Cr_2O_3, NiO, and CoO in molten Na_2SO_4.

Experimental Section

Stability Range of Manganese Oxides. An important question to be addressed is the stoichiometry of the oxide whose solubility is to be measured. According to the most recent critical review[10] of thermodynamic data for manganese compounds, Mn_2O_3 is the stable oxide at 0.2 atm of O_2 from 477 to 1027 °C. However, a more recent experimental study of manganese oxide equilibria[11] shows that Mn_2O_3 transforms to Mn_3O_4 at 879 °C in air. We have confirmed this latter result by heating Mn_2O_3 thermogravimetrically (Mettler thermogravimetry apparatus), observing the expected weight loss, cooling the oxide under vacuum, and identifying the resulting Mn_3O_4 by its X-ray powder pattern. Therefore, the oxide whose solubility is measured in NaCl at 830 °C is Mn_2O_3 and in Na_2SO_4 at 930 °C is Mn_3O_4.

Stability of Manganese Melts. The 20 wt % melts of $MnCl_2$ in NaCl and $MnSO_4$ in Na_2SO_4 were prepared from high-purity anhydrous manganese salts (Alfa Inorganics) and vacuum-dried (450 °C) alkali-metal salts in a glovebox (Vacuum Atmospheres Corp.) filled with a dry and CO_2-free 20% O_2-in-helium mixture. The respective mixtures were heated in porcelain crucibles for 30 h, and the remaining material was then analyzed by X-ray diffraction. In the chloride system only Mn_2O_3 was observed; in the sulfate system, although some Mn_2SO_4–Na_2SO_4 melt remained, oxide was found at the upper edge of the crucible. Since the melts were unstable, coulometric titrations, as previously carried out for the nickel, cobalt, and yttrium systems, could not be performed.

Solubility of Manganese Oxides. In a glovebox containing 20% O_2, samples of Mn_2O_3 in NaCl and Mn_3O_4 in Na_2SO_4 were equilibrated in high-purity (99.8%) alumina crucibles. The oxide activity was monitored by using the cell

Ag|melt + AgCl or Ag_2SO_4 (10m/o)|Na^+ mullite|NaCl or
Na_2SO_4 + Na_2O|stab. ZrO_2|O_2|Pt (1)

The details and interpretation of this measurement were fully discussed elsewhere.[7] After 20 h the EMF became constant, indicating that equilibrium had been achieved. The melt was then sampled at intervals of ~3 h by dipping a cold, high-purity alumina rod into the melt and quickly withdrawing it. The adhering frozen melt was analyzed by atomic absorption (Perkin-Elmer Model 360) and atomic emission (Spectrospan III D.C. argon plasma spectrometer). Results of the two methods were in good agreement.

Results and Discussion

Based on the known chemistry of manganese compounds,[12] the solution reactions are

$$Mn_2O_3(s) + 4NaCl(l) = 2MnCl_2(sol) + 2Na_2O(sol) + {}^1/_2O_2(g) \quad (2)$$

$$Mn_3O_4(s) + 3Na_2SO_4(l) = 3MnSO_4(sol) + 3Na_2O(sol) + {}^1/_2O_2(g) \quad (3)$$

Note that in both reactions the solution reaction involves a valence change for manganese and that the solubility depends on the O_2 pressure.

Table I

	$G°_f$, kcal mol^{-1}		
	1100 K	1200 K	ref
NaCl(l)	−74.268		13
Na_2SO_4(l)		−212.612	13
Na_2O(l)	−61.126	−58.089	13
Mn_2O_3(s)	−160.75		10
Mn_3O_4(s)		−230.4	10
$MnCl_2$(l)	−82.7		10
$MnSO_4$(l)		−145.3	10

Since the EMF of cell is directly related to the activity of Na_2O, and manganese is expressed as a concentration, it was necessary to convert the oxide activity to concentration (mole fraction scale). The required activity coefficients, 1.7×10^{-4} in NaCl and 4.5×10^{-4} in Na_2SO_4 (on a mole fraction scale) were measured previously.[4] For reaction 2 the experimentally determined equilibrium constant is

$$K_x = X_{MnCl_2}{}^2 X_{Na_2O}{}^2 P_{O_2}{}^{1/2} = (6.6 \pm 2.2) \times 10^{-23}$$

and for reaction 3

$$K_x = X_{MnSO_4}{}^3 X_{Na_2O}{}^3 P_{O_2}{}^{1/2} = (9.5 \pm 2.5) \times 10^{-30}$$

assuming $X_{NaCl} = X_{Na_2SO_4} = 1$ in these dilute melts. The values of K_x above are average values with the uncertainty given as a standard deviation. The thermodynamic equilibrium constants of reactions 2 and 3 can be calculated from the Gibbs energies of formation given in Table I. From these data, $K_2 = 1.56 \times 10^{-34}$, and $K_3 = 2.86 \times 10^{-48}$. A comparison of the thermodynamic constants with the respective K_x's gives the activity coefficient of the manganese salts: $K_2/K_{x_2} = (\delta_{MnCl_2}\delta_{Na_2O})^2$, $K_3/K_{x_3} = (\delta_{MnSO_4}\delta_{Na_2O})^3$. Since δ_{Na_2O} is known, this relationship gives $\delta_{MnCl_2} = 9.0 \times 10^{-3}$ in NaCl and $\delta_{MnSO_4} = 1.5 \times 10^{-3}$ in Na_2SO_4. These values are similar to previously reported activity coefficients of $NiCl_2$ and $CoCl_2$ in NaCl and $NiSO_4$ and $CoSO_4$ in Na_2SO_4.[3] A comparison of the solubilities of the manganese oxides with those of the oxides of nickel,[4] cobalt,[4] and yttrium[5] shows that under an ambient oxygen pressure they are all equal to within 1 order of magnitude. Any marked differences exhibited by the oxides in conferring corrosion resistance is therefore likely to involve factors other than solubility.

Registry No. Mn_2O_3, 1317-34-6; Mn_3O_4, 1317-35-7; NaCl, 7647-14-5; Na_2SO_4, 7757-82-6.

---

(8) Stroud, W. P.; Rapp, R. A. In "High Temperature Metal Halide Chemistry"; Hildenbrand, D. L., Cubicciotti, D. D., Eds.; The Electrochemical Society: Princeton, NJ, 1978; p 547.
(9) Gupta, D. K.; Rapp, R. A. *J. Electrochem. Soc.* **1980**, *127*, 2194.
(10) Mah, A. D. *U.S., Rep. Invest.—Bur. Mines* **1960**, 5600.
(11) Otto, E. M. *J. Electrochem. Soc.* **1964**, *111*, 88.
(12) Stern, K. H.; Weise, E. L. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1966**, *NSRDS-NBS 7*.
(13) "JANAF Thermochemical Tables", 2nd ed.; U.S. National Bureau of Standards: Washington, D.C., 1971; NSRDS-NBS 37.

Contribution from the Departments of Chemistry,
University of Northern Iowa, Cedar Falls, Iowa 50614,
and Northern Illinois University, DeKalb, Illinois 60115

Tetraamine Complexes of Chromium(III). 4. Kinetics of the Aquation of the *cis*-Aquabis(ethylenediamine)iodochromium(III) Cation

James C. Chang*[1a] and Joe W. Vaughn*[1b]

Received August 17, 1981

Although the kinetics of the aquation of the *cis*-dichloro-, *cis*-dibromo-, *cis*-aquachloro-, and *cis*-aquabromobis(ethylenediamine)chromium(III) cations have been extensively studied,[2-7] there is no indication of similar studies of the

---

(1) (a) University of Northern Iowa. (b) Northern Illinois University.
(2) Selbin, J.; Bailar, J. C. *J. Am. Chem. Soc.* **1957**, *79*, 4285.

corresponding iodo complexes. In 1976 Vaughn and Yoeman[8] reported the first apparently successful preparation and isolation of the corresponding iodo complexes. In this paper we report the aquation kinetics of the *cis*-aquabis(ethylenediamine)iodochromium(III) cation.

Experimental Section

cis-Aquabis(ethylenediamine)iodochromium(III) iodide hydrate was prepared by the method of Vaughn and Yoeman.[8] Anal. Calcd for $[CrI(H_2O)(C_2H_8N_2)_2]I_2{\cdot}H_2O$: Cr, 8.83; C, 8.16; N, 9.51; H, 3.42; total I, 64.64; ionic I, 43.09. Found: Cr, 8.53; C, 8.11; N, 9.20; H, 3.41; total I, 64.3; ionic I, 43.5. *cis*-Diaquabis(ethylenediamine)chromium(III) cation was isolated by ion-exchange chromatography from aquated solutions of *cis*-$[CrI(H_2O)(en)_2]I_2{\cdot}H_2O$ on columns of Sephadex SP-C25-120 at ca. 2 °C, with use of the technique previously reported.[9] In this work the eluting agent was $HClO_4$ instead of HNO_3.

Chromium was determined by the alkaline–peroxide method,[10] and iodide was determined by standard iodometric titration.[11] Total iodide was determined after the compound was burned in a Schöniger flask, and ionic iodide was determined by chromatographing a solution of the compound as previously reported.[9] Carbon, nitrogen, and hydrogen were determined by microanalysis.

The rate of aquation was measured spectrophotometrically by following the decrease in the absorbance at 540 nm, with a procedure previously reported.[9]

Results and Discussion

Since the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation aquates at a rapid rate ($t_{1/2}$ = *ca.* 10 min at 25 °C), its visible absorption spectrum was established by measuring a series of spectra in 0.001 M $HClO_4$ ($\mu = 0.10$ ($NaClO_4$)) at 10 °C and extrapolating to zero time. The spectrum obtained resembled somewhat that of the *cis*-$[CrI(H_2O)(NH_3)_4]^{2+}$ cation.[12] The absorption maxima and minima above 400 nm, listed in λ in nm (ϵ in L mol^{-1} cm^{-1}), are as follows: *cis*-$[CrI(H_2O)(NH_3)_4]^{2+}$, 446 (18.0), 471 (34.0), 483 (30.0), 546 (62.3); *cis*-$[CrI(H_2O)(en)_2]^{2+}$, 444 (27.9), 482 (65.2), 489 (63.5), 534 (94.4). Below 400 nm the spectrum exhibited very high absorptivities because of the presence of coordinated iodide, and the UV spectrum was not determined in this work.

When repeated spectral scans of aqueous $HClO_4$ solutions of *cis*-$[CrI(H_2O)(en)_2]^{2+}$ were superimposed upon one another, two isobestic points were observed. These isobestic points are the same, within experimental error, as the intersecting points of the spectra of *cis*-$[CrI(H_2O)(en)_2]^{2+}$ and *cis*-$[Cr(H_2O)_2(en)_2]^{3+}$ cations. The observed and calculated isobestic points are as follows: observed 440 (30.5), 487 (62.7); calculated 400 (30.2), 487 (63.3).

Although the spectral changes suggested that the aquation product was the *cis*-$[Cr(H_2O)_2(en)_2]^{3+}$ cation, the product itself was further isolated and characterized by ion-exchange chromatography of partially aquated solutions of *cis*-$[CrI(H_2O)(en)_2]^{2+}$ on columns of Sephadex SP-C25-120. After the ionic iodide was rinsed out, only two colored bands could be obtained from the material adsorbed on the column. A purple band was eluted by 0.1 M $HClO_4$ and was identified as the unreacted *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation. An orange band was eluted by 0.3 M $HClO_4$, and its visible spectrum was identical with that reported for the *cis*-$[Cr(H_2O)_2(en)_2]^{3+}$ cation.[13–15] No other colored complex was isolated from the chromatography column. If a hydroxo complex resulted from base hydrolysis, it could not be isolated because the eluting agent was acid. However, the reactions were studied mostly at acid concentrations greater than 0.1 M; therefore base hydrolysis, although suspected (vide infra), could not be important enough to interfere with the study of the aquation kinetics. The chromatographic studies coupled with the isobestic points determinations strongly suggested that the reaction path is not complicated by simultaneous Cr–N bond rupture to produce a partially unwrapped species.

Table I. Rate Constants for the Aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ Cation

t, °C	$[H^+]$, M	μ, M	10^3k, s^{-1} [a]
30	0.01	1.0	2.35 ± 0.02[b]
25	0.001	1.0	2.46 ± 0.01[b]
	0.01	0.10	1.72 ± 0.01[c]
	0.01	0.50	1.70 ± 0.01[b]
	0.01	1.0	1.46 ± 0.01[b]
	0.10	0.10	1.48 ± 0.01[c]
	0.10	0.50	1.45 ± 0.01[c]
	0.10	1.0	1.42 ± 0.01[d]
	0.20	1.0	1.40 ± 0.01[c]
	0.30	1.0	1.40 ± 0.01[c]
	0.40	1.0	1.35 ± 0.01[c]
	0.50	1.0	1.35 ± 0.01[c]
	0.80	1.0	1.35 ± 0.01[c]
	1.0	1.0	1.30 ± 0.01[e]
20	0.10	0.10	0.854 ± 0.002[c]
	0.10	1.0	0.805 ± 0.002[c]
	1.0	1.0	0.773 ± 0.006[c]
15.5	0.10	0.10	0.490 ± 0.001[c]
	0.10	1.0	0.474 ± 0.001[c]
	1.0	1.0	0.420 ± 0.008[c]
15	0.01	1.0	0.403 ± 0.003[b]
10	0.01	1.0	0.222 ± 0.002[b]
	0.10	0.10	0.218 ± 0.001[c]
	0.10	1.0	0.216 ± 0.001[c]
	1.0	1.0	0.193 ± 0.001[c]

[a] Obtained from least-squares analyses; errors given are statistical standard deviations. [b] $C_0 = (1.08\text{–}1.14) \times 10^{-2}$ M. [c] $C_0 = (1.30\text{–}1.35) \times 10^{-3}$ M. [d] $C_0 = (0.133\text{–}1.15) \times 10^{-2}$ M. [e] $C_0 = (1.30\text{–}6.80) \times 10^{-3}$ M.

The rates of aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation were followed by noting the change in the absorbance at 540 nm, and the rate constants were evaluated from the slopes of the pseudo-first-order rate plots of ln ($A_t - A_\infty$) vs. time. These rate constants are summarized in Table I. Most of these values are averages of rate constants of two or more runs under the same conditions but with complex concentrations varying by factors from 5 to 8.5. The rate constants found, with different complex concentrations under the same conditions, were the same within experimental error, except in 0.001 M $HClO_4$ (vide infra).

From the data in Table I, it can be seen that the rate constant increases with decreasing acid concentration but becomes essentially constant at acid concentrations greater than 0.4 M. There is but a slight increase in the rate constant when the acid concentration is decreased to 0.1 M, but the rate constant in 0.001 M $HClO_4$ is almost twice that in 1.0 M $HClO_4$. A similar variation of rate constant with acid concentration was also observed in the aquation of the *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ cation,[16] but the variation was not as great as that found for the aquation of *cis*-$[CrI(H_2O)(en)_2]^{2+}$. For

---

(3) MacDonald, D. J.; Garner, C. S. *J. Am. Chem. Soc.* **1961**, *83*, 4152.
(4) MacDonald, D. J.; Garner, C. S. *Inorg. Chem.* **1962**, *1*, 20.
(5) Quinn, L. P.; Garner, C. S. *Inorg. Chem.* **1964**, *3*, 1348.
(6) Bratushko, Yu. I.; Nazarenko, Yu. P. *Zh. Neorg. Khim.* **1967**, *12*, 2122.
(7) Maes, N. A.; Nozari, M. S.; McLean, J. A., Jr. *Inorg. Chem.* **1973**, *12*, 750.
(8) Vaughn, J. W.; Yoeman, A. M. *Inorg. Chem.* **1976**, *15*, 2320.
(9) Malek, D.; Chang, J. C. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1313.
(10) Chang, J. C. *J. Inorg. Nucl. Chem.* **1968**, *30*, 945.
(11) Ingram, G. "Method of Organic Elemental Microanalysis"; Chapman and Hall: London, 1962; pp 204–206.
(12) Hoppenjans, D. W.; Gordon, G.; Hunt, J. B. *Inorg. Chem.* **1971**, *10*, 754.
(13) Schläfer, H. L.; Kling, O. *Z. Anorg. Allg. Chem.* **1956**, *287*, 296.
(14) Schläfer, H. L.; Kollrack, R. *Z. Phys. Chem.* (*Wiesbaden*) **1958**, *18*, 348.
(15) Woldbye, F. *Acta Chem. Scand.* **1958**, *12*, 1079.
(16) Chang, J. C. *Inorg. Chem.* **1982**, *21*, 837.

Table II. Effect of Complex Concentration on the Rate Constant of the Aquation of *cis*-$[CrI(H_2O)(en)_2]^{2+}$ in 0.001 M $HClO_4$ ($\mu = 1.0$, $NaClO_4$)

C_0, M	10^3k, s^{-1} [a]	C_0, M	10^3k, s^{-1} [a]
0.021 5	2.42 ± 0.02	0.005 00	2.71 ± 0.03
0.011 4	2.46 ± 0.01	0.001 36	3.52 ± 0.04
0.005 20	2.74 ± 0.03	0.001 33	3.57 ± 0.03

[a] Obtained from least-squares analyses; errors given are statistical standard deviations.

Table III. Activation Parameters for the Aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ Cation

$[H^+]$, M	μ, M	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}
0.01	1.0	83.0 ± 1.2[a]	−21.5 ± 2.1[a]
0.10	0.10	87.1 ± 2.3	−6.8 ± 7.8
0.10	1.0	85.6 ± 1.7	−12.2 ± 5.7
1.0	1.0	87.7 ± 2.3	−5.5 ± 7.8

[a] The error is the standard deviation evaluated from the least-squares analysis.

the aquation of the bromo complex, the rate constants in 0.1 M $HClO_4$ were 7–9% higher than those in 1 M $HClO_4$. Aquation of the iodo complex, on the other hand, gave rate constants in 0.1 M $HClO_4$ 9–12% higher than those in 1 M $HClO_4$.

Plots of k_{obsd} vs. $[H^+]$ are parabolic in nature with an essentially limiting value reached for k_{obsd} above a $[H^+]$ of 0.4 M. The nature of this plot suggests that the acid hydrolysis is accompanied by another competing side reaction. The higher rate constants in lower acid concentrations may be attributed to two competing side reactions: (1) the direct base hydrolysis of the *cis*-$[CrX(H_2O)(en)_2]^{2+}$ cation (X = Br^- or I^-)

$$cis\text{-}[CrX(H_2O)(en)_2]^{2+} + OH^- \rightarrow cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + X^- \quad (1)$$

(2) the aquation of the hydroxo complex in equilibrium with the aqua complex

$$cis\text{-}[CrX(H_2O)(en)_2]^{2+} + H_2O \rightleftharpoons cis\text{-}[CrX(OH)(en)_2]^{+} + H_3O^+ \quad (2)$$

$$cis\text{-}[CrX(OH)(en)_2]^{+} + H_2O \rightarrow cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + X^- \quad (3)$$

$$cis\text{-}[Cr(OH)(H_2O)(en)_2]^{2+} + H_2O \rightarrow cis\text{-}[Cr(H_2O)_2(en)_2]^{3+} + OH^- \quad (4)$$

or some combination of these schemes. Of the two possible sequences, base catalysis would appear to be more plausible for the following reasons.

Base hydrolysis (eq 1) of Co(III) complexes can occur even in weakly acidic solutions; but for Cr(III) complexes direct base hydrolysis is normally important only in basic solutions.[17] However, base catalysis may occur for Cr(III) complexes if the substrate has at least one aqua ligand whose acidity is greater than the amine ligand. In the case of *cis*-$[Cr(H_2O)(en)_2]^{3+}$ the pK_a values for the loss of the protons from the coordinated water molecules are 4.8 and 7.2,[15] respectively, while the corresponding trans complex has pK_a values of 4.1 and 7.5.[15] The pK_a values for the loss of a proton from the amine ligand is not known; but, since the acidities of Co(III) and Cr(III) complexes are similar,[18] it is not unreasonable to expect the pK_a values for the Cr(III) complex to be >14. Thus the relative acidities of the ligands are such that base catalysis could easily occur.

The decrease in the rate constant with increasing ionic strength is similar to that observed by Rogers and Staples[19] in their study of the hydrolysis of $[CrCl(RNH_2)_5]^{2+}$ complexes over the $[H^+]$ range 0.005–1 M $HClO_4$ and is consistent with base catalysis.

In 0.001 M $HClO_4$ ($\mu = 1.0$), the rate constants were observed to increase with decreasing complex concentration as shown by the data in Table II. Thus in 0.001 M $HClO_4$ and perhaps even at acid concentrations less than 0.1 M, the rate law is given as eq 5, which yields $k_1 \approx 1.65 \times 10^{-6}$ mol L^{-1}

$$-\frac{d[\text{complex}]}{dt} = k_{obsd}[\text{complex}] = \left(\frac{k_1}{[\text{complex}]} + k_2\right)[\text{complex}] \quad (5)$$

s^{-1} and $k_2 \approx 2.35 \times 10^{-3}$ s^{-1}. It would appear that k_2 represents the direct aquation of the complex and that k_1 is related to the base-catalyzed side reaction at low acid concentrations. Thus at acid concentrations which do not favor base catalysis, k_1 decreases rapidly and direct aquation is the observed reaction. The value of 2.35×10^{-3} s^{-1} for k_2 in 0.001 M $HClO_4$ is larger than the limiting value of k_2; thus it would appear that there is a slight contribution to k_2 via a yet undetermined pathway at low acid concentrations.

The activation parameters for the aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation were calculated from rate constants at four different temperatures, and the values are listed in Table III. Within experimental error, the enthalpies of activation in 0.10 and 1.0 M $HClO_4$ are the same. The lower value of the enthalpy of activation in 0.01 M $HClO_4$ may be attributed to contributions by base catalysis.

Acknowledgment. J.C.C. wishes to thank the Committee on Research of the University of Northern Iowa for the partial support of this work and Miss Kimberly Henkle for her assistance. J.W.V. wishes to thank Mr. Thomas Zupancic for his assistance.

Registry No. *cis*-$[CrI(H_2O)(en)_2]^{2+}$, 81097-63-4.

---

[17] Garner, C. S.; House, D. A. in "Transition Metal Chemistry"; Carlin, R. L., Ed.; Marcel Dekker: New York, 1970; Vol. 6, p 211.

[18] Garner, C. S.; House, D. A. *Ibid.*, p 177.

[19] Rogers, G. A.; Staples, P. J. *J. Chem. Soc.* **1965**, 6834.

Contribution from the Department of Chemistry,
Indiana-Purdue University at Fort Wayne,
Fort Wayne, Indiana 46805

The Trichlorocuprate(I) Ion in Aqueous Solution. Dependence of CTTS Absorption Band and Formation Constant on Temperature

C. R. Davis and K. L. Stevenson*[1]

Received October 20, 1981

In our studies of the photooxidation of chloro complexes of copper(I) in aqueous solution,[2-5] we concluded that the initial step in such a reaction is the absorption of a photon in a charge-transfer-to-solvent (CTTS) transition in the tri-

---

[1] To whom correspondence should be addressed.

[2] K. L. Stevenson and D. D. Davis, *Inorg. Nucl. Chem. Lett.*, **12**, 905 (1976).

[3] D. D. Davis, G. K. King, K. L. Stevenson, E. R. Birnbaum, and J. H. Hageman, *J. Solid State Chem.*, **22**, 63 (1977).

[4] D. D. Davis, K. L. Stevenson, and C. R. Davis, *J. Am. Chem. Soc.*, **100**, 5344 (1978).

[5] K. L. Stevenson, D. M. Kaehr, D. D. Davis, and C. R. Davis, *Inorg. Chem.*, **19**, 781 (1980).