these asymmetrical niobium and tantalum mixed peroxides. This information can lead to a better understanding of the stabilization displayed by additional oxygen or nitrogen chelates, reflected in chemical properties of these complexes.

Potentiometric Studies on Tetrahalonickelate(II) Ions in Molten Dimethyl Sulfone[1a,b]

By C. H. LIU,[1c] L. NEWMAN,[1d] and J. HASSON[1d]

The 4:1 halide–nickel(II) ratio in and the mononuclear nature of the tetrahalonickelate(II) ions in dimethyl sulfone at 125° were demonstrated potentiometrically. Amalgamated and pure nickel coils served as the indicator electrodes while the silver(I)–silver system provided the reference potential. The formation constants of the chloride, bromide, and iodide complexes were measured; the stability followed the order Br > Cl > I. The application of the information obtained in this solvent to molten halide salt systems was discussed.

Crystalline tetrahalonickelate(II) salts with large organic cations are well known.[2–4] The solution spectra of nickel(II) in some molten halides[5,6] and organic solvents with added alkali halides[3] were reported to be those of essentially tetrahedral complexes. In a recent publication,[7] the spectra of the halide complexes of nickel(II) in molten dimethyl sulfone at 125° were measured and shown to be virtually identical with those of nickel(II) in molten substituted ammonium, phosphonium, and arsonium halides. Ligand field interpretation of the spectra indicated that these complexes were tetrahedral in structure. Since the oxygen atoms of the solvent dimethyl sulfone molecules possess only weak coordinating capacity, they are easily and completely replaced from the coordination sphere of dissolved transition metal ions when an excess of alkali halides is added. Thus, dimethyl sulfone can be considered as "inert" diluent in these cases. Its use as solvent allows the study of the halide concentration dependence of the transition metal ion–halide interaction and should be of great value in clarifying the chemistry of these metal ions in molten halides. In the present work, the compositions and the over-all formation constants of the nickel(II)–halide complexes in molten dimethyl sulfone at 125° were determined potentiometrically. Lithium perchlorate at a concentration of 2 M was used as inert electrolyte.

There was no detectable interaction between perchlorate and the solvated nickel(II) ion. A silver(I)–silver electrode furnished the reference potential, and amalgamated and pure nickel wires served as the indicator electrodes. These measurements represent the first quantitative evaluation of the stability of the tetrahalonickelate(II) ions.

Assuming that at sufficiently high halide concentrations a limiting complex, $Ni_qX_p{}^{2q-p}$, is the predominant species, it can be shown by appropriate substitutions into the Nernst equation that at 125°

$$E = E° + \frac{0.07899}{2} \log C_{Ni}{}^{1/q} - \frac{0.07899}{2} \log [X^-]^{p/q} - \frac{0.07899}{2} \log (\beta^{1/q} q^{1/q})$$

where E is the electrode potential at the nickel indicator electrode in volts, $E°$ is the formal potential of the nickel(II)–nickel system in volts relative to the same chosen reference electrode, C_{Ni} is the total nickel(II) concentration in moles per liter, $[X^-]$ is the equilibrium concentration of the halide of interest in moles per liter, β is the over-all formation constant, and p and q are coefficients described in the equations

$$qNi(II) + pX^- \rightleftharpoons Ni_qX_p{}^{2q-p}$$

$$\beta = \frac{[Ni_qX_p{}^{2q-p}]}{[Ni(II)]^q[X^-]^p}$$
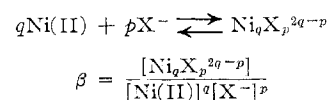
A plot of the potential of the nickel indicator electrode at a high constant halide concentration *vs.* the logarithm of the total nickel(II) concentration should be a straight line with a slope equal to $0.0395/q$. A plot of the potential of the nickel indicator electrode at a constant total nickel(II) concentration *vs.* the logarithm of the halide ion concentration should also be a straight line. The slope is equal to $-0.0395p/q$, and β can easily be calculated from the intercept.

(1) (a) This work was done under the auspices of the United States Atomic Energy Commission; (b) parts of this paper are based upon the Ph.D. thesis of J. Hasson, Polytechnic Institute of Brooklyn, 1967; (c) Department of Chemistry, Arizona State University, Tempe, Ariz. (d) Brookhaven National Laboratory, Upton, N. Y.

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Experimental Section

Chemicals. Dimethyl Sulfone.—Commercial reagent was recrystallized once from water and three times from methanol and vacuum dried.

Lithium Perchlorate.—Perchloric acid was treated with lithium carbonate to form the desired salt, which was dehydrated in the molten state at 240°. A detailed procedure has been described elsewhere.[8]

Lithium Chloride, Bromide, and Iodide.—Commercial reagent grade chemicals were vacuum desiccated with gradual application of heat below the melting point.

Nickel Perchlorate Hexahydrate.—Perchloric acid was allowed to react slowly with an excess of nickel carbonate. After filtration and evaporation, the hexahydrate separated out as green needles from the filtrate.

Nickel Perchlorate Solution in Dimethyl Sulfone.—A weighed amount of nickel perchlorate hexahydrate was added to enough dimethyl sulfone in a glass container to give a concentrated solution. This solution was placed in the furnace, heated to 150°, and flushed overnight vigorously with dry argon. The resulting solution exhibited a golden yellow color distinctly different from the green color of the aquo complex. Analysis indicated a water content less than 0.01%. When the flushing was completed, the solution was diluted with dimethyl sulfone and lithium perchlorate to give the desired concentration of nickel(II).

Silver Perchlorate.—Perchloric acid was allowed to react slowly with silver carbonate to form the product which was dried at 170°. A detailed procedure has been described.[9]

Argon.—Ultrahigh-purity argon was passed over copper turnings in a furnace at 600° and then through a column of magnesium perchlorate.

Electrodes. Silver, Platinum, and Nickel.—These electrodes were made of fine-grade metal wires 1 mm in diameter. They were coiled to give a calculated area of approximately 10 cm².

Amalgamated Nickel.—The nickel electrodes were placed in an aqueous nickel plating bath (0.5 M nickel sulfate, 0.25 M ammonium chloride, and 0.25 M boric acid) and polarized cathodically against a platinum electrode. While the current was still flowing, the coil of nickel wire was immersed in a saturated amalgam at the bottom of the cell. The wire amalgamated quickly. It was later found that electrodes prepared with mercury instead of the amalgam were identical in performance. The electrodes were stored in the plating solution. Prior to use, they were shaken free of excess amalgam, carefully rinsed with distilled water, dried in acetone, and then wiped free of the remaining excess amalgam by twisting a piece of tissue around the wire and running it along the length of the coil. They were introduced into the inert atmosphere of the sample cell as quickly as possible after the last wiping.

Saturated Nickel Amalgam Pools.—These electrodes were prepared by depositing nickel into triply distilled mercury pools from the aqueous nickel plating bath previously described. The amalgam was considered saturated when it became viscous and developed a gritty solid phase.

Apparatus and Equipment. Furnace.—The furnace was of the crucible type with a cylindrical opening at the top 10 cm in diameter and 14 cm in depth. Nichrome wire elements furnished the heating, and temperature control was provided by a Wheelco Indicating Controller (Barber-Coleman Co., Rockford, Ill.) to within ±1° at 125° in the electrolytic cell.

Constant-Current Source.—The constant-current source was built by the Instrument Division of the Brookhaven National Laboratory. The precision of current delivered was ±0.1%.

Experimental Procedures.—The following description applies specifically to the nickel chloride system, but is typical of all of the experiments. A 200-ml solution containing 2 M lithium perchlorate in dimethyl sulfone at 125° was prepared by weighing the solid materials at room temperature and using the pycnometrically determined value of 1.257 g/cm³ for the density of the

solution at 125°. This mixture was quickly melted with a heat gun. Most of this electrolyte solution was poured into a Pyrex cylindrical container, which fit snugly into the furnace aperture. This electrolyte served the dual purpose of a temperature bath and a salt bridge connection between the various electrode compartments. The reference and auxiliary electrode compartments were made from tubes 10 cm long and 1 cm in diameter, sealed at one end. The sample or indicator electrode compartment was 10 cm long and 3.5 cm in diameter. A 1-cm diameter fine-porosity sintered-glass frit was sealed in the wall of each compartment about 2 cm from the closed end. Electrodes, bubblers, and thermometers were placed through holes in the rubber stoppers used to close the other end of the compartments.

The compartments were weighed and then filled to a depth of about 5 cm with portions of the remaining electrolyte solution. The weight of material added was obtained by reweighing the compartments, and the volumes were calculated from the weight gain. The reference, sample, and auxiliary compartments were placed in the electrolyte bath. A thermometer and an argon conduit were placed in the sample compartment, and the solution was outgassed for 5 min. Once the system was maintained at 125°, an amalgamated nickel wire electrode was placed in the sample compartment, a silver electrode in the reference compartment, and a platinum electrode in the auxiliary compartment. The level of the bath was adjusted to be about 1 or 2 mm below that of the sample and reference solutions to minimize the chance of cross contamination between the compartments, *via* the bath solution. On the other hand, the solution level of the auxiliary compartment was adjusted to be below that of the bath to prevent unnecessary contamination of the bath with the electrolysis products from the platinum electrode. The constant-current source was connected between the silver and the auxiliary electrodes and silver(I) ions were generated for the time necessary to give a concentration of 0.0100 M in the calculated volume of the reference solution. The constant-current source was then connected between the nickel indicator and the auxiliary electrodes, and nickel ions were generated for a time necessary to give the desired concentration of nickel, usually in increments of 1×10^{-4} M. The constant current source was disconnected, and the potentiometer was connected between the nickel indicator and the reference electrode. The potential was checked for agreement with the Nernst equation.

Milligram amounts of lithium chloride were then added successively by direct weighing and the potential was measured after each addition. The potential usually took about 10–15 min to attain a constant value after the addition of the chloride. Additions of the lithium chloride were made until the concentration was approximately 0.5 M. The volume increase due to the halide was considered negligible.

Results

The Silver(I)–Silver Reference Electrode.—The silver(I)–silver system showed highly reversible behavior in dimethyl sulfone. A silver coil electrode in silver(I) solutions at 2 M LiClO₄ gave potentials which obey the Nernst equation. In these measurements, a 0.01 M silver(I)–silver electrode was used as the reference electrode. This system was previously reported to be a satisfactory polarographic reference.[10] Silver(I) can be added to the solution coulometrically or as silver perchlorate. Figure 1 shows the Nernst plot; the slope of the straight line is 0.079 V. The formal potential of the silver(I)–silver system found from the Nernst plot is 0.158 V *vs.* the 0.01 M silver reference electrode as predicted by theory. The 0.01 M silver(I)–silver reference electrode was used in all of the potentiometric measurements in this work and provided a highly

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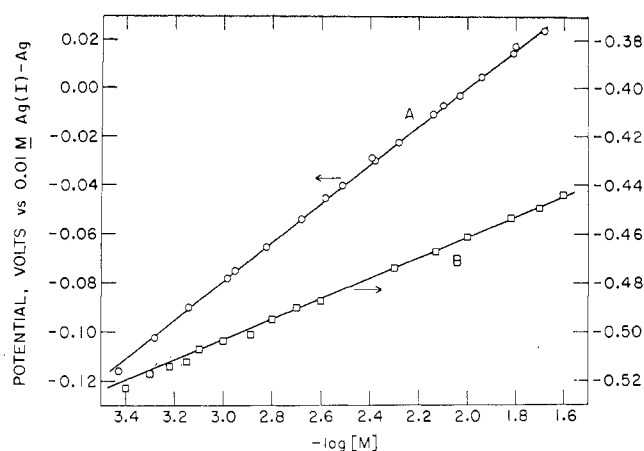
Figure 1.—Nernst-equation plots: (A) Ag(I)–Ag; (B) Ni(II)–Ni(Hg).

Figure 2.—Nernst-equation plots for the $NiX_4{}^{2-}$–Ni(Hg) systems at constant halide concentrations: (A) chloride; (B) bromide.

Figure 3.—Nernst-equation plots for the $NiX_4{}^{2-}$–Ni(Hg) systems at constant Ni(II) concentrations: (A) iodide; (B) chloride; (C) bromide.

stable and reproducible reference potential. Asymmetry potentials among several replicates were less than 0.002 V within 15 min after they were prepared.

The Nickel(II)–Nickel Amalgam Electrode.—Pure nickel electrodes were highly polarizable in nickel(II) perchlorate solutions in dimethyl sulfone. It was found that a coil of nickel wire coated with mercury gave the same potential as saturated nickel amalgam pool electrodes. These electrodes gave potentials which followed the Nernst equation at various nickel(II) concentrations. The nickel(II) ions were generated at a nickel amalgam electrode coulometrically at constant current for measured periods of time. The current efficiency was determined by measuring the nickel(II) in solution colorimetrically with dimethyl glyoxime and found to be essentially 100% within experimental error. Figure 1 shows a typical Nernst plot. The slope of the line was 0.0409 V, and a value of −0.380 V was obtained for the formal potential *vs.* the silver reference electrode.

A further check on the performance of the amalgamated nickel wire electrode was made by preparing a series of nickel(II) solutions from the anhydrous nickel perchlorate stock solution and measuring their potentials with the amalgamated nickel wire electrode. The results were in good agreement with those obtained by coulometric generation of nickel(II).

Nickel(II) Chloride and Bromide Complexes.—The nickel halides were virtually insoluble in dimethyl sulfone but dissolved readily in the presence of a large excess of halide. At a constant chloride or bromide concentration, the potential at an amalgamated nickel wire electrode was a linear function of the logarithm of the total nickel(II) concentration as shown in Figure 2. For convenience in plotting together the results from several experiments, data for halide concentrations ranging between 0.2 and 0.7 *M* were normalized to 1 *M* by the use of the Nernst equation. The lines were obtained by regression analysis. The slopes of the linear plots were 0.0390 and 0.0384 V for chloride and bromide, respectively. Figure 3 shows the plot of the potential at the amalgamated nickel wire electrode against the logarithm of the chloride and bromide
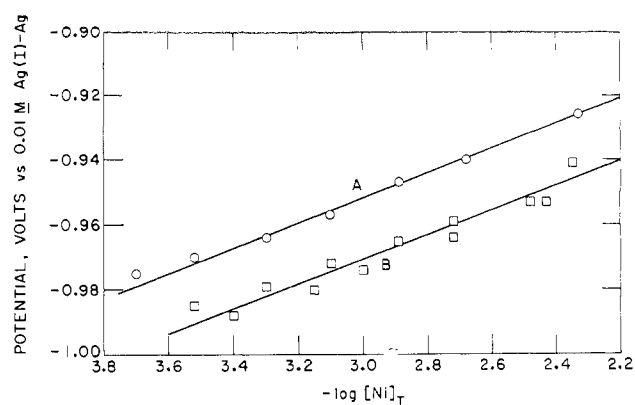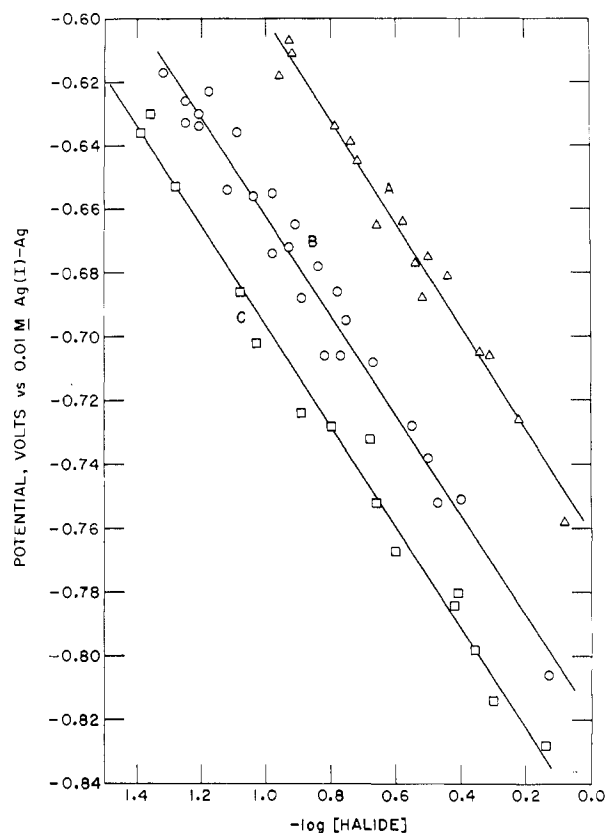
concentrations at a constant nickel(II) concentration. In these plots, data for nickel concentrations ranging between 4×10^{-4} and 1×10^{-3} *M* were normalized to 1 *M* by the use of the Nernst equation. The lines were obtained by regression analysis. The slopes of the least-squares lines were −0.155 and −0.156 V and the logarithms (base 10) of the over-all formation constants were 11.08 ± 0.21 and 11.97 ± 0.18 for tetrachloronickelate(II) and tetrabromonickelate(II), respectively.

Nickel(II) Iodide Complexes.—When studying the iodide system, it was found that the mercury of the

amalgamated nickel wire electrode reduced the red tetraiodonickelate(II) anion to metallic nickel. It was also observed that pure nickel electrodes behaved reversibly in nickel(II) solutions in the presence of a large excess of chloride or bromide. The potential at the nickel electrode obeys the Nernst equation as a function of nickel(II) and halide concentrations. Since the pure nickel electrode was polarized in nickel perchlorate solutions, the formal potential could not be measured directly. It was obtained by measuring the potential difference between the amalgamated nickel wire electrode and the pure nickel electrode in solutions of different concentrations of nickel(II) and halides. The chloride and bromide systems gave results in good agreement. The average value of the difference between the electrodes in these solutions was 0.040 V, with the pure nickel electrode being more negative. The average formal potential of the pure nickel electrode was therefore −0.420 V *vs.* the silver reference electrode.

The pure nickel electrode was less poised than the amalgamated nickel wire electrode and tended to drift somewhat, but this tendency could be suppressed by cathodizing it with a current of 1 μA between the potential measurements.

Figure 3 shows the plot of the potential at the pure nickel wire electrode against the logarithm of the iodide concentration at a constant nickel(II) concentration. Again, data for nickel concentrations between 1×10^{-3} and 5×10^{-3} M were normalized to 1 M, and for ease of comparison with the chloride and bromide systems, the potential at the pure nickel electrode was normalized to that at the amalgamated nickel electrode by applying the factor 0.040 V. The line with a slope of −0.161 V was obtained by regression analysis. The logarithm of the over-all formation constant of tetraiodonickelate(II) was found to be 9.66 ± 0.17.

Discussion

These potentiometric measurements have established the 4:1 halide–nickel(II) ratios in the halo complexes. In dimethyl sulfone with excess added lithium halides, as well as in molten halides, the reduction of nickel(II) has been shown to be a two-electron process. Thus, the halo complexes are mononuclear with respect to nickel(II); that is, q is equal to 1. Since the slopes of the plots in Figure 3 should be equal to $-0.0395p/q$, the value of p must be 4. The spectra of nickel(II) in melts of low-melting halide salts of large organic cations and in dimethyl sulfone with excess added lithium halides are virtually identical and are very similar to the crystal spectra of tetrahalonickelate(II) salts.[7] Since nickel(II) can be complexed only to halides in the halide melts, it is reasonable to suppose that the solvent dimethyl sulfone molecules are completely displaced in the halo complexes and that we are dealing with tetrahedral tetrahalonickelate(II) ions in all cases.

At the high ionic strengths employed in the experiments, there was undoubtedly ion pairing to a considerable extent. It has been shown that in molten chlorides

containing cations of large charge-size ratios, such as lithium(I) and magnesium(II), the spectra of nickel(II) are affected significantly by changes in concentration of these cations and by changes in operating temperature.[11] As the concentration of these cations increases, nickel(II) tends to form complexes of approximate octahedral geometry in equilibrium with the tetrahedral complexes. As the temperature increases, the tetrahedral geometry is favored and the behaviors of lithium(I) and magnesium(II) differ in much less significant ways from those of larger cations such as cesium(I) and potassium(I). These phenomena are at least partly attributable to the polarizing power of the small cations of high charge density. In going from chloride to bromide to iodide, the equilibrium shifts in favor of the tetrahedral geometry.[12] Evidently, steric hindrance becomes more severe as the size of the coordinating halide increases. In dimethyl sulfone at 125°, there was no evidence of the formation of octahedral halo complexes, and, except for the lower attainable chloride concentration due to lower solubilities, the use of cesium and potassium chlorides in place of lithium chloride produced essentially the same results both potentiometrically and spectrophotometrically. Apparently, the alkali metal ions are solvated, and ion pairing has little effect on the structure of the tetrahalonickelate(II) ions. The use of dimethyl sulfone as "inert" diluent helps elucidate the nickel(II)–halide interactions, and the information thus obtained should prove valuable in studying the effect of solvent cations on these interactions in molten halide systems.

In these potentiometric experiments, it is assumed that, in the presence of lithium perchlorate at a high concentration, changes in junction potential and in activity coefficient due to differences in nickel(II) and halide concentrations are within experimental errors. As evidenced by the linearity of the Nernst equation plots, these assumptions appear to be quite valid.

The stability of the bromo complex is greater than that of the chloro complex. However, this trend is reversed in going from bromide to iodide which forms the least stable 4:1 complex among the three halides under consideration. As pointed out by Leden and Chatt,[13] the stability of halide complexes follows the order $I^- > Br^- > Cl^-$ for those metal ions which are capable of forming π bonds of the d_π–d_π type with the halides. Metal ions which show this behavior include silver(I), bismuth(III), copper(I), cadmium(II), mercury(II), platinum(II), and thallium(III). Of these metal ions, cadmium(II) and mercury(II) possess stereochemistry somewhat similar to that of nickel(II). However, the ionic radius of nickel(II) is much smaller than those of the others. Thus, the large size of the iodide ion and the resulting steric hindrance undoubtedly play an important role in the reversal of stability

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for tetraiodonickelate(II). This explanation is consistent with the observation that in molten salt systems, iodide is incapable of forming octahedral nickel(II) complexes while bromide does so with considerably more difficulty than chloride, which already prefers the tetrahedral geometry.[11,12]

Substitution Reactions of Oxalato Complex Ions. VIII. The Kinetics of the Anation Reaction of Diaquobis(ethylenediamine)cobalt(III) Ion by Oxalate in Acidic Aqueous Solution[1]

BY P. M. BROWN AND G. M. HARRIS

The reaction appears to proceed by a typical SN1 ion-pairing mechanism. The rate-limiting water dissociation reaction has a rate constant, k_0, very similar in magnitude and temperature dependence to that for water exchange under comparable conditions. The association constants for the reactant pairs $Co(en)_2(H_2O)_2^{3+}-H_2C_2O_4$ and $Co(en)_2(H_2O)_2^{3+}-HC_2O_4^-$ are 11 and 100, respectively, at 50°. These values are several times greater than predicted by simple point-charge interaction theory, as might be expected for large-ion systems amenable to hydrogen-bonding effects. The constant k_0 is increased more or less linearly by a factor of about 4 when the "inert" nitrate salt concentration is increased from zero to 3 M. This is typical of a nonspecific medium effect in this kind of reaction.

The water replacement reactions of various anionic nucleophiles with stable aquo cations are believed by many researchers to involve the prior establishment of an ion-pairing associative equilibrium between the reacting species. This is followed by ligand–water rate-determining dissociation, whereupon the nearby nucleophile slips into the position vacated by the leaving water molecule. Typical examples are afforded by the series of anation reactions symbolized by

$$Co(NH_3)_5(H_2O)^{3+} + X^{n-} \longrightarrow Co(NH_3)_5X^{(3-n)+} + H_2O$$
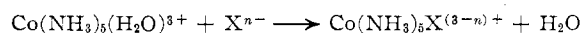
where X^{n-} may be SO_4^{2-}, $H_2PO_4^-$, Cl^-, SCN^-, etc.[2] Only two similar studies of the ion $Co(en)_2(H_2O)_2^{3+}$ have thus far been reported—those of anation by sulfate[3a] and by phosphate.[3b] In these cases, the expected SN1 ion-pairing mechanism also appears to be applicable, as suggested by the near equivalence of the ligand–water isotopic exchange rates and the limiting anation rates at high anion concentration. Study of the reaction of $Co(en)_2(H_2O)_2^{3+}$ with oxalate offers another interesting possibility, since rapid and complete chelation is involved in formation of the final product.[4] The question thus arises as to what limits the rate of the substitution—water dissociation or chelation of monodentate oxalate. Of further significance is the fact that the product cation, $Co(en)_2C_2O_4^+$, is completely stable in strongly acidic solution,[5] unlike several analogous cobaltammine oxychelates (such as with SO_4^{2-}, CO_3^{2-}, PO_4^{3-}), all of which aquate readily in strong acid. Thus, in the present study it has been possible to observe "anation" by the uncharged species $H_2C_2O_4$ as well as by ionic oxalate. The investigation is also of interest relative to the recently reported[6] reaction of ionic oxalate with the complex anion $Cr(C_2O_4)_2(H_2O)_2^-$. For this process, the question of preequilibration of the reactants is somewhat controversial, since both are negatively charged. In the present study, conventional ion association is possible, but the data indicate considerable reinforcement of this process by factors which are probably independent of ionic charge. The reactant association mechanism assumed in the interpretation of the anation of bis(oxalato)diaquochromium(III) anion by oxalate is thus offered indirect support.

Experimental Section

cis-$Co(en)_2(H_2O)_2(NO_3)_3 \cdot CH_3OH$ was prepared and crystallized from methanol solution by the procedure of Dwyer, Sargeson, and Reid.[7] The results of a commercial analysis[8] follow. *Anal.* Calcd for *cis*-$Co(en)_2(H_2O)_2(NO_3)_3 \cdot CH_3OH$: C, 13.86; H, 5.58; N, 22.63; Co, 13.60. Found: C, 13.86; H, 5.70; N, 23.18; Co, 13.35. Aqueous solutions of the product gave extinction coefficients which compared well with those reported by Bjerrum and Rasmussen.[9] To test for possible impurities which might catalyze the reaction, the material was also prepared by the method described by Tong and Yankwich.[10] Observed reactivity data for the two different materials agreed within experimental error. All other reagents were commercial

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(4) No evidence has previously been presented for anything but the fleeting existence of aquooxalato complexes of the type Co(bidentate ligand)₂-(C₂O₄)(H₂O)⁺.

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