

Autoxidation of free phosphines has been demonstrated to be a radical chain process.²²⁻²⁴ It may be that the iron complexes serve to initiate this process. The observation that certain amounts of the iron dithiolene complexes are destroyed during these reactions

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(24) However coordination of phosphines and arsine to Lewis acids markedly affects their oxidation. For example $(C_6H_5)_3AsAlCl_3$ is more rapidly oxidized by air to $(C_6H_5)_3AsO$ than is $(C_6H_5)_3As$ under similar conditions: D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 666 (1942). Aerial oxidation of coordinated phosphine in $CoCl_2(P(C_6H_5)_3)_2$ has been reported to produce only the phosphine oxide, whereas oxidation of free alkylphosphines produces approximately equal quantities of R_3PO and $R_2P(O)OR$: D. D. Schmidt and J. T. Yoke, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 5, 1969, No. INOR 203. What effect coordination has on the mechanism of the oxygenation reactions described herein is not clear, but coordination alone cannot be of overriding importance since the apical bases in the cobalt adducts are not activated.

suggests that the activating agent may not be the parent complexes themselves. We have attempted the oxidation of triphenylphosphine in the presence of $FeCl_3$ in acetone and in the presence of $Na_2S_2C_2(CN)_2$. Traces of triphenylphosphine oxide and triphenylphosphine sulfide were obtained in the latter case, but neither reagent was nearly as effective in promoting oxidation on a synthetic scale as was $Fe_2S_8C_8(CN)_8^{2-}$ or $FeS_6C_6(CN)_6^{2-}$. Other compounds formed from the parent complexes may be agents that are active in promoting these oxidations.

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Octahedral Chromium(III) Complexes in Dipolar Aprotic Solvents. III.¹ Ion Association Studies in *N,N*-Dimethylformamide, *N,N*-Dimethylacetamide, and Dimethyl Sulfoxide by Conductance Measurements²

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Ion-pair association constants have been determined from conductance measurements for the association of chloride, bromide, iodide, perchlorate, and thiocyanate ions with a series of cations of the type *cis*- and *trans*- $CrXY(en)_2^+$, where "en" represents ethylenediamine or an *N*-methyl-substituted ethylenediamine, and X and Y represent monodentate monovalent negative ligands. The data have been treated by the equation of Fuoss, Onsager, and Skinner.³ The solvents investigated are *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO). In order to extend the comparison with our previous work on the analogous cobalt(III) complexes⁴ some results are presented for selected rhodium(III) complexes. The results are presented together with limiting ionic conductances at 25°. The results confirm the previous conclusions regarding the importance of the dipolar nature of the complexes and the role of H bonding to the ethylenediamine nitrogen protons.⁴ The association constants show remarkable independence of the identity of the metal ion and also show clearly that it is naive to overemphasize interionic electrostatic terms in comparing ion association constants, since in doing so one for the most part is emphasizing enthalpy terms associated with interionic interactions which, even when comparing these simple analogous systems, may not predominate over the corresponding modifications introduced in solvation energies.

Since the initial recognition by Taube and Posey⁵ of the role of ion aggregates in substitution mechanisms of cationic octahedral complexes the importance of such fast ion association reactions as a prelude to rate-determining phenomena has been firmly established. As we have previously emphasized,⁶ the weakness of ion association in aqueous systems of monovalent ions, the only ions for which precise conductance-based association constants are obtainable at the time, has made it diffi-

cult to compare the ion association constants, established as compatible with rate data, with independently established values. Ion association constants in water have been established through spectrophotometric methods based on the charge-transfer spectrum of the ion pair⁷ but have given widely scattered values⁸ and have been better applied either to systems involving highly charged cations, such as $Co(NH_3)_6^{3+}$ with halide ions,⁹ or to ion pairs in poorly solvating solvents, such as tetramethylene sulfone,⁶ than to the systems treated here.

The advantage of investigating the role of ion association in mechanisms by using dipolar aprotic solvents has

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been emphasized previously.¹⁰⁻¹² Because of poor anion solvation in these solvents, which is largely uncompensated by the improved cation solvation,¹² the ion association constants of univalent ion combinations, such as $[\text{MCl}_2(\text{en})_2]^+\text{Cl}^-$, are easily investigated by conductance measurements.⁴ The values obtained have been shown to be compatible with those obtained from fitting kinetic data⁶ but in addition have proven to be of interest in themselves in that they have emphasized the importance of dipolar forces as well as such short-range forces as the hydrogen bond in determining the magnitude of the ion association constant and the stereochemistry of the aggregate.

The present work was aimed at establishing the generality of the conclusions drawn as a result of the cobalt(III) studies and at increasing, in chromium(III) studies, the available anions to include iodide ion which is found to reduce many of the cobalt(III) cations. The rhodium(III) complexes have allowed us to study the effects of *N*-methyl substitution on the ethylenediamine ligands. Here we have used the ligands *N,N'*-dimethylethylenediamine (sdmen) and *N,N,N',N'*-tetramethylethylenediamine (tetmen).

Experimental Section

(a) **Preparation of Complexes.**—Salts of *cis*- $\text{CrCl}_2(\text{en})_2^+$ were prepared from *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}\cdot\text{H}_2\text{O}$ made following Rollinson and Bailar¹³ by crystallizing *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ with NH_4Br , *cis*- $[\text{CrCl}_2(\text{en})_2]\text{I}$ with NaI , *cis*- $[\text{CrCl}_2(\text{en})_2]\text{ClO}_4$ with LiClO_4 , and *cis*- $[\text{CrCl}_2(\text{en})_2]\text{SCN}$ with NH_4SCN . All salts were recrystallized at least twice from water, washed with ethanol and ether, and dried by vacuum desiccation. All compounds were stored for minimum periods, always in the dark. *Anal.* Calcd for *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}\cdot\text{H}_2\text{O}$: C, 16.2; H, 6.1; N, 18.8; Cl, 35.8. Found: C, 16.2; H, 6.1; N, 18.7; Cl, 35.8. Calcd for *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: Cl, 20.8; Br, 23.4. Found: Cl, 20.7; Br, 23.4. Calcd for *cis*- $[\text{CrCl}_2(\text{en})_2]\text{I}$: Cl, 19.2; I, 34.3. Found: Cl, 19.4; I, 33.9. Calcd for *cis*- $[\text{CrCl}_2(\text{en})_2]\text{ClO}_4$: C, 14.0; H, 4.7; N, 16.4; Cl, 20.7. Found: C, 14.1; H, 4.7; N, 16.3; Cl, 20.7. Calcd for *cis*- $[\text{CrCl}_2(\text{en})_2]\text{SCN}$: Cl, 23.5. Found: Cl, 23.8.

Salts of *trans*- $\text{CrCl}_2(\text{en})_2^+$ were prepared from *trans*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$ made after Pfeiffer, *et al.*,¹⁴ or Vaughn, *et al.*¹⁵ *Anal.* Calcd for *trans*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$: Cl, 38.1. Found: Cl, 38.2. Calcd for *trans*- $[\text{CrCl}_2(\text{en})_2]\text{Br}$: Cl, 22.0; Br, 24.7. Found: Cl, 22.1; Br, 24.9. Calcd for *trans*- $[\text{CrCl}_2(\text{en})_2]\text{ClO}_4$: C, 14.0; H, 4.7; N, 16.4; Cl, 20.7. Found: C, 14.1; H, 4.7; N, 16.3; Cl, 20.7.

cis- $[\text{CrBr}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ was prepared by the method of Quinn and Garner.¹⁶ *Anal.* Calcd for *cis*- $[\text{CrBr}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: C, 11.2; H, 4.2; N, 13.0; Br, 55.8. Found: C, 11.1; H, 4.2; N, 13.0; Br, 55.4.

trans- $[\text{CrBr}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ was prepared after Vaughn, *et al.*¹⁵ *Anal.* Calcd for *trans*- $[\text{CrBr}_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: Br, 55.8. Found: Br, 55.5.

cis- $[\text{CrCl}(\text{SCN})(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ was prepared by the method of House and Garner.¹⁷ *Anal.* Calcd for *cis*- $[\text{CrCl}(\text{SCN})(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: Br, 22.0. Found: Br, 21.9. *cis*- $[\text{CrBrCl}(\text{en})_2]\text{Br}$

H_2O was prepared by the analogous method. *Anal.* Calcd for *cis*- $[\text{CrBrCl}(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: C, 12.5; H, 4.7; N, 14.5; total halogen, 50.7. Found: C, 12.7; H, 4.8; N, 14.3; total halogen, 51.0.

trans- $[\text{CrBrCl}(\text{en})_2]\text{Br}$ was prepared after Jackson and Fee.¹⁸ *Anal.* Calcd for *trans*- $[\text{CrBrCl}(\text{en})_2]\text{Br}$: C, 13.1; H, 4.4; N, 15.3; total halogen, 53.1. Found: C, 13.5; H, 4.8; N, 15.6; total halogen, 53.8.

cis- $[\text{Cr}(\text{SCN})_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ was prepared by the method of Pfeiffer, *et al.*¹⁴ *Anal.* Calcd for *cis*- $[\text{Cr}(\text{SCN})_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: Br, 20.7. Found: Br, 21.0. The *trans* isomer was also prepared by the method of Rollinson and Bailar.¹³ *Anal.* Calcd for *trans*- $[\text{Cr}(\text{SCN})_2(\text{en})_2]\text{Br}$: C, 19.6; H, 4.4; N, 22.8; S, 17.4. Found: C, 20.0; H, 4.9; N, 22.8; S, 17.6.

cis- $[\text{Cr}(\text{NO}_2)_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$ was prepared after Fee, Garner, and Harrowfield.¹⁹ *Anal.* Calcd for *cis*- $[\text{Cr}(\text{NO}_2)_2(\text{en})_2]\text{Br}\cdot\text{H}_2\text{O}$: Br, 22.1. Found: Br, 21.9. The $[\text{CrCl}_2(\text{DMSO})_4]\text{ClO}_4$ salt was prepared by the method of Lo and Watts.²⁰ *Anal.* Calcd for $[\text{CrCl}_2(\text{DMSO})_4]\text{ClO}_4$: C, 18.0; H, 4.5; S, 24.0; Cl, 13.3. Found: C, 18.1; H, 4.6; S, 22.8; Cl, 13.1.

cis- and *trans*- $[\text{RhCl}_2(\text{en})_2]\text{Cl}\cdot\text{H}_2\text{O}$ were prepared following Basolo and Johnson.²¹ *Anal.* Calcd for *cis*- $[\text{RhCl}_2(\text{en})_2]\text{Cl}\cdot\text{H}_2\text{O}$: Cl, 30.6. Found: Cl, 30.6. Calcd for *trans*- $[\text{RhCl}_2(\text{en})_2]\text{Cl}$: Cl, 32.3. Found: Cl, 32.5. *cis*- $[\text{RhCl}_2(\text{sdmen})_2]\text{Cl}$ and *cis*- $[\text{RhCl}_2(\text{tetmen})_2]\text{Cl}$ were prepared after Watt and Alexander.²² *Anal.* Calcd for *cis*- $[\text{RhCl}_2(\text{sdmen})_2]\text{Cl}$: Cl, 27.6. Found: Cl, 28.1. Calcd for *cis*- $[\text{RhCl}_2(\text{tetmen})_2]\text{Cl}$: Cl, 24.1. Found: Cl, 24.0.

cis- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Br}$ was prepared as described previously²³ for the chloride salt, with NH_4Br substituted for NH_4Cl in the final conversion of the nitrate salt. *Anal.* Calcd for *cis*- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Br}$: Br, 26.7. Found: Br, 26.6.

(b) **Solvent Purification.**—All solvents were purified as before and reached the previous standards of purity.⁴

(c) **Cell Constant Determination.**—Tetrabutylammonium tetrphenylboride was prepared after Accasina, Petrucci, and Fuoss,²⁴ and the cell constant was determined by their method.

(d) **Conductance Measurements.**—These measurements were made on equipment as previously described⁴ making similar allowances for solvolysis reactions by extrapolation of all measurements at all frequencies to zero time. These solvolysis reactions were found in general to be slower than in the cobalt(III) systems and thus produced less uncertainty. A number of complexes, in particular those of Rh(III), were sufficiently inert to allow a first-order extrapolation of resistance to zero time. However on the whole the standard deviations of results in the present systems were slightly greater than in the cobalt(III) systems. The source of this greater error is logically traced to the greater inherent difficulties associated with the chromium and rhodium preparations and at least in the chromium case with the photochemical instability of the complexes.²⁵

Duplicate runs using both the anhydrous and monohydrate forms of the *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$ complex gave identical results indicating the presence of water in such small concentrations did not affect the conductivity.

In the present work a deliberate attempt has been made to obtain association constants for weakly associating anions such as perchlorate and iodide which were not previously studied.

In some cases the Fuoss–Onsager–Skinner treatment of the results for weakly associating ion pairs gave negative association constants. This is not a function of our data since the data of

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Sears, Lester, and Dawson²⁶ for such weakly associating electrolytes as NaNO₃, NaClO₄, and NaI in DMSO when treated by this equation also yield negative association constants. The occurrence of negative values using this treatment has been fully discussed by Fuoss, Onsager, and Skinner³ in the presentation of their conductance equation. It is sufficient to mention that for association constants greater than 10, reproducible values were obtained within the computed standard deviations in K_{IP} from duplicate runs. The simpler Fuoss-Kraus equation²⁷ was tested in these cases and gave realistic association constants in most cases as indicated in the tabulated results. The results for these systems were also tested for compatibility with the Fuoss two-parameter equation for totally dissociated electrolytes³ and these results are also tabulated. The weakness of the association in these cases is emphasized by their linear Λ vs. \sqrt{c} plots. The fact that the incompatibility of the conductance data and the Fuoss-Onsager-Skinner equation indicated very weak association proved to be consistent with the expectations of our established generalizations. The viscosities and dielectric constants used were as previously, except where specified in the tables.

Results

The molar conductance (Λ) results were extrapolated to zero time and then to infinite frequency for various molar concentrations (c). Conductance and concentration ranges for each salt are presented in Table I. Table II gives tabulated values of Λ_0 , K_{IP} , and the standard free energies of association (ΔG°_{IP}), together with the constants for the Fuoss-Onsager-Skinner equation.²⁸

Table III presents limiting molar ionic conductances which were calculated as previously⁴ using the then acknowledged data for chloride and bromide ion except where indicated in the table.

Discussion

The previous results on cobalt(III) complexes in the same solvents established the following trends whose generalities were under test in the present study: (a) in all three solvents chloride ion associates more strongly than bromide ion and both would be predicted to associate more strongly than iodide ion; (b) trans ions exhibit association constants very much lower than the isomeric cis ions; (c) for cis salts in DMSO, association constants decrease in the order $cis\text{-CoCl}_2(\text{en})_2^+ > cis\text{-CoBrCl}(\text{en})_2^+ > cis\text{-CoBr}_2(\text{en})_2^+$ for association with both chloride and bromide ions; that is, association constants decrease with decreasing dipole moment of the cation; (e) ion association constants for the same ion pair vary with solvent being greatest for DMA and decreasing in the order DMA > DMF > DMSO; (f) all the association constants were considerably greater than those found for ions of similar size but not possessing acidic protons which provide specific sites for H-bonding interactions with anions.

All these observations were rationalized purely in terms of factors which influence the magnitude of the

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(28) $\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + E'c\gamma \ln(6E'ic\gamma) + Lc\gamma - K_{IP}c\gamma_{\pm}^2\Lambda$, where c is molar concentration, Λ is molar conductance, Λ_0 is limiting molar conductance, γ is the degree of dissociation, f_{\pm} is the mean molar activity coefficient (f_{\pm} was calculated according to the equation described by Fuoss, Onsager, and Skinner³ and the values were provided for each concentration as part of the computer output), and S , E' , E' , and L are parameters as previously defined.³

TABLE I
THE RANGE OF MOLAR CONCENTRATIONS AND MOLAR CONDUCTANCES USED FOR EACH SALT IN DMSO, DMF, AND DMA AT 25°

Salt	10 ⁴ c, M	Λ , (intern. ohm) ⁻¹ cm ² mol ⁻¹
DMSO Solvent		
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	0.8492-32.53	32.52-21.06
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	1.194-37.44	32.84-27.40
<i>cis</i> -[CrCl ₂ (en) ₂]I	1.461-36.54	32.56-29.87
<i>cis</i> -[CrBrCl(en) ₂]Br·H ₂ O	2.658-39.10	32.70-27.09
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	0.7209-15.68	33.70-30.39
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	1.792-23.15	31.46-27.46
<i>cis</i> -[Co(NO ₂) ₂ (NH ₃) ₄]Br	1.468-51.07	33.13-28.95
<i>trans</i> -[CrCl ₂ (en) ₂]Cl	1.538-48.79	34.29-30.30
<i>trans</i> -[CrCl ₂ (en) ₂]Br	1.391-36.14	33.54-31.24
<i>trans</i> -[CrCl ₂ (en) ₂]ClO ₄	1.193-26.34	34.15-32.45
<i>trans</i> -[CrBrCl(en) ₂]Br	1.655-34.75	35.44-32.36
<i>trans</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	1.200-27.91	33.75-32.09
<i>trans</i> -[Cr(SCN) ₂ (en) ₂]Br	2.248-39.16	32.09-29.72
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O (30°)	1.001-32.40	35.85-23.25
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O (35°)	1.084-31.68	39.16-25.54
<i>cis</i> -[RhCl ₂ (en) ₂]Cl·H ₂ O	1.285-29.41	30.28-20.29
<i>cis</i> -[RhCl ₂ (sdmen) ₂]Cl	0.7739-35.97	37.55-33.73
<i>cis</i> -[RhCl ₂ (tetmen) ₂]Cl	1.754-21.76	34.13-32.72
<i>trans</i> -[RhCl ₂ (en) ₂]Cl	2.327-30.59	32.98-30.51
DMF Solvent		
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	0.9618-46.44	54.64-13.52
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	1.617-37.32	67.66-35.24
<i>cis</i> -[CrCl ₂ (en) ₂]I	2.160-29.54	71.83-61.22
<i>cis</i> -[CrCl ₂ (en) ₂]SCN	2.665-25.63	79.37-71.57
<i>cis</i> -[CrCl ₂ (en) ₂]ClO ₄	0.7037-33.91	75.47-67.56
<i>cis</i> -[CrBrCl(en) ₂]Br·H ₂ O	1.045-30.73	70.58-37.04
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	1.008-24.98	70.92-38.68
<i>cis</i> -[CrCl(SCN)(en) ₂]Br·H ₂ O	0.9274-22.59	67.17-38.04
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	0.7891-21.52	68.53-38.68
<i>cis</i> -[Cr(NO ₂) ₂ (en) ₂]Br·H ₂ O	1.181-38.64	70.99-35.74
<i>cis</i> -[CoBr ₂ (en) ₂]Br·H ₂ O	0.9970-30.30	68.39-33.55
[CrCl ₂ (DMSO) ₄]ClO ₄	0.8547-14.03	68.79-65.16
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O (15°)	1.174-46.82	45.80-12.17
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O (35°)	1.189-46.91	58.48-15.59
DMA Solvent		
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^a	0.9516-28.50	37.30-9.894
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	1.139-41.61	54.60-22.88
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	1.064-26.79	57.69-26.93

^a The results for this system were treated using the Fuoss-Kraus equation²² which, as found previously,⁴ behaves better with data for very strongly associated electrolytes.

interaction between the associating anion and cation; that is, there appeared to be a good correspondence between the free energy of ion-pair formation and the magnitude of electrostatic interactions between the associating ions. This is perhaps best expressed by saying that modification in the charge nature of a singly charged positive ion by the introduction of a dipole moment or local H-bonding sites has a more noticeable effect on interionic interactions than on the interactions of this ion with the dipolar solvents. Generally the ion association constants lack the precision necessary to produce temperature-dependent data from which reliable enthalpy and entropy terms can be deduced. When comparing these similar cations in closely similar reactions it is likely that the free energy of association is less sensitive to the types of changes we have introduced

TABLE II
LIMITING MOLAR CONDUCTANCES (Λ_0), ASSOCIATION CONSTANTS (K_{IP}), AND STANDARD FREE ENERGIES OF ASSOCIATION (ΔG°_{IP}) FOR ALL SYSTEMS STUDIED TOGETHER WITH THE CONSTANTS FITTING THE FUOSS-ONSAGER-SKINNER EQUATION AND THE STANDARD DEVIATIONS (RESULTS AT 25° EXCEPT WHERE SPECIFIED)

Salt	Λ_0 , (intern. ohm) ⁻¹ cm ² mol ⁻¹	S	E'	L	K_{IP}	σ_A	$-\Delta G^\circ_{IP}$, kcal mol ⁻¹
DMSO Solvent							
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	33.75 ± 0.02	52.62	25.57	224.2	291 ± 5	0.02	3.36
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	33.70 ± 0.02	52.59	25.51	1488	123 ± 6	0.03	2.85
<i>cis</i> -[CrCl ₂ (en) ₂]I	33.10 ± 0.06	52.29	24.86	-1067	-52 ± 11 ^e	0.06	
	33.32 ± 0.09 ^f	52.40	25.09	53.47		0.13	
	33.13				5 ± 2 ^g		0.96
<i>cis</i> -[CrClBr(en) ₂]Br·H ₂ O	34.16 ± 0.04	52.82	26.02	822.4	99 ± 6	0.03	2.72
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	34.25 ± 0.04	52.86	26.11	394.6	61 ± 23	0.04	2.44
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	32.53 ± 0.07	52.00	24.23	309.4	70 ± 21	0.05	2.52
<i>cis</i> -[Co(NO ₂) ₂ (NH ₃) ₄]Br	33.85 ± 0.07	52.67	25.68	51.21	10 ± 10	0.08	1.37
<i>trans</i> -[CrCl ₂ (en) ₂]Cl	35.04 ± 0.03	53.26	26.98	379.6	25 ± 6	0.03	1.91
<i>trans</i> -[CrCl ₂ (en) ₂]Br	34.21 ± 0.04	52.84	26.07	412.6	12 ± 9	0.04	1.47
<i>trans</i> -[CrCl ₂ (en) ₂]ClO ₄	34.71 ± 0.05	53.10	26.62	-999.6	-52 ± 17 ^e	0.05	
	34.84 ± 0.05 ^f	53.16	26.77	264.5		0.08	
<i>trans</i> -[CrClBr(en) ₂]Br	36.29 ± 0.00	53.89	28.36	1404	66 ± 0.2	0.00	2.48
<i>trans</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	34.34 ± 0.03	52.91	26.22	1112	34 ± 9	0.02	2.09
<i>trans</i> -[Cr(SCN) ₂ (en) ₂]Br	32.83 ± 0.03	52.15	24.56	-267.1	-19 ± 5 ^e	0.02	
	32.91 ± 0.04 ^f	52.20	24.65	122.0		0.05	
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^{a,d}	37.34 ± 0.07	52.55	27.27	19.29	285 ± 13	0.05	3.41
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^{b,d}	40.86 ± 0.07	57.83	30.13	-192.2	270 ± 12	0.07	3.43
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^d	33.71 ± 0.02	46.97	24.45	235.9	298 ± 5	0.02	3.37
<i>cis</i> -[RhCl ₂ (en) ₂]Cl·H ₂ O	31.91 ± 0.13	51.69	23.55	-192.3	259 ± 31	0.11	3.29
<i>cis</i> -[RhCl ₂ (sdmen) ₂]Cl	38.14 ± 0.05	54.81	30.38	1221	60 ± 11	0.05	2.43
<i>cis</i> -[RhCl ₂ (tetmen) ₂]Cl	34.77 ± 0.01	53.13	26.69	-550.4	-33 ± 5 ^e	0.01	
	34.83 ± 0.03 ^f	53.16	26.75	291.7		0.04	
<i>trans</i> -[RhCl ₂ (en) ₂]Cl	33.83 ± 0.02	52.66	25.66	174.2	9 ± 6	0.02	1.30
	33.81 ± 0.01 ^f	52.64	25.63	-23.61		0.02	
DMF Solvent							
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	77.06 ± 1.79	154.27	127.46	16.92	5,969 ± 371	0.97	5.15
	77.10				5,984 ^g		5.15
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	75.65 ± 0.48	153.27	124.31	-255.7	641 ± 42	0.34	3.83
<i>cis</i> -[CrCl ₂ (en) ₂]I	74.64 ± 0.06	152.54	122.03	-400.8	26 ± 6	0.05	1.93
<i>cis</i> -[CrCl ₂ (en) ₂]SCN	83.11 ± 0.13	158.61	141.05	4886	124 ± 14	0.07	2.86
<i>cis</i> -[CrCl ₂ (en) ₂]ClO ₄	76.80 ± 0.07	154.09	126.88	-19.36	-7 ± 6 ^e	0.07	
	76.87 ± 0.05 ^f	154.14	127.05	296.3		0.07	
	76.80				2 ± 1 ^g		0.41
<i>cis</i> -[CrClBr(en) ₂]Br·H ₂ O	76.91 ± 0.31	154.71	127.14	-37.01	727 ± 31	0.26	3.90
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	77.99 ± 0.22	154.94	129.56	1718	913 ± 24	0.15	4.04
<i>cis</i> -[CrCl(SCN)(en) ₂]Br·H ₂ O	72.86 ± 0.26	151.27	118.05	-255.2	747 ± 39	0.21	3.92
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	73.82 ± 0.20	151.95	120.20	865.5	836 ± 29	0.14	3.99
<i>cis</i> -[Cr(NO ₂) ₂ (en) ₂]Br·H ₂ O	77.57 ± 0.47	154.64	128.60	-109.0	655 ± 42	0.36	3.84
<i>cis</i> -[CoBr ₂ (en) ₂]Br·H ₂ O	75.54 ± 0.47	153.19	124.06	126.4	953 ± 37	0.26	4.06
[CrCl ₂ (DMSO) ₄]ClO ₄	70.22 ± 0.14	149.37	112.11	-1623	-48 ± 40 ^e	0.13	
	70.35 ± 0.10 ^f	149.47	112.41	740.5		0.13	
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^{c,h}	65.97 ± 2.59	133.20	103.94	225.3	5,319 ± 536	1.33	4.91
	66.50				5,540 ^g		4.94
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O ^{b,h}	85.32 ± 1.58	175.11	146.45	397.6	5,591 ± 263	0.75	5.28
	85.40				5,632 ^g		5.29
DMA Solvent							
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	64.41				13,180 ^g		5.61
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	61.56 ± 0.58	126.83	89.56	-133.9	1,082 ± 64	0.47	4.14
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	65.35 ± 1.35	129.43	97.36	-374.2	1,231 ± 186	1.00	4.22

^a Results at 30°. ^b Results at 35°. ^c Results at 15°. ^d Using dielectric constants and viscosity data of G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.*, **73**, 5731 (1951). ^e Results not compatible with Fuoss-Onsager-Skinner equation;³ negative values of K_{IP} arise from weakly associated electrolytes. ^f Λ_0 and parameters calculated from Fuoss two-parameter equation.³ ^g Results which yield very high or negative values for K_{IP} were calculated, as in Co(III) complex results in DMA,⁴ from the simple Fuoss-Kraus equation.²⁷ ^h Temperature-dependent viscosity data were kindly supplied by Professor P. G. Sears.

because of an anticipated favorable entropy of association which must be taken in conjunction with an unfavorable enthalpy, for changes within the one solvent system.²⁹ However, the effect of hydrogen bonding is

likely to have a more significant effect on the enthalpy term.³⁰

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TABLE III

TOTAL AND IONIC LIMITING CONDUCTANCES AT 25° ((INTERN. OHM)⁻¹ CM² MOL⁻¹) AND CORRESPONDING STOKES RADII FOR THE COMPLEX CATIONS (Å)

	λ_0	λ_0^-	λ_0^+	R_{ST}
DMSO Solvent				
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	33.75	24.9 ^a	8.9	4.7
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	33.70	24.7	9.0	4.7
<i>cis</i> -[CrCl ₂ (en) ₂]I	33.10	24.3	8.8	4.7
	33.32	24.3	9.0 ^c	4.7
<i>cis</i> -[CrBrCl(en) ₂]Br·H ₂ O	34.16	24.7	9.5	4.4
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	34.25	24.7	9.6	4.3
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	32.53	24.7	7.8	5.4
<i>cis</i> -[Co(NO ₂) ₂ (NH ₃) ₄]Br	33.85	24.7	9.2	4.5
<i>trans</i> -[CrCl ₂ (en) ₂]Cl	35.04	25.5 ^a	9.5	4.4
<i>trans</i> -[CrCl ₂ (en) ₂]Br	34.21	24.7	9.5	4.4
<i>trans</i> -[CrCl ₂ (en) ₂]ClO ₄	34.71	25.2	9.5	4.4
	34.84	25.2	9.6	4.3
<i>trans</i> -[CrBrCl(en) ₂]Br	36.29	24.7	11.6	3.6
<i>trans</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	34.34	24.7	9.6	4.3
<i>trans</i> -[Cr(SCN) ₂ (en) ₂]Br	32.83	24.7	8.1	5.2
	32.91	24.7	8.2 ^c	5.1
<i>cis</i> -[RhCl ₂ (en) ₂]Cl·H ₂ O	31.91	24.9	7.0 ^b	6.0
<i>cis</i> -[RhCl ₂ (sdmen) ₂]Cl	38.14	24.9	13.2 ^b	3.2
<i>cis</i> -[RhCl ₂ (tetmen) ₂]Cl	34.77	24.9	9.9 ^b	4.2
	34.83	24.9	9.9 ^{b,c}	4.2
<i>trans</i> -[RhCl ₂ (en) ₂]Cl	33.83	24.9	8.9 ^b	4.7
	33.81	24.9	8.9 ^{b,c}	4.7
DMF Solvent				
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	77.06	55.1	22.0	4.7
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	75.65	53.6	22.1	4.7
<i>cis</i> -[CrCl ₂ (en) ₂]I	74.64	52.3	22.3	4.6
<i>cis</i> -[CrCl ₂ (en) ₂]SCN	83.11	59.7	23.4	4.4
<i>cis</i> -[CrCl ₂ (en) ₂]ClO ₄	76.80	52.4	24.4	4.2
	76.87	52.4	24.5 ^c	4.2
<i>cis</i> -[CrBrCl(en) ₂]Br·H ₂ O	76.91	53.6	23.3	4.4
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	77.99	53.6	24.4	4.2
<i>cis</i> -[CrCl(SCN)(en) ₂]Br·H ₂ O	72.86	53.6	19.3	5.3
<i>cis</i> -[Cr(SCN) ₂ (en) ₂]Br·H ₂ O	73.83	53.6	20.2	5.1
<i>cis</i> -[Cr(NO ₂) ₂ (en) ₂]Br·H ₂ O	77.57	53.6	24.0	4.3
<i>cis</i> -[CoBr ₂ (en) ₂]Br·H ₂ O	75.54	53.6	21.9	4.7
[CrCl ₂ (DMSO) ₄]ClO ₄	70.22	52.4	17.8	5.8
	70.35	52.4	18.0 ^c	5.7
DMA Solvent				
<i>cis</i> -[CrCl ₂ (en) ₂]Cl·H ₂ O	64.41	46.0 ^a	18.4	4.8
<i>cis</i> -[CrCl ₂ (en) ₂]Br·H ₂ O	61.56	43.2	18.4	4.8
<i>cis</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	65.35	43.2	22.2	4.0

^a The values of λ_0^- for chloride ion were calculated from the average value of λ_0^+ calculated for similar cations. ^b The value for λ_0^+ was derived from the values for λ_0^- of the chloride ion estimated above. ^c Results using the Fuoss two-parameter equation.³

The present results confirm the conclusions (a), (b), (c), (e), and (f), but (c), which one might reasonably have expected to apply to measurements in all three solvents, is not found to hold in the present results in DMF and DMA. In addition to these previous generalizations it can now be said that ion association constants for univalent cobalt(III) complexes are for the most part slightly greater than for the analogous chromium(III) complexes which in turn, on less evidence, are greater than for analogous rhodium(III) complexes. These differences are small, as exemplified by K_{IP} for the analogous series of ion pairs *cis*-[CoCl₂(en)₂]⁺Cl⁻, *cis*-[CrCl₂(en)₂]⁺Cl⁻, and *cis*-[RhCl₂(en)₂]⁺Cl⁻ for which values of 397 ± 10, 291 ± 5, and 259 ± 31 were obtained in DMSO at 25°. The results also show, in

addition to confirming (a) in relation to the relative associating properties of chloride and bromide ions, that one can extend this generality to Cl⁻ > Br⁻ > SCN⁻ > I⁻ > ClO₄⁻ although, for the most part, attempts to evaluate constants for ClO₄⁻ have produced meaningless negative values. Such an order is consistent with the anticipations of Parker, *et al.*^{12,31} Although it would appear that (b) will prove to be universally applicable and that dipolar cations of the *cis* configuration will more strongly associate with anions, the results in DMF, where an extended range of coordinated ligands has been employed, suggest that generalizations of the type (c) are not valid. Clearly the variation in solvation energy produced by substituting a bromide or a thiocyanate ligand for one of two *cis* chloride ligands can be at least as important as the coincident change in interionic interaction. Thus the change in dipole moment through a series of complexes of the type *cis*-MXY(en)₂⁺ will not necessarily produce a correlation between the complex dipole moment and the ion association constant which is independent of other factors. This is clearly shown by the series of complexes *cis*-CrCl₂(en)₂⁺, *cis*-CrBrCl(en)₂⁺, and *cis*-CrBr₂(en)₂⁺ which in this order show a gradual decrease in K_{IP} in DMSO and an equally significant increase in K_{IP} in DMF. The importance of the variation in solvation energy is emphasized by the low association constant for the *cis*-[Co(NO₂)₂(NH₃)₄]⁺Br⁻ ion pair in DMSO. Here the extra nitrogen protons, compared with the "en" complexes, while not significant in increasing the interaction of the anion with the cation, provide a series of sites for hydrogen bond enhanced solvation.

In DMSO we also attempted, for the more weakly associating *trans* isomers, to see if increasing polarizability of the anionic ligands would correlate with a predominance of the greater solvation energy of the cation and thus a weaker ion association. Alternatively a correlation could have been expected with the introduction of a dipole moment into the *trans* series. A comparison of the results for the ion pairs *trans*-[CrCl₂(en)₂]⁺Br⁻, *trans*-[CrBrCl(en)₂]⁺Br⁻, *trans*-[CrBr₂(en)₂]⁺Br⁻, and *trans*-[Cr(SCN)₂(en)₂]⁺Br⁻ clearly shows that no such correlation is valid, although it is certainly significant that the introduction of a dipole moment into a *trans* complex increases K_{IP} over the value for the symmetrical complex irrespective of the nature of the anionic ligands.

The role of the nitrogen protons *trans* to *cis*-oriented anionic ligands in facilitating ion association, (f) above, has been emphasized by kinetic results,^{6,32} by the magnitude of ion association constants,⁴ and by observation of the chemical shift associated with these protons in the pmr spectrum.⁴ The results for the complexes *cis*-RhCl₂(en)₂⁺, *cis*-RhCl₂(sdmen)₂⁺, and *cis*-RhCl₂(tetmen)₂⁺ add further weight to these conclusions. The *N*-methyl substitution has a considerably larger effect on the association constant than would be

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expected from the 1.00:1.23:1.28 relative increase in ion size predicted by models. The total substitution of the N protons leads us again into the region of weak ion association where our results are not compatible with this treatment. All these effects are also emphasized in the results for the complex salt $[\text{CrCl}_2(\text{DMSO})_4]^+\text{ClO}_4^-$ in DMF.

It is tempting to speculate on the order found for the dependence of K_{IP} on the metal, namely, $K_{\text{IP}}(\text{Co(III)}) > K_{\text{IP}}(\text{Cr(III)}) > K_{\text{IP}}(\text{Rh(III)})$. Because of the overall size of the solvated cations which must be taken, at least at first, as invariant and because of the identity of the charge type, one might have expected a dependence either on the dipole moment of the complexes, which would be dependent on the polarizability of the metal ($\text{Cr} > \text{Co} > \text{Rh}$), or on the acidity of the nitrogen protons (probably $\text{Rh} > \text{Cr} > \text{Co}$).³³ The present results suggest that neither of these two effects predominates. It may be significant that the order of rates of base hydrolysis is $\text{Co(III)} \gg \text{Cr(III)} > \text{Rh(III)}$.

In DMSO and DMF a temperature-dependent study was attempted for the *cis*- $[\text{CrCl}_2(\text{en})_2]^+\text{Cl}^-$ ion pair. The variation of K_{IP} in DMSO for a 10° range in temperature was just beyond the limit of standard deviation in K_{IP} and gave ΔH° and ΔS° for ion association of $-2.1 \pm 0.4 \text{ kcal mol}^{-1}$ and $4.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$ as previ-

ously published. These results closely resemble the thermodynamic data derived from spectrophotometric techniques by Millen and Watts³⁴ for the association of *cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ in DMSO. However, the results in DMF show that the variation in K_{IP} over a 10° range in temperature is not beyond the standard deviation and casts doubt on the value for DMSO. An improvement in the precision of determination or the use of solvolysis-resistant complexes allowing the use of a greater temperature range appears essential to develop this aspect further.

The limiting molar ionic conductances of these chromium and rhodium complex cations are for the most part experimentally indistinguishable from the values previously obtained for the analogous Co(III) complexes. This can only serve to emphasize that the solvation of the analogous complexes is closely similar and lends support to our tendency to ascribe changes in ion association constants to predominant effects in the anion-cation interaction. It is notable that the new complexes involving larger more polarizable anionic ligands, such as SCN^- , show significantly smaller values of λ_0^+ , correlating with increased solvation.

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Kinetics of the First-Stage Aquation of *trans*-Dichlorobis(propylenediamine)chromium(III) Cation

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The first-order rate constant for the disappearance of *trans*- $\text{Cr}(\text{pn})_2\text{Cl}_2^+$ in 0.10 *F* HNO_3 at $35.04 \pm 0.04^\circ$ in the absence of light was found to be $(12.62 \pm 0.03) \times 10^{-6} \text{ sec}^{-1}$. The first-stage aquation of this complex gave three products—*trans*- $\text{Cr}(\text{pn})_2(\text{OH}_2)\text{Cl}^{2+}$, pink $\text{Cr}(\text{pn})(\text{OH}_2)_2\text{Cl}_2^+$, and *cis*- $\text{Cr}(\text{pn})_2(\text{OH}_2)\text{Cl}^{2+}$ with first-order rate constants of formation of $(8.14 \pm 0.18) \times 10^{-5}$, $(1.01 \pm 0.01) \times 10^{-5}$, and $(3.42 \pm 0.38) \times 10^{-5} \text{ sec}^{-1}$, respectively. The two former products are previously unreported and were isolated in solution and their visible absorption spectra were determined. The chloride release rate constant for *trans*- $\text{Cr}(\text{pn})_2\text{Cl}_2^+$ was studied under the same conditions as the rate of disappearance of the complex and found to be $(11.62 \pm 0.07) \times 10^{-6} \text{ sec}^{-1}$.

Following the successful synthesis of *trans*-dichlorobis(propylenediamine)chromium(III) chloride,² the kinetics of the aquation of this complex has been investigated. The present study provides a means of (a) checking some of the possible reaction paths postulated for the acid hydrolysis of *cis*-dichlorobis(propylenediamine)chromium(III) cation,³ (b) comparing this bis-

(propylenediamine)chromium(III)⁴ complex with its ethylenediamine analog,⁵ and (c) determining whether Cr–N bond breakage competes significantly with Cr–Cl bond breaking as has been reported for some similar systems.^{5,6} A combination of techniques including ion-exchange chromatography, spectrophotometric identification of eluted fractions, and chloride release

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