the higher melting component of the stable pair, and an immiscibility gap is found.[2,4]

The first factor, ΔG°, has been used in correlations by Russian investigators[2,4] although they utilize ΔG° and sometimes ΔH° for the exchange reaction of the solids at room temperature. The other two factors, $\Sigma\lambda_{ij}$ and liquidus temperatures, provide a justification of many of the empirical correlations given by the Russian workers. For example, when the cations are polarizable, it has been observed that an immiscibility gap will occur for smaller values of ΔG° [2,4] than when the cations are not polarizable. Values of λ_{ij} tend to be more positive (or less negative)[7,13,18] and the melting points of salts are lower when the cations are polarizable. Both factors are in the right direction so as to agree with the observed data. The positive contributions to λ_{ij} which are related to cation polarizabilities have been discussed theoretically[7,18,19] in terms of the van der Waals (or London) interactions between ions. Thus, one can relate the appearance of immiscibility gaps theoretically to fundamental interactions between the ions. Conversely, the prediction of immiscibility gaps can be made from values of λ_{ij} obtained from a theoretical calculation based on a knowledge of the ionic interactions or from independent measurements of the binary systems.

Conclusion

Many of the significant topological features of phase diagrams including immiscibility gaps can be correlated with the conformal ionic solution theory. Although the theory is approximate, it provides a simple and fundamental basis for many of the empirical rules stated by previous workers.

(19) (a) M. Blander, *J. Chem. Phys.*, **36**, 1092 (1962); (b) J. Lumsden, *Discussions Faraday Soc.*, **32**, 138 (1961).

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The Kinetics of Formation and Aquation of Bis(oxalato)bis(dimethyl sulfoxide)chromate(III)

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The compound potassium *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III) has been prepared, and the visible absorption spectrum in water solution is reported. The kinetics of formation of the compound from *cis*-bis(oxalato)diaquochromate(III) in DMSO has been investigated. The solvolysis in DMSO is a two-step process with both steps independent of water concentration up to 1.03 *M* water concentration at 45°. The rate constants for the faster step are 4.61×10^{-4}, 8.20×10^{-4}, 21.9×10^{-4}, and 40.6×10^{-4} sec^{-1} at 30, 35, 40, and 45°, respectively. The activation parameters for this step are $\Delta H^* = 28.5 \pm 1.1$ kcal/mole and $\Delta S^* = 20.1 \pm 3.4$ cal/deg mole. For the slower step the rate constants at 30, 35, 40, 45, 50, and 55° are 1.52×10^{-4}, 3.43×10^{-4}, 7.55×10^{-4}, 16.1×10^{-4}, 34.7×10^{-4}, and 70.3×10^{-4} sec^{-1}, respectively. The activation parameters are $\Delta H^* = 29.7 \pm 0.1$ kcal/mole and $\Delta S^* = 21.9 \pm 0.3$ cal/deg mole. The aquation of the *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III) was found to be pH independent between pH 1.0 and 4.0 at 55°. A two-step process was also observed for the aquation reaction. The activation parameters for the fast step are $\Delta H^* = 12.3 \pm 0.6$ kcal/mole and $\Delta S^* = -30.2 \pm 1.9$ cal/deg mole. The associated rate constants are 25.1×10^{-4}, 51.0×10^{-4}, and 86.2×10^{-4} sec^{-1} at 35, 45, and 55°, respectively. For the slow step the rate constants are 3.03×10^{-4}, 8.04×10^{-4}, 18.9×10^{-4}, and 45.7×10^{-4} sec^{-1} at 25, 35, 45, and 55°, respectively. The activation parameters are $\Delta H^* = 17.0 \pm 0.8$ kcal/mole and $\Delta S^* = -17.6 \pm 2.6$ cal/deg mole.

Compounds of cobalt and chromium containing dimethyl sulfoxide (DMSO) as a ligand have been reported by various workers.[1] Usually only the spectral characteristics of the compounds were discussed. Schläfer investigated the equilibrium between the ions dichlorotetrakis(dimethyl sulfoxide)chromium(III) and trichlorotris(dimethyl sulfoxide)chromium(III) in DMSO.[2] Tobe and Watts[3] have investigated systems in which the chloro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion was present. To date, with the exception of Tobe and Watts, no one has investigated the rate of formation of any complex containing DMSO.

In an attempt to find a suitable nonaqueous solvent in which to study the *trans–cis* isomerization of the bis(oxalato)diaquochromate(III) ion it was observed that DMSO reacted with the complex. This paper reports the results of the investigation of the rate of aquation and the rate of formation of potassium *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III).

Experimental Section

The potassium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.[4] The product

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[1] (a) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960); (b) H. L. Schläfer and H. P. Opitz, *Z. Anorg. Allgem. Chem.*, **313**, 178 (1961); (c) R. S. Drago, D. W. Meek, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

[2] H. L. Schläfer and H. P. Opitz, *Z. Chem.*, 216 (1962).

[3] (a) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1962); (b) D. W. Watts, L. F. Chin, and W. A. Millen, *Australian J. Chem.*, **18**, 453 (1965).

[4] A. Werner, *Ann.*, **406**, 216 (1914).

was air dried and analyzed as previously described.[5] Potassium *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III) was prepared by dissolving potassium *trans*-bis(oxalato)diaquochromate(III) in DMSO at 100° and maintaining the solution at this temperature for 10 min. The solution was cooled to room temperature and allowed to sit for 30 min at 20°. The crystals which formed were filtered and washed with absolute ethanol and anhydrous ethyl ether. This product was recrystallized once from hot (100°) DMSO.

A preliminary examination of the compound to establish purity was made by dissolving 3 mmoles of the compound in water and passing it into an anion-exchange column containing Dowex 1-X8 resin in the nitrate form. The resin was washed with several bed volumes of water, and the effluent was passed through another similar anion-exchange column. The second effluent was treated with silver nitrate and ammonium peroxydisulfate. A barely perceptible yellow indicated the presence of a very small amount of cationic and/or neutral species present as impurities. The first column then was washed with 0.1 *N* sodium nitrate. One broad band consisting of bis(oxalato)bis(dimethyl sulfoxide)chromate(III) and the aquation products was eluted. At the top of the column there remained an extremely small amount of material, which was not adequate in quantity for identification but may have consisted of polymeric material or tris(oxalato)chromate(III).

Two additional recrystallizations from hot DMSO were performed to purify the material further. The compound was analyzed for chromium as has been previously described.[5] A DMSO analysis was done based on a method described by Douglas.[6] In this method, a sample containing about 1.5 mmoles of DMSO was dissolved in 200 ml of 1.0 *N* sulfuric acid. Fifty milliliters of 0.1 *N* potassium permanganate was added and after mixing thoroughly 50 ml of 0.1 *N* ferrous ammonium sulfate and 30 ml of concentrated phosphoric acid were added. This solution was titrated to a faint pink end point using 0.1 *N* potassium permanganate. Sulfur, carbon, and hydrogen were determined by Galbraith Laboratories. *Anal.* Calcd for $K[Cr(C_2O_4)_2(DMSO)_2]\cdot 2DMSO$: Cr, 8.98; DMSO, 53.9; S, 22.2; C, 24.9; H, 4.14. Found: Cr, 8.88; DMSO, 54.1; S, 22.3; C, 24.6; H, 4.08.

Two different experiments were performed in an attempt to determine if the bis(oxalato)bis(dimethyl sulfoxide)chromate(III) was a mixture of isomers or a single compound. In the first experiment about 1 mmole of the complex was run into an anion-exchange column with an exchange capacity of about 10 mequiv. The column was enclosed in a water jacket through which water at about 2° was circulated. The material was eluted with 0.05 *M* $NaNO_3$ at a flow rate of about 3 ml/hr. As the material passed down the column three ill-defined bands began to develop. These bands separated only enough to allow conclusive spectral identification of the first and third. The first band containing the major amount of the material to be eluted was $[Cr(C_2O_4)_2(DMSO)_2]^-$ and the third band was *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ which had undoubtedly been formed by aquation. There was no evidence in detailed looking at the first band that it consisted of more than a single compound. The intermediate broad band could not be identified. It was spread out as would be expected when the aquation was occurring while the material moved down the column.

The second experiment performed was nonaqueous column chromatography on the bis(oxalato)bis(dimethyl sulfoxide)chromate(III). An anion-exchange column of about 10-mequiv capacity was prepared using DMSO instead of water. At room temperature a solution of about 1 mmole of bis(oxalato)bis(dimethyl sulfoxide)chromate(III) in DMSO was run onto the column and eluted at a flow rate of about 3 ml/hr with 0.1 *M* $NaNO_3$ in DMSO. Only a single band developed in this experiment. This implies the presence of only one isomer.

The visible spectrum of a solution of bis(oxalato)bis(dimethyl sulfoxide) chromate(III) in DMSO does not change with time. This means that the thermodynamically stable isomer or mixture of isomers has been isolated.

For the kinetic runs, all solutions used were mixed in a 25-ml flask that was partially submerged in a constant-temperature bath. A Teflon-coated stirring bar and submergible, air driven magnetic stirrer were used. By this means, no change in temperature occurred throughout the mixing. To adjust the pH, reagent grade perchloric acid was used. The runs in water were made at pH 3.0 with no added electrolyte. In those runs in which the pH was varied no inert electrolyte was added to maintain a constant ionic strength. The concentration of bis(oxalato)bis(dimethyl sulfoxide)chromate(III) used in the kinetic runs was 1 m*M*. For the kinetic runs in DMSO the concentration of potassium bis(oxalato)diaquochromate(III) tetrahydrate was 2.2 m*M*. It was found that unless excess water of crystallization was in the potassium bis(oxalato)diaquochromate(III) a cloudy solution developed when the complex was added to the DMSO. The DMSO used in the kinetic runs was Matheson Coleman and Bell anhydrous grade which contained a maximum of 0.05% water.

In those runs in which the effect of water on the solvolysis in DMSO was investigated, the solutions of DMSO containing various concentrations of water were made by adding the proper amount of water to a volumetric flask and diluting to volume with DMSO. In calculating the amount of water to add to the DMSO it was assume that the water concentration of the anhydrous grade DMSO was 0.05%.

Kinetic runs were made on a Beckman Model DU spectrophotometer fitted with a constant-temperature block that completely surrounded the 10-cm cells used. The temperature was maintained within ±0.1° of the desired temperature by water circulating through the block from a constant-temperature bath. The change in absorbance was measured at a wavelength of 600 mμ. This wavelength was used because the greatest change in absorbance occurred here. The precision obtained for rate constants would be lower at any other wavelength; however, the complete spectrum does not indicate anything to make one believe the results would be substantially different.

All rate constants are the average of at least duplicate runs. The method of determining the value of the larger rate constant in both reactions did not give good precision. The average of the relative precision for the larger rate constants was about 20% while for the smaller rate constants the average of the relative precision was under 10%.

Complete absorption spectra were run over the wavelength range from 350 to 600 mμ for freshly dissolved bis(oxalato)bis(dimethyl sulfoxide)chromate(III), for solutions that had reacted for various lengths of time, and for the completely aquated solution. To calculate the molar absorptivities of the beginning compound, the freshly dissolved compound at 2° was run within 2 min after mixing. The spectrum of the completely aquated compound was identical with that of a solution of *cis*-bis(oxalato)diaquochromate(III).

Results

The over-all reactions studied were

$$cis\text{-}[Cr(C_2O_4)_2(H_2O)_2]^- \xrightarrow{DMSO} cis\text{-}[Cr(C_2O_4)_2(DMSO)_2]^- + 2H_2O \quad (1)$$

$$cis\text{-}[Cr(C_2O_4)_2(DMSO)_2]^- \xrightarrow{H_2O} cis\text{-}[Cr(C_2O_4)_2(H_2O)]^- + 2DMSO \quad (2)$$

Neither one of the reactions followed simple first-order kinetics. Therefore it was assumed that the reaction occurred stepwise.

For a series of consecutive first-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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(5) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 609 (1953).

(6) T. B. Douglas, *ibid.*, **68**, 1972 (1946).

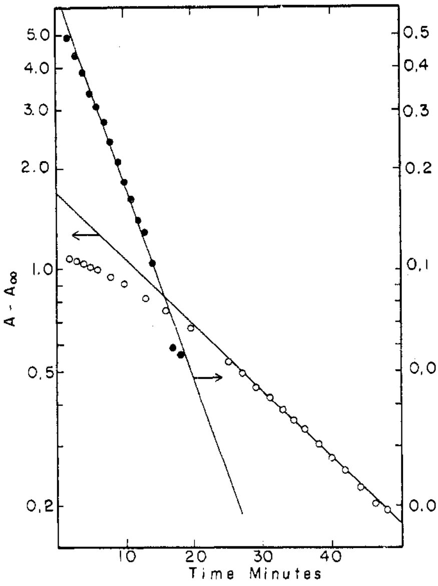


Figure 1.—Plot of experimental data for determination of aquation rates when dissolving *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ in water.

it can be easily demonstrated by solving the associated system of differential equations that the following equations give the concentrations of the species at any time t, where A_0 is the initial concentration of species A

$$[A] = A_0e^{-k_1t} \tag{3}$$

$$[B] = \frac{A_0k_1}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) \tag{4}$$

$$[C] = A_0\left(1 - \frac{k_2}{k_2 - k_1}e^{-k_1t} + \frac{k_1}{k_2 - k_1}e^{-k_2t}\right) \tag{5}$$

Since the absorbance, A, at any time t is given by

$$A = b(\epsilon_A[A] + \epsilon_B[B] + \epsilon_C[C]) \tag{6}$$

where ϵ_i is the molar absorptivity of the ith species, $[X_i]$ is the concentration of the ith species, and b is the cell length, the following equation can be derived.

$$(A - A_\infty) = a_1e^{-k_1t} + a_2e^{-k_2t}$$

where A_∞ is the absorbance at time infinity and a_1 and a_2 are constants composed of the rate constants, molar absorptivities, and cell length.

Figure 1 shows a typical rate plot of log $(A - A_\infty)$ *vs.* time t, from which the rate constants were obtained. The straight-line segment of the graph at the longer times was extrapolated to time zero. The logarithm of the difference between the experimental $(A - A_\infty)$ and the $(A - A_\infty)'$ from the straight line is plotted *vs.* time. The specific rate constant for the slow reaction is 2.303 times the slope of the first line. The specific rate constant for the fast reaction is 2.303 times the slope of the second line. No more than two rate constants were obtained for a reaction at any temperature investigated. The rate constants are contained in Tables I and II.

The activation parameters were determined by plotting $-\ln k_rh/kT$ against $1/T$. These plots permitted the calculation of ΔH^* and ΔS^* which are also given in Tables I and II.

TABLE I

AQUATION OF *cis*-BIS(OXALATO)BIS(DIMETHYL SULFOXIDE)CHROMATE(III) IN WATER

Temp, °C	pH	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}
25	3.0	. . .	3.03
35	3.0	25.1	8.04
45	3.0	51.0	18.9
55	1.0	86.3	45.3
55	2.0	87.0	45.1
55	3.0	82.3	45.8
55	4.0	89.0	46.5
ΔH^*, kcal/mole		12.3 ± 0.6^a	17.0 ± 0.8^a
ΔS^*, cal/deg mole		-30.6 ± 1.9^a	-17.6 ± 2.6^a

[a] Standard deviation.

TABLE II

SOLVOLYSIS OF *cis*-BIS(OXALATO)DIAQUOCHROMATE(III) IN DMSO

Temp, °C	H_2O concn, *M*	10^4k_{fast}, sec^{-1}	10^4k_{slow}, sec^{-1}
30	0.03	4.61	1.52
35	0.03	8.20	3.43
40	0.03	21.9	7.55
45	0.03	40.6	16.1
45	0.14	36.9	15.4
45	0.25	35.2	18.9
45	1.03	36.4	18.1
50	0.03	. . .	34.7
55	0.03	. . .	70.3
ΔH^*, kcal/mole		28.5 ± 1.1^a	29.7 ± 0.1^a
ΔS^*, cal/deg mole		20.1 ± 3.4^a	21.9 ± 0.3^a

[a] Standard deviation.

Figure 2 shows the spectral changes during aquation of *cis*-bis(oxalato)bis(dimethyl sulfoxide)chromate(III). The spectral changes during the solvolysis in DMSO of *cis*-bis(oxalato)diaquochromate(III) are similar.

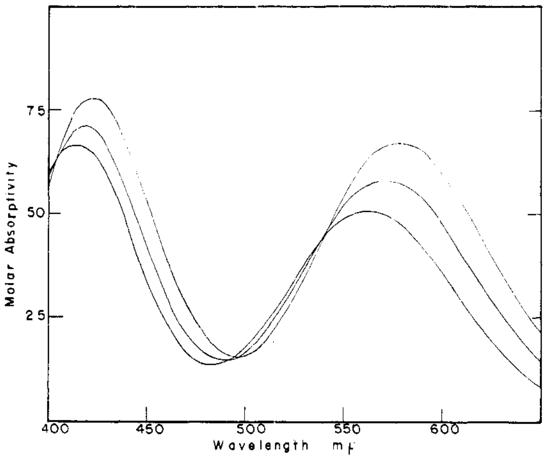


Figure 2.—Spectra during aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ with absorption at peaks decreasing. Times are 0, 184, and 1200 min after solution.

In Figure 3 are given the spectra of *trans*- and *cis*-bis(oxalato)diaquochromate(III) and *cis*-bis(oxalato)-bis(dimethyl sulfoxide)chromate(III) and the calculated spectrum of the intermediate in the aquation of the last compound.

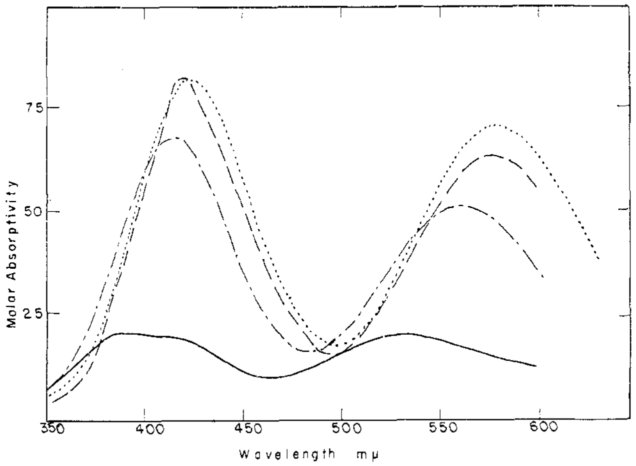


Figure 3.—Absorption spectra: ———, *trans*-$[Cr(C_2O_4)_2(H_2O)_2]^-$; –·–·–·, *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$; . . . . . . , *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$; – – – –, intermediate in aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$, probably *cis*-$[Cr(C_2O_4)_2H_2O(DMSO)]^-$.

The spectrum of the intermediate was calculated using the data from the aquation reaction and eq 3–6. The calculations were made at an optimum time in order to have reasonable concentrations of the various species present. Implicit in these calculations was the assumption that there was only one intermediate species. The calculation was performed in two ways. In the first method the larger of the two rate constants was assigned to the first step, and the smaller rate constant was assigned to the second step. The result of this calculation was the spectrum shown in Figure 3. The second method of calculation assigned the rate constants in the reverse order. The result of this assignment gave a spectrum with maxima at unexpected wavelengths (420 and 610 mμ) and gave molar absorptivities which were absurdly large at these wavelengths and gave molar absorptivities which were negative between 340 and 380 mμ. One must conclude from these results that the faster rate process occurs first and the slower second. The close comparison of the spectrum of the intermediate to that of the two *cis* compounds permits the identification of the intermediate as a *cis* isomer.

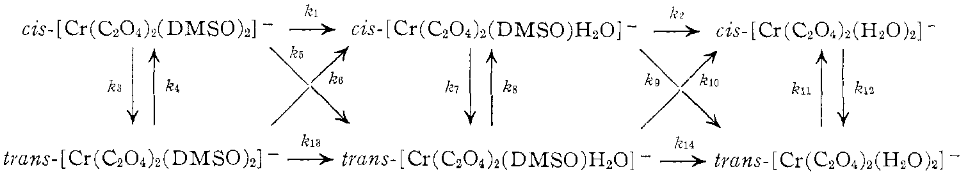
When similar calculations were performed for the solvolysis of *cis*-bis(oxalato)diaquochromate(III) in DMSO, the results were not clearly defined because of the low solubility of the starting compound in DMSO. The accuracy of the calculations was very poor. When the smaller rate constant was assigned to the first step and the larger to the second step, a very large negative molar absorptivity (−107) was obtained at one wavelength. When the larger rate constant was assigned to the first step and the smaller to the second step, the accuracy of the calculations was so poor that it would be impossible to infer exactly where the maxima and minima of the spectrum were. Therefore we have tentatively assumed that the faster reaction occurs first followed by the slower.

Discussion

Spectra.—The spectra of the *cis*- and *trans*-bis(oxalato)diaquochromate(III) in Figure 3 are very similar to the spectra of other *cis* and *trans* isomers of chromium compounds.[7] Immediately obvious also is the similarity of the spectra for $[Cr(C_2O_4)_2(DMSO)_2]^-$ and the intermediate compound in the aquation. Because of the similarty of the spectra of these two compounds and their comparison to the spectrum of *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ and because of the failure to separate isomers in column chromatographic experiments, the *cis* configuration is assumed both for the bis(dimethyl sulfoxide) compound and the intermediate in the aquation experiments.

Aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$.—The possible reactions that must be considered are shown in Scheme I.

Scheme I



The numbers applied to the rate constants are also used as the designation for that reaction. There was no isomerization of the *cis* isomer of the starting compound in DMSO solution, and it seems reasonable to expect that the same behavior would prevail in water. This rules out path 3. Since the starting compound has been assumed to be the *cis* isomer on the basis of absorption spectrum, this also rules out paths 4, 6, and 13. In water *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ is the stable isomer and in DMSO *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ is the stable isomer. Reasoning by analogy, *cis*-$[Cr(C_2O_4)_2(DMSO)H_2O]^-$ might be expected to be the more stable in water or in DMSO. The calculated spectrum of the intermediate is in agreement with this conclusion. This argument eliminates paths 5, 7, 8, 10, 12, and 14.

The *trans–cis* isomerization of *trans*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ has been investigated.[5] From this work the values for k_{11} and the associated activation parameters are known. Neither one of the observed rate constants for the aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ corresponds to the known isomerization rate, and the activation parameters are significantly different. This eliminates steps 9 and 11, leaving only reactions 1 and 2, where k_1 must be the larger rate constant and k_2 must be the smaller rate constant.

The aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ is pH independent over the pH range 1.0–4.0 at 55°, as

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(7) C. S. Garner and J. M. Weigel, *Inorg. Chem.*, **4**, 1569 (1965).

demonstrated by the data in Table I. The pK values for *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ are about 6.4 and 9.8.[8] One would expect that the pK for *cis*-$[Cr(C_2O_4)_2(DMSO)H_2O]^-$ would be not less than 6.4 and, therefore, the species studied in the pH range 1–4 would not change.

The activation parameters for the first step of the aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ imply a mechanism with more bond making than bond breaking in the transition state. This is consistent with the idea that the activation enthalpy should be lower if the entering group is forming a bond with the metal during the transition state. If the entering group is forming a bond in the transition state, stringent steric requirements have to be met and the entropy of activation should be relatively negative. The second step in the aquation reaction has activation parameters which imply more of a concerted reaction.

Solvolysis of *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ in DMSO.—The possible reaction scheme for the solvolysis of *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ in DMSO would be a set of reactions similar to those presented for the aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$. The arguments with respect to the *cis* isomers being the more stable thermodynamically have been presented. There can be no argument that the spectrum of the intermediate supports this because of the inaccuracy of the calculated intermediate spectrum.

The activation parameters for this solvolysis reaction in DMSO, shown in Table II, have small standard deviations in general and probably indicate a dissociation mechanism. The data taken with small amounts of water added to DMSO indicate no importance due to presence of water in DMSO. If the observed rate constants are composites of several different rate constants, the several different rate constants must have activation parameters that are within experimental error of the observed activation parameters, because the standard deviation of the observed parameters is quite small.

Acknowledgment.—The authors wish to express their thanks to the University Research Committee of Washington State University for funds to support this research.

[8] R. E. Hamm and D. M. Grant, *J. Am. Chem. Soc.*, **78**, 3006 (1956).

CONTRIBUTION FROM THE SCHOOL OF CHEMICAL SCIENCES, UNIVERSITY OF EAST ANGLIA,
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The Stereospecific Coordination of Sarcosine

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The classical resolution[1] of the (±)sarcosinatobis(ethylenediamine)cobalt(III) ion has been repeated, and the mutarotation of the optically active coordinated sarcosine was not observed. Circular dichroism, rotatory dispersion, and pmr evidence has been collected to show that sarcosine is coordinated stereospecifically, and this result is supported by a conformational analysis of the possible isomers.

Introduction

The possibility of resolving a quaternary ammonium salt where one of the substituents is a metal ion probably was entertained first by Meisenheimer and co-workers.[1] These authors claimed to have resolved the $(Co(en)_2sar)^{2+}$ ion (en = ethylenediamine, sar = sarcosine) where both the configuration about the cobalt and that about the N atom are asymmetric (Figure 1). This work is quoted widely as an outstanding example of asymmetry engendered in the ligand by coordination, and some discussion of its experimental validity is relevant here since at least two attempts to reproduce some of Meisenheimer's most significant results have been unsuccessful.[2]

Disregarding the conformations of the ligands there are four possible isomeric forms of the ion, $(+)(Co(en)_2(+)sar)^{2+}$, $(+)(Co(en)_2(-)sar)^{2+}$, $(-)(Co(en)_2(+)sar)^{2+}$, and $(-)(Co(en)_2(-)sar)^{2+}$, denoted by Meisenheimer as (Co+N+) (Co+N−), (Co−N+), and (Co−N−). This nomenclature will be retained to avoid confusion with the original literature. Meisenheimer, *et al.*, resolved the complex with the π-bromocamphorsulfonate ion ((+)BCS) and obtained two BCS diastereoisomers designated as (Co−N±), $[M]_D$ −923°, and (Co+N±), $[M]_D$ +2020°, respectively, containing variable amounts of water and alcohol. They maintained that although the cobalt configurations were separated the internal diastereoisomers arising from the coordinated sarcosine were not. However, in one instance recrystallization of a diastereoisomer fraction, $[M]_D$ +2020°, from water gave a fraction, $[M]_D$ +2290°, whose rotation in aqueous solution decreased to +2130° after 2 hr and then to +2020° on standing overnight. The authors considered that this fraction contained the (Co+N+)

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[1] J. Meisenheimer, L. Angermann, and H. Holsten, *Ann.*, **438**, 261 (1924).

[2] (a) F. Basolo, Ph.D. Thesis, University of Illinois; (b) this work.