

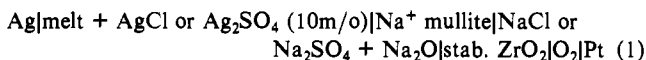
studying manganese oxide solubility because MnCl_2 - NaCl (830 °C) and MnSO_4 - Na_2SO_4 (930 °C) solutions were found to be unstable. We have therefore used a potentiometric technique in which the appropriate oxide and molten salt are equilibrated, the oxide activity is measured potentiometrically, 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 review¹⁰ 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 equilibria¹¹ 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.

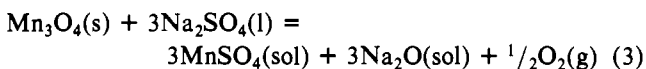
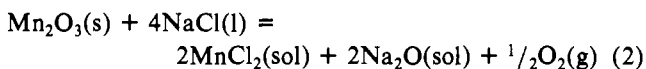
Solubility of Manganese Oxides. In a glovebox containing 20% O_2 , samples of Mn_2O_3 in NaCl and Mn_3O_4 in Na_2SO_4 were equilibrated in high-purity (99.8%) alumina crucibles. The oxide activity was monitored by using the cell



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



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

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

Table I

	G°_f , kcal mol ⁻¹		ref
	1100 K	1200 K	
$\text{NaCl}(\text{l})$	-74.268		13
$\text{Na}_2\text{SO}_4(\text{l})$		-212.612	13
$\text{Na}_2\text{O}(\text{l})$	-61.126	-58.089	13
$\text{Mn}_2\text{O}_3(\text{s})$	-160.75		10
$\text{Mn}_3\text{O}_4(\text{s})$		-230.4	10
$\text{MnCl}_2(\text{l})$	-82.7		10
$\text{MnSO}_4(\text{l})$		-145.3	10

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

$$K_x = X_{\text{MnCl}_2}^2 X_{\text{Na}_2\text{O}}^2 P_{\text{O}_2}^{1/2} = (6.6 \pm 2.2) \times 10^{-23}$$

and for reaction 3

$$K_x = X_{\text{MnSO}_4}^3 X_{\text{Na}_2\text{O}}^3 P_{\text{O}_2}^{1/2} = (9.5 \pm 2.5) \times 10^{-30}$$

assuming $X_{\text{NaCl}} = X_{\text{Na}_2\text{SO}_4} = 1$ 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: $K_2/K_x = (\delta_{\text{MnCl}_2} \delta_{\text{Na}_2\text{O}})^2$, $K_3/K_x = (\delta_{\text{MnSO}_4} \delta_{\text{Na}_2\text{O}})^3$. Since $\delta_{\text{Na}_2\text{O}}$ is known, this relationship gives $\delta_{\text{MnCl}_2} = 9.0 \times 10^{-3}$ in NaCl and $\delta_{\text{MnSO}_4} = 1.5 \times 10^{-3}$ 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 yttrium⁵ 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.

(13) "JANAF Thermochemical Tables", 2nd ed.; U.S. National Bureau of Standards: Washington, D.C., 1971; NSRDS-NBS 37.

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

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Although the kinetics of the aqueation of the *cis*-dichloro-, *cis*-dibromo-, *cis*-aquadichloro-, and *cis*-aquadibromobis(ethylenediamine)chromium(III) cations have been extensively studied,²⁻⁷ there is no indication of similar studies of the

(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.

(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 Yoeman⁸ reported the first apparently successful preparation and isolation of the corresponding iodo complexes. In this paper we report the aquation kinetics of the *cis*-aquadis(ethylenediamine)iodochromium(III) cation.

Experimental Section

cis-Aquadis(ethylenediamine)iodochromium(III) iodide hydrate was prepared by the method of Vaughn and Yoeman.⁸ Anal. Calcd for $[\text{Cr}(\text{H}_2\text{O})(\text{C}_2\text{H}_8\text{N}_2)_2\text{I}_2 \cdot \text{H}_2\text{O}]$: 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*-Diaquadis(ethylenediamine)-chromium(III) cation was isolated by ion-exchange chromatography from aquated solutions of *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+} \cdot \text{H}_2\text{O}$ 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*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cation aquates at a rapid rate ($t_{1/2} = \text{ca. } 10 \text{ min}$ 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*- $[\text{CrI}(\text{H}_2\text{O})(\text{NH}_3)_4]^{2+}$ cation.¹² The absorption maxima and minima above 400 nm, listed in λ in nm (ϵ in $\text{L mol}^{-1} \text{cm}^{-1}$), are as follows: *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{NH}_3)_4]^{2+}$, 446 (18.0), 471 (34.0), 483 (30.0), 546 (62.3); *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$, 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*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ 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*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ and *cis*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ 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*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ cation, the product itself was further isolated and characterized by ion-exchange chromatography of partially aquated solutions of *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ 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*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cation. An orange band was eluted by 0.3 M HClO_4 , and its visible spectrum was

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

$t, ^\circ\text{C}$	$[\text{H}^+], \text{M}$	μ, M	$10^3 k, \text{s}^{-1} \text{ }^a$	
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	
20	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	
	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
0.01		1.0	0.222 ± 0.002^b	
10	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 $C_0 = (1.08-1.14) \times 10^{-3} \text{ M}$. ^c $C_0 = (1.30-1.35) \times 10^{-3} \text{ M}$. ^d $C_0 = (0.133-1.15) \times 10^{-2} \text{ M}$. ^e $C_0 = (1.30-6.80) \times 10^{-3} \text{ M}$.

identical with that reported for the *cis*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$ 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.

The rates of aquation of the *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ 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 $\ln(A - A_\infty)$ 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*- $[\text{CrBr}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cation,¹⁶ but the variation was not as great as that found for the aquation of *cis*- $[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$. 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.

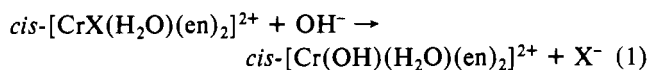
Table II. Effect of Complex Concentration on the Rate Constant of the Aquation of $cis\text{-}[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ in 0.001 M HClO_4 ($\mu = 1.0$, NaClO_4)

C_0 , M	$10^3 k$, s^{-1} ^a	C_0 , M	$10^3 k$, s^{-1} ^a
0.0215	2.42 ± 0.02	0.00500	2.71 ± 0.03
0.0114	2.46 ± 0.01	0.00136	3.52 ± 0.04
0.00520	2.74 ± 0.03	0.00133	3.57 ± 0.03

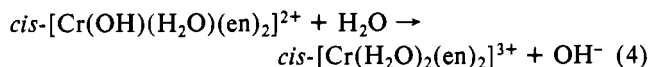
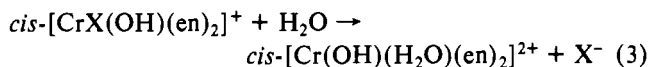
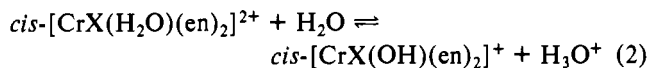
^a Obtained from least-squares analyses; errors given are statistical standard deviations.

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. $[\text{H}^+]$ are parabolic in nature with an essentially limiting value reached for k_{obsd} above a $[\text{H}^+]$ 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 $cis\text{-}[\text{CrX}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cation ($\text{X} = \text{Br}^-$ or I^-)



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



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 $cis\text{-}[\text{Cr}(\text{H}_2\text{O})(\text{en})_2]^{3+}$ the $\text{p}K_a$ 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 $\text{p}K_a$ values of 4.1 and 7.5.¹⁵ The $\text{p}K_a$ 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 $\text{p}K_a$ 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 Staples¹⁹ in their study of the hydrolysis of $[\text{CrCl}(\text{RNH}_2)_5]^{2+}$ complexes over the $[\text{H}^+]$ 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

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

$[\text{H}^+]$, M	μ , M	ΔH^\ddagger , kJ mol^{-1}	ΔS^\ddagger , $\text{J K}^{-1} \text{mol}^{-1}$
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.

perhaps even at acid concentrations less than 0.1 M, the rate law is given as eq 5, which yields $k_1 \approx 1.65 \times 10^{-6} \text{ mol L}^{-1}$

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

s^{-1} and $k_2 \approx 2.35 \times 10^{-3} \text{ s}^{-1}$. 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 $2.35 \times 10^{-3} \text{ s}^{-1}$ 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 $cis\text{-}[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ 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.

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Registry No. $cis\text{-}[\text{CrI}(\text{H}_2\text{O})(\text{en})_2]^{2+}$, 81097-63-4.

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

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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).

(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.