

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

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Abstract. Ion-pair association constants have been determined from conductance measurements for the association of chloride and bromide ions with cations of the type *cis*- and *trans*-[CoXY(en)₂]⁺, where "en" represents ethylenediamine, and X and Y represent either of the ligands chlorine or bromine. The data have been treated by the equation of Fuoss, Onsager, and Skinner.² The solvents investigated are N,N-dimethylformamide, N,N-dimethylacetamide, and dimethyl sulfoxide. The results are presented together with limiting ionic conductances at 25°. The results emphasize that both the dipolar nature of the *cis* complexes and the hydrogen-bond donor properties of the weakly acid nitrogen protons of the ethylenediamine ligands are important in the association process.

During the past decade it has been firmly established that ion association plays an important role in the mechanism of solution reactions. This feature has become more apparent because of the development of research into the mechanism of reaction of coordination compounds where a great proportion of the work has involved the study of ionic reactions.

Taube and Posey³ emphasized the importance of fast ion association equilibria prior to rate-determining processes in substitution in coordination compounds in water, and since then much has been recorded on such reactions in both aqueous and nonaqueous media.⁴⁻⁸ Basolo, Henry, and Pearson⁹ elegantly showed that ion association was important in the reactions of the dichlorobis(ethylenediamine)cobalt(III) complexes in the protic solvent methanol and at the same time pointed to hydrogen bonding as an important contributing factor in this ion association for basic anions such as azide. They concluded that hydrogen bonding could lead to the establishment of specific association sites on the surface of large cations and also suggested that such interactions would increase the stability of dissociative intermediates by polarization of the complex ion.

The increasing importance of aprotic solvents as media for substitution studies has emphasized the significance of ion association in all fields of kinetics.^{10,11} Although the aprotic solvents, N,N-dimethylformamide

(DMF), N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and tetramethylene sulfone (TMS) have dielectric constants comparable to the protic solvent methanol,¹⁰ they are found relative to methanol to promote ion association. This trend is greater for small anions because there is poor anion solvation when the solvent cannot act as a hydrogen-bond donor.¹⁰

Although many effects have been explained by invoking ion association, there have been only a few attempts to investigate in detail the physical chemistry of solutions actually involved in the systems of kinetic interest. The reasons for this lie in the difficulties of making accurate time-consuming measurements on reacting solutions and in the uncertainties involved in the extrapolation for zero-time data.

The mechanism of reaction of complexes of the type *cis*- and *trans*-[CoXY(en)₂]⁺ has been much investigated in both protic¹² and aprotic⁸ solvents. These results had indicated considerable ion association and suggested that the systems would make an excellent model for the investigation of ion association by conductance and spectrophotometric^{5b} techniques, especially in that the lability is such that measurements can be extrapolated with the required certainty to zero time.

In this study we have investigated complexes of both *cis* and *trans* configuration where X and Y are the ions chloride and bromide and the associated anion is either chloride or bromide in the solvents DMF, DMA, and DMSO. Since we have in the collection of results both symmetrically charged cations, asymmetrically charged cations of varying dipole, and associating anions of differing hydrogen-bond acceptor properties, it has been possible to establish some generalizations of wide application.

Experimental Section

Preparation of Complexes. (a) The preparation of these complexes has been described in previous publications of this group⁸ or is well established.¹³ All complexes were recrystallized from ice

(1) (a) Part XI: I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, in press; (b) part X: W. R. Fitzgerald and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 815 (1967).

(2) R. M. Fuoss, L. Onsager, and J. R. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

(3) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(4) M. L. Tobe, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **27**, 79 (1966).

(5) (a) M. N. Hughes and M. L. Tobe, *J. Chem. Soc.*, 1204 (1953);

(b) M. L. Tobe and D. W. Watts, *ibid.*, 4614 (1962); 299 (1964).

(6) S. C. Chan and F. Leh, *ibid.*, Sect. A, 126, 129, 134, 138, 142 (1966).

(7) B. Bosnich, J. Ferguson, and M. L. Tobe, *ibid.*, 1636 (1966).

(8) (a) D. W. Watts, *et al.*, *Australian J. Chem.*, **18**, 453 (1965);

(b) *ibid.*, **19**, 43 (1966); (c) *ibid.*, **19**, 51 (1966); (d) *J. Am. Chem. Soc.*, **89**, 821 (1967).

(9) F. Basolo, P. M. Henry, and R. G. Pearson, *ibid.*, **79**, 5379, 5582 (1957).

(10) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(11) A. J. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967).

(12) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(13) A. Werner, *Ann.*, **386**, 1 (1912).

water using either tetraethylammonium chloride or bromide as a precipitant, as appropriate. Carbon, hydrogen, and nitrogen analyses agreed to better than 1% and free and coordinated halide analyses to better than 0.5%. Some compounds were recrystallized as hydrates and used in this form since absolute drying in many cases led to decomposition or substitution of free anion for coordinated anion. This small amount of water had no detectable effect on the conductance or association results. The ethylenediamine complexes were used in the following forms: *cis*-[CoCl₂(en)₂]Cl·H₂O, *cis*-[CoCl₂(en)₂]Br·H₂O, *cis*-[CoBrCl(en)₂]Cl·0.5H₂O, *cis*-[CoBrCl(en)₂]Br, *cis*-[CoBr₂(en)₂]Br·H₂O, *trans*-[CoCl₂(en)₂]Cl, and *trans*-[CoCl₂(en)₂]Br.

The triethylenetetramine (trien) complexes (*cis*- α -[CoCl₂(trien)]Cl and *cis*- β -[CoCl₂(trien)]Cl·0.5H₂O) were prepared by the method of Searle¹⁴ and were supplied by Fitzgerald.¹⁵

(b) The solvents DMF, DMA, and DMSO were purified as previously; the final distillation was always at <2 mm pressure and <40°. Solvents were stored in the dark under dry nitrogen but never for more than 24 hr. Typical densities, refractive indices, and conductances are given in Table I. 1,2-Dichloroethane used in the cell-constant determination was distilled sharply at 83.3° at atmospheric pressure.

Table I. Solvent Properties at 25°

	Density	Refractive index	Conductance, ohm ⁻¹ cm ⁻¹	Dielectric constant
DMA	0.9362 ₄	1.4373 ₂	3.0–5.0 × 10 ⁻⁸	37.8 ^c
DMF	0.9440 ₆	1.4300 ₆	0.6–1.0 × 10 ⁻⁷	37.2 ^b
DMSO	1.0955 ₆	1.4767 ₄	2.5–7.0 × 10 ⁻⁸	48.0 ^a

^a H. L. Schaffer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960). ^b S. J. Bass, W. I. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 503 (1964). ^c G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

(c) Tetrabutylammonium tetraphenylborate, which was used in the cell-constant determination was prepared by the method of Accasina, Petrucci, and Fuoss¹⁶ and melted in the range 236–237°.

(d) The conductance cell requirements for this type of work have been discussed by Fuoss and Nichol,¹⁷ and their cell design with the following two modifications was used in this work. Firstly, a Teflon rod was machined to fit inside the outer tube electrode lead. This supported the platinum wire lead to the inner concentric electrode. This use of Teflon eliminated the glass tubing and thus glass-platinum seals used in the Nichol and Fuoss cell. Secondly, instead of the standard Teflon taper originally used for the cell cap, our electrode system was fitted to a glass disk 8.8 cm in diameter and 0.8 cm thick. Apertures in the disk were fitted with B14 cones and standard 4BA terminals. This entire disk fitted the cell vessel which was cylindrical, 7.0 cm in diameter and 10.5 cm in height flattened at the top to give a ground rim 1 cm broad. The system was sealed by B14 ground-glass stoppers and around the rim by a neoprene gasket and a set of three metal clips. The cell constant varied from 0.04628 to 0.04631 cm⁻¹ during the study.

Thermostated conditions ($\pm 0.002^\circ$) were maintained in an insulated oil bath using a mercury-toluene regulator coupled with a Sunvic control system. Temperatures were measured to 0.002°, using a 36-cm, 6°-range thermometer calibrated against a platinum resistance thermometer.

A Jones conductivity bridge (Leeds and Northrup No. 4666) was used with a variable-frequency oscillator as the source of alternating voltage and a three-stage tuned amplifier as the detector coupling the amplified out-of-balance signal to the Y plates of a double-beam cathode ray oscilloscope. This setup has been previously described.¹⁸

(e) The procedure developed for the conductance measurements was chosen because of the unstable nature of the solutions. The reactions in all cases involved solvolysis and isomerization; however, as they occurred in the conductance cells, they were faster

than the rate constants previously measured⁸ would have suggested. This appears to be associated with catalysis at the platinum electrode surfaces.

About 230 ml of pure solvent was weighed into the cell vessel. The whole cell was placed into the thermostat so that the level of the solvent was 6 cm below the oil surface. A calibrated resistor (9960.1 ohms at 25°) was connected in parallel with the cell. After allowing 20 min for thermal equilibration, the solvent was thoroughly stirred by means of a rotating Teflon-covered bar magnet inside the cell. The resistance of the parallel system was measured and the solvent conductance thus obtained.

A weighed amount of solute was introduced through a B14 aperture by means of a platinum bucket and suspended above the solvent. The stirring magnet was again activated and the bucket firstly tipped to introduce the solute and then immersed in the solvent. At this stage a stopclock was started. Stirring was continued for from 3 to 15 min, depending on the speed of the solution process. When the solution process was judged complete, resistance measurements were commenced, recording values at known times from the commencement of the solution process at frequencies 556, 1250, and 5000 cps and over a period of 15–20 min. The values were extrapolated by a best-fit, second-order polynomial to zero time and then after Nichol and Fuoss¹⁷ by a best-fit, second-order polynomial in inverse root frequency to infinite frequency.

The unweighted molar concentration (*c*) and molar conductance (Λ) data were fitted to the Fuoss–Onsager–Skinner² function for associated electrolytes

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + E'c\gamma \ln(6E_1'c\gamma) +$$

$$Lc\gamma - K_{IP}c\gamma f_{\pm}^2\Lambda$$

where Λ_0 is the limiting molar conductance, γ is the degree of dissociation, f_{\pm} is the mean molar activity coefficient, and *S*, E_1' , E' , and *L* are parameters as defined previously.²

Because of the low concentrations used, solvent densities and viscosities were used in lieu of solution values in all calculations. This function was found not applicable for *cis*-[CoCl₂(en)₂]⁺Cl⁻ association in DMA where the association constant was too high. In this case the simpler Fuoss expression¹⁹

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Delta f_{\pm}^2}{K_{IP}\Lambda_0^2 F(z)}$$

where all symbols are as above except *F*(*z*), which has been defined,¹⁹ was used. The results for *cis*-[CoCl₂(en)₂]⁺Cl⁻ in DMF were treated by both functions and gave identical results.

Failures were not infrequent in these experiments because of solubility difficulties associated with the state of subdivision of the solute. In some cases the solute accumulated into large lumps whose solution rate was far too slow to give meaningful results.

All computations were carried out on a PDP-6 high-speed computer.

Results

The molar conductance (Λ) results after extrapolation to zero time and infinite frequency for various molar concentrations (*c*) are presented in Table II together with the computed degree of dissociation (γ) and the differences ($\Delta\Lambda$) between the measured molar conductance and that calculated from the Fuoss–Onsager–Skinner equation. Table III 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.

Discussion

The association constants show five main trends, some of which have been seen in the limited results previously available:^{8b,c,9} (a) in all three solvents chloride ion associates more strongly than bromide ion, (b) *trans* ions exhibit association constants very much lower than the corresponding *cis* ions; (c) for *cis* salts

(19) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

(14) C. H. Searle, Ph.D. Thesis, Australian National University, Canberra, Australian Capital Territory, 1963.

(15) W. R. Fitzgerald, The University of Western Australia.

(16) F. Accasina, S. Petrucci, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1301 (1959).

(17) J. C. Nichol and R. M. Fuoss, *J. Phys. Chem.*, **58**, 696 (1954).

(18) G. Jones, K. J. Hysels, and W. Judd, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

Table II. Molar Conductances and Degrees of Dissociation of Salts in DMSO, DMF, and DMA at 25°

10 ³ c, M	Λ intern. ohm ⁻¹ cm ² mole ⁻¹	γ	Δ/Λ	10 ³ c, M	Λ intern. ohm ⁻¹ cm ² mole ⁻¹	γ	Δ/Λ
	<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O in DMSO				<i>cis</i> - β -[CoCl ₂ (trien)]Cl·0.5H ₂ O in DMSO (Continued)		
1.031	32.88	0.9642	0.01	8.341	25.88	0.7780	0.11
4.723	29.18	0.8719	-0.01	11.57	24.10	0.7290	-0.05
5.238	28.80	0.8622	0.00	14.26	23.02	0.6995	0.04
7.112	27.55	0.8296	0.01				
9.116	26.43	0.8002	0.03		<i>trans</i> -[CoCl ₂ (en) ₂]Cl in DMSO		
17.10	23.18	0.7135	0.03	1.061	34.82	0.9909	0.02
	<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O in DMSO			2.277	34.40	0.9794	-0.02
0.5566	33.38	0.9919	0.05	3.768	34.04	0.9675	-0.02
1.103	32.95	0.9800	-0.06	4.989	33.82	0.9590	-0.01
5.886	31.23	0.9192	-0.02	8.073	33.37	0.9392	0.03
5.973	31.22	0.9187	0.00	17.85	32.39	0.8861	0.00
7.118	30.95	0.9073	0.03		<i>trans</i> -[CoCl ₂ (en) ₂]Br in DMSO		
16.69	29.20	0.8279	-0.01	1.026	34.66	0.9982	0.01
	<i>cis</i> -[CoBrCl(en) ₂]Cl·0.5H ₂ O in DMSO			1.091	34.62	0.9975	-0.01
0.9537	32.72	0.9726	-0.02	4.998	33.83	0.9901	-0.01
1.188	32.49	0.9674	0.00	7.800	33.47	0.9860	0.01
4.482	29.78	0.8996	0.04	17.30	32.52	0.9710	-0.01
4.919	29.46	0.8911	0.00	18.04	32.47	0.9702	0.00
11.43	26.14	0.8018	-0.09		<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O in DMF		
15.47	24.79	0.7650	0.03	1.185	47.10	0.6363	-0.08
	<i>cis</i> -[CoBrCl(en) ₂]Br in DMSO			1.977	40.72	0.5521	0.12
1.078	32.96	0.9881	0.02	3.564	33.46	0.4558	-0.09
2.381	32.37	0.9732	-0.02	4.976	29.74	0.4063	0.17
4.321	31.73	0.9597	-0.02	9.588	23.01	0.3164	-0.26
7.643	30.92	0.9289	0.03	15.64	18.89	0.2612	0.11
9.244	30.54	0.9160	-0.01		<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O in DMF		
12.38	29.95	0.8949	-0.01	0.9609	68.48	0.9373	0.05
	<i>cis</i> -[CoBr ₂ (en) ₂]Br·H ₂ O in DMSO			1.957	64.28	0.8882	0.09
2.137	32.62	0.9862	0.00	3.472	59.29	0.8278	-0.21
5.392	31.65	0.9677	0.00	5.870	54.09	0.7645	0.09
6.503	31.37	0.9617	-0.01	10.21	47.72	0.6856	0.29
7.661	31.13	0.9568	0.02	17.43	41.07	0.6020	0.20
8.071	31.03	0.9545	0.01		<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O in DMA		
9.267	30.76	0.9483	-0.01	1.191	29.83	0.5576	^a
17.81	29.29	0.9134	0.00	1.939	25.28	0.4877	
	<i>cis</i> - α -[CoCl ₂ (trien)]Cl in DMSO			3.053	21.24	0.4236	
0.9969	33.24	0.9699	0.00	4.470	18.21	0.3749	
2.469	32.34	0.9332	0.00	8.759	13.67	0.3006	
4.360	31.49	0.8943	0.01	17.24	10.07	0.2404	
7.788	30.37	0.8383	-0.01		<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O in DMA		
11.59	29.52	0.7912	0.00	0.6118	55.91	0.9178	0.06
	<i>cis</i> - β -[CoCl ₂ (trien)]Cl·0.5H ₂ O in DMSO			1.163	52.23	0.8617	-0.08
0.9277	32.77	0.9587	-0.01	2.331	46.95	0.7799	-0.03
2.014	31.22	0.9197	0.01	3.128	44.36	0.7394	0.06
5.937	27.37	0.8179	-0.06	5.287	39.24	0.6583	0.03
				10.27	32.54	0.5511	0.02

^a The results for this system were treated using the simpler Fuoss equation.¹⁹

in DMSO, association constants decrease in the order *cis*-[CoCl₂(en)₂]⁺ > *cis*-[CoBrCl(en)₂]⁺ > *cis*-[CoBr₂(en)₂]⁺ for association with both chloride and bromide ion; (d) the association constant for *cis*- β -[CoCl₂(trien)]⁺ is significantly greater than for *cis*- α -[CoCl₂(trien)]⁺; (e) ion association constants for the same ion pair vary with solvent, being greatest in DMA and decreasing in the order DMA > DMF > DMSO.

Pattern a would be expected from all classical theories²⁰ of ion association and in these terms is an expression of the greater radius or smaller ionic potential of the bromide ion. In fact, aprotic solvents alone show this pattern because in protic solvents such as methanol the greater electrostatic attraction of the smaller chloride ion for an associating cation is more

than compensated for by the greater solvation energy of chloride ion in these solvents where hydrogen-bonding energies are important.¹⁰ These points have recently been formalized by the work of Parker^{10,11} and are emphasized by the determination of ion association constants for tetramethylammonium chloride and bromide in methanol, where the values of K_{IP} are 7 and 14, respectively, at 25°. ²¹ These results are typical of the association constants for a range of tetraalkylammonium halides in methanol. ²¹ The results of Evans and Nancollas²² for the [Co(NH₃)₆]³⁺Cl⁻ and [Co(NH₃)₆]³⁺Br⁻ ion pairs (K_{IP} = 74 and 46, respectively, at 25°) in water do not support these conclusions. However,

(21) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).

(22) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

(20) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5099 (1958).

Table III. Limiting Molar Conductances (Λ_0), Association Constants (K_{IP}), and Standard Free Energies of Association ($-\Delta G^\circ_{IP}$) for All the Systems Studied Together with the Constants Fitting the Fuoss–Onsager–Skinner Equation and Standard Deviation (σ_A)

Solvent	Salt	Λ_0 , intern. ohm ⁻¹ cm ² mole ⁻¹	<i>S</i>	<i>E'</i>	<i>L</i>	K_{IP}	$-\Delta G^\circ_{IP}$, kcal mole ⁻¹	σ_A
DMSO	<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O	34.66 ± 0.04	53.07	26.57	-70.07	397 ± 10	3.54	0.03
	<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O	33.92 ± 0.05	52.70	25.75	2514	182 ± 25	3.08	0.05
	<i>cis</i> -[CoBrCl(en) ₂]Cl·0.5H ₂ O	34.15 ± 0.07	52.82	26.01	145.7	309 ± 31	3.40	0.06
	<i>cis</i> -[CoBrCl(en) ₂]Br	33.77 ± 0.04	52.62	25.59	1430	125 ± 29	2.86	0.03
	<i>cis</i> -[CoBr ₂ (en) ₂]Br·H ₂ O	33.80 ± 0.02	52.64	25.62	367.2	72 ± 8	2.53	0.01
	<i>cis</i> - α -[CoCl ₂ (trien)]Cl	34.31 ± 0.02	52.90	26.19	5150	336 ± 12	3.45	0.01
	<i>cis</i> - β -[CoCl ₂ (trien)]Cl·0.5H ₂ O	34.70 ± 0.11	53.09	26.61	61.70	510 ± 47	3.69	0.08
	<i>trans</i> -[CoCl ₂ (en) ₂]Cl	35.48 ± 0.04	53.48	27.47	2147	100 ± 19	2.73	0.03
	<i>trans</i> -[CoCl ₂ (en) ₂]Br	35.24 ± 0.01	53.36	27.21	382.0	22 ± 7	1.83	0.01
	DMF	<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O	75.35 ± 0.87	151.32	118.20	690.7	8061 ± 273	5.33
<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O ^a		75.35				8062	5.33	
<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O		74.65 ± 0.36	150.84	116.72	-487.0	824 ± 57	3.98	0.25
DMA	<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O ^a	63.10				20200	5.87	
	<i>cis</i> -[CoCl ₂ (en) ₂]Br·H ₂ O	61.86 ± 0.11	127.04	90.18	900.6	1704 ± 36	4.41	0.07

^a Results calculated from the simple Fuoss equation.

it should be emphasized that hydrogen-bonding interactions between the nitrogen protons of the complex and the associating anion are likely to be important in these cases and that these interactions would be greater for the chloride ion.

Observation b is quite general and has been commented upon before.^{8,9} The *cis* complexes with the two anionic ligands occupying one edge of the octahedron possess a dipole in addition to their charge and thus will present a more favorable site than is available in *trans* complexes for ion pairing at the edge remote from the anionic ligands. The symmetrical *trans* complex has no dipole. Here the site of ion pairing is likely to be within the plane containing the four nitrogen ligand atoms and on the edges between the nitrogen atoms of different ethylenediamine molecules.

This correlation of ion association constants with dipole moment is emphasized by the pattern c above, where it is clear that because of the difference in electronegativity between chlorine and bromine the magnitude of the dipole moment of the complex will decrease in the order *cis*-[CoCl₂(en)₂]⁺ > *cis*-[CoBrCl(en)₂]⁺ > *cis*-[CoBr₂(en)₂]⁺. The small difference in cation size brought about by the replacement of chloride by bromide is unlikely to have an appreciable effect on K_{IP} , particularly as the site of ion pairing is remote from the halogen ligands.

The influence of the dipole moment of *cis* complexes and the consequent existence of a specific favorable site for ion association is further emphasized by the significant difference in association properties of the *cis*- α - and *cis*- β -[CoCl₂(trien)]⁺ complexes which are shown in Figure 1. Clearly the *cis*- β isomer at the site of ion pairing closely resembles the *cis*-[CoCl₂(en)₂]⁺ ion; however, this edge of the octahedron in the case of the *cis*- α -[CoCl₂(trien)]⁺ ion is blocked by the -C-C-bridge of the trien ligand.

All of these generalizations are significant and cognizance must be taken of them in the interpretation of any substitution kinetics, particularly in relation to steric course. However, perhaps the most startling feature of the present results is the magnitude of the association constants compared with those determined for systems of similarly sized ions of the same charge.

Fuoss²⁰ has developed the following expression for K_{IP} in a solvent of dielectric constant (*D*) for ions of charge *z*, and of distance of closest approach *a*, where *e* is the electronic charge and *N* Avogadro's number

$$K_{IP} = \frac{4\pi a^3 N}{3000} \exp\left(\frac{z^2 e^2}{a D k T}\right)$$

This equation predicts a value of K_{IP} of 3 l. mole⁻¹ for the *trans*-[CoCl₂(en)₂]⁺Cl⁻ ion pair in DMSO at 25° using *a* = 4.6 Å, a value which seems realistic from the crystallographic data of Nakatsu, Saito, and Kuroya²³ and Nakahara, Saito, and Kuroya.²⁴ The value determined here is 100 l. mole⁻¹.

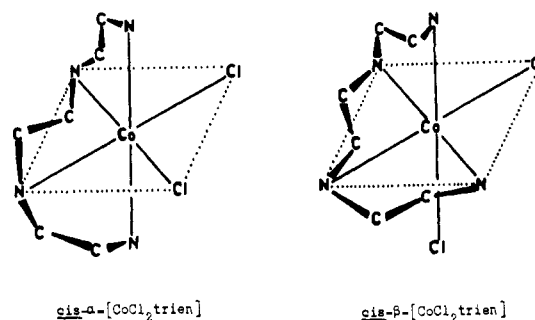


Figure 1. Structural diagrams of the *cis*- α - and *cis*- β -[CoCl₂(trien)]⁺ ions.

That the present set of constants are extraordinarily high is more clearly shown by comparison of these results with K_{IP} values determined for other salts in these solvents.²⁵ Sears, Lester, and Dawson²⁵ have studied a wide range of simple 1:1 electrolytes in DMSO and find all salts "to be completely dissociated." Sears, *et al.*,^{26,27} found that Me₄N⁺Cl⁻ and Et₄N⁺Br⁻ ion

(23) K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **29**, 428 (1956).

(24) A. Nakahara, Y. Saito, and H. Kuroya, *ibid.*, **25**, 331 (1952).

(25) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(26) P. G. Sears, E. D. Wilhoit, and L. R. Dawson, *ibid.*, **59**, 373 (1955).

(27) G. R. Lester, T. A. Gover, and P. G. Sears, *ibid.*, **60**, 1076 (1956).

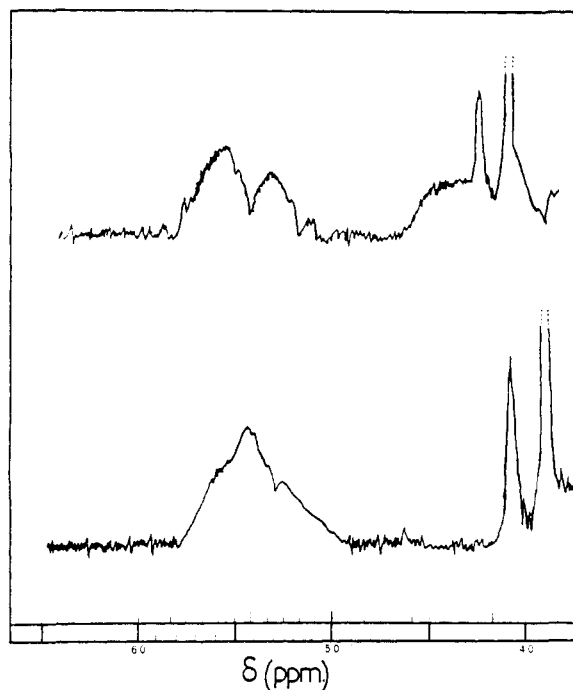


Figure 2. Pmr spectra of solutions of *cis*-[CoCl₂(en)₂]ClO₄ (upper) and *cis*-[CoCl₂(en)₂]Cl (lower) in DMSO (0.1 M solutions).

association constants were 37 and 16 in DMF and that K_{IP} for Et₄N⁺Br⁻ in DMA was 20. The comparable K_{IP} values for *trans*-[CoCl₂(en)₂]⁺Br⁻ in DMA and DMF were not determined because of solubility difficulties, but the value in DMSO of 22 suggests that the value would be in excess of 100 in DMF and of the order 200 in DMA.

Because of the effect of the dipole of the *cis* complexes, it is not reasonable to compare these association constants with symmetrical tetraalkylammonium ions; however, it is impressive that the Fuoss theoretical expression for K_{IP} predicts a value of only 44 for the association of a doubly charged cation ($a = 4.6 \text{ \AA}$) with Cl⁻ in DMSO.

It is clear then that the interactions in these systems are more than simple charge-charge and charge-dipole interactions. A comparable enhancement of ion association in partially substituted ammonium ions has been previously observed by Wynne-Jones,²⁸ who elegantly established the role of hydrogen bonding between acidic nitrogen protons in the cation and the associating anion. Similar conclusions have been reached for studies in DMF by Sears, Wolford, and Dawson.²⁹ Basolo, Henry, and Pearson⁹ have considered hydrogen bonding in ethylenediamine complexes in explaining "the residual rate" in the attack of N₃⁻ on *cis*-[CoCl₂(en)₂]⁺ in acidified methanol.

If hydrogen bonding is accepted as accounting for the present high K_{IP} values, then the -C-C- chain in the *cis*- α -[CoCl₂(trien)]⁺ leads to a lower association than for the *cis*- β -[CoCl₂(trien)]⁺ in that orientation for hydrogen bonding is more difficult.

In order to verify that specific interactions occurred between associating anions and the nitrogen protons, we have studied the pmr spectra of the *cis*-[CoCl₂(en)₂]⁺

(28) W. F. K. Wynne-Jones, *J. Chem. Soc.*, 795 (1931).

(29) P. G. Sears, R. K. Wolford, and L. R. Dawson, *J. Electrochem. Soc.*, 103, 633 (1956).

in the presence of ClO₄⁻ (not a hydrogen-bond acceptor and shown to be completely dissociated^{30,31}) and Cl⁻ ions. A similar study of *trans* complexes was prevented by the low solubility of *trans*-[CoCl₂(en)₂]Cl in the dipolar aprotic solvents.

Figure 2 shows the pmr spectra of solutions of *cis*-[CoCl₂(en)₂]ClO₄ and *cis*-[CoCl₂(en)₂]Cl. Recently Sargeson, *et al.*,^{30,31} and Lantzke and Watts³² have systematized the pmr of these compounds and the assignment of protons in Table IV is in accord with this previous work.³² Although the signals are broadened by quadrupole interaction, it is clear, however, that two protons (H₆ and H₈) are more deshielded in the presence of Cl⁻, and as a result their signal is shifted to lower fields. Such a shift is consistent with hydrogen bonding with the nitrogen protons H₆ and H₈, which have previously been assigned to the edge of the octahedron remote from the halogen ligands.

Table IV. Chemical Shifts (δ), Peak Areas, and Proton Assignments in DMSO

Compound	δ , ppm	$W_{1/2}$, cps	Area	Proton assignment
<i>cis</i> -[CoCl ₂ (en) ₂]ClO ₄	5.55	15	4	H ₁ H ₃ , H ₂ H ₄
	5.3	13	2	H ₅ H ₇
	4.3 ^a		2	H ₆ H ₈
<i>cis</i> -[CoCl ₂ (en) ₂]Cl	5.45	25	8	H ₁ H ₃ , H ₂ H ₄ , H ₅ H ₇ , H ₆ H ₈

^a This signal is partly obscured by solvent bands, and the assignment of chemical shift is only approximate. For this reason it is difficult to determine the area of this signal.

The explanation of observation e, that the magnitude of the association constants decreases from a maximum in DMA in the order DMA > DMF > DMSO, would at first sight lie in the variation of the ability of these solvents to solvate cations. This type of reasoning is supported by observations on the solubility of salts of the type *cis*- and *trans*-[CoCl₂(en)₂]ClO₄ in these solvents,³³ which decrease in the order DMSO > DMF > DMA. Inherent in this thinking is that the solvation forces involving the anion and the ion pair are similar in all three solvents.¹⁰

It should be emphasized that this variation of K_{IP} is a function of the solvation energies of the ion pair as well as both the free ions. Parker and Alexander³⁴ have recently published relevant information on the solvation free energies of a series of ions in these solvents, and these results show that anion solvation free energies may vary more in these systems than do the cation and ion-pair energies. Theoretical calculations based on a modified Born equation³⁵ support this and suggest that the cation solvation energies actually decrease in the order DMA > DMF > DMSO. We are at present undertaking a comprehensive study of solubilities³⁶ in these solvents which with the results presented here

(30) D. A. Buckingham, L. J. Durham, and A. M. Sargeson, *Australian J. Chem.*, 20, 257 (1967).

(31) S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, 5, 2103 (1966).

(32) I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, 20, 35 (1967).

(33) D. W. Watts, unpublished results.

(34) A. J. Parker and R. Alexander, *J. Am. Chem. Soc.*, 89, 5549 (1967).

(35) W. A. Millen and D. W. Watts, *ibid.*, 89, 6051 (1967).

(36) A. J. Parker and D. W. Watts, unpublished results.

and the results of Parker and Alexander³⁴ will give a clear understanding of relative solvation in these solvents of the cations, anions, and ion pairs.

Table V shows the division of total limiting conductances into ionic limiting conductances (λ_0). For DMF the values for Cl^- and Br^- limiting conductances as determined by Prue and Sherrington³⁷ from transport numbers have been used. In DMSO and DMA no transport based data are available, and the values of λ for bromide of 24.7 and 43.2 intern. $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ for DMSO and DMA, respectively, have been accepted. This follows Prue and Sherrington³⁷ and is based on the results of Sears, *et al.*,^{25,27} and the assumption that $\lambda_0^+ = \lambda_0^-$ for tetrabutylammonium triphenylborofluoride.³⁸ To evaluate single ionic conductances for *cis*- α - and *cis*- β - $[\text{CoCl}_2(\text{trien})]^+$ cations for which the bromide salts have not been treated, an average value of 25.2 intern. $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ for chloride ion has been used.

Table V. Total and Ionic Limiting Conductances (intern $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)

Compound	Λ_0	λ_0^-	λ_0^+
Solvent: DMSO			
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$	34.7	25.5	9.2
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Br} \cdot \text{H}_2\text{O}$	33.9	24.7	9.2
<i>cis</i> - $[\text{CoBrCl}(\text{en})_2]\text{Cl} \cdot 0.5\text{H}_2\text{O}$	34.2	25.1	9.1
<i>cis</i> - $[\text{CoBrCl}(\text{en})_2]\text{Br}$	33.8	24.7	9.1
<i>cis</i> - $[\text{CoBr}_2(\text{en})_2]\text{Br} \cdot \text{H}_2\text{O}$	33.8	24.7	9.1
<i>cis</i> - α - $[\text{CoCl}_2(\text{trien})]\text{Cl}$	34.3	25.2	9.1
<i>cis</i> - β - $[\text{CoCl}_2(\text{trien})]\text{Cl} \cdot 0.5\text{H}_2\text{O}$	34.7	25.2	9.5
<i>trans</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl}$	35.5	25.0	10.5
<i>trans</i> - $[\text{CoCl}_2(\text{en})_2]\text{Br}$	35.2	24.7	10.5
Solvent: DMF			
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$	75.3	55.1	20.2
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Br} \cdot \text{H}_2\text{O}$	74.7	53.6	21.1
Solvent: DMA			
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$	63.1	44.4	18.7
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Br} \cdot \text{H}_2\text{O}$	61.9	43.2	18.7

Table VI. Stokes' Crystallographic Radii for the Complex and Halide Ions

Ion	$r_s, \text{\AA}$	$r_c, \text{\AA}$
Solvent: DMSO		
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]^+$	4.6	3.6
<i>cis</i> - $[\text{CoBrCl}(\text{en})_2]^+$	4.6	3.6
<i>cis</i> - $[\text{CoBr}_2(\text{en})_2]^+$	4.6	3.6
<i>cis</i> - α - $[\text{CoCl}_2(\text{trien})]^+$	4.6	3.6
<i>cis</i> - β - $[\text{CoCl}_2(\text{trien})]^+$	4.4	3.6
<i>trans</i> - $[\text{CoCl}_2(\text{en})_2]^+$	4.0	3.6
Cl^-	1.7	1.64
Br^-	1.7	1.80
Solvent: DMF		
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]^+$	5.0	3.6
Cl^-	1.9	1.64
Br^-	1.9	1.80
Solvent: DMA		
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]^+$	4.8	3.6
Cl^-	2.0	1.64
Br^-	2.1	1.80

Table VI gives the Stokes' radii (r_s) together with best estimate of the crystallographic radii. The crystallo-

(37) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

(38) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

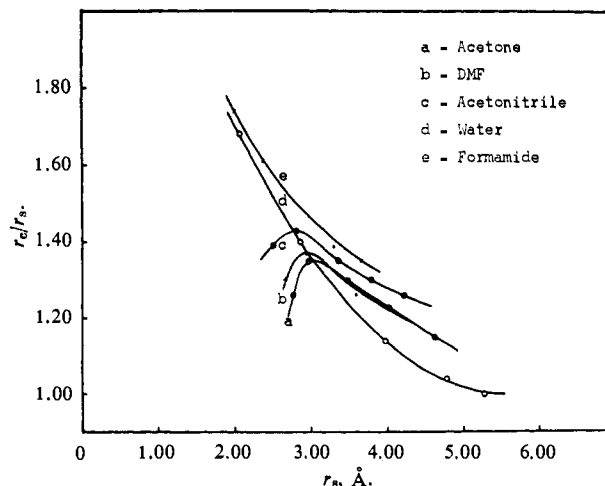


Figure 3. Correction factors for Stokes' radii in the solvents formamide, water, acetone, DMF, and acetonitrile at 25° as a function of Stokes' radius.

graphic radii for chloride and bromide are those of Gourary and Adrian.³⁹ The figure of 3.6 Å for the complex ions is based on the limited crystallographic data available, which show the maximum radius through the Co-C-H directions to be 3.6 Å in both $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ²³ and *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$.²⁴

Unambiguous interpretation of Stokes' radii is difficult. Absolute r_s values as obtained directly from the Stokes' equation are not truly representative of ions in motion in the solvent. This point is emphasized by Robinson and Stokes,⁴⁰ who suggest that the law is applicable in water only for particles greater than 5 Å in radius. For smaller particles the law gives radii which are far too small when compared with radii estimated from molecular models. Robinson and Stokes suggest a correction factor to give correlation of Stokes' radii in water with crystallographic radii for tetraalkylammonium ions which are considered not to carry solvent with them in the transport process. This correction factor is normally plotted against Stokes' radius and used to estimate solvated ionic radii.

It should be emphasized that the form of the correction curve is expected to be solvent dependent, and thus the Robinson and Stokes' curve is not applicable to other solvents although Gopal and Husain⁴¹ have applied the curve to radii of ions in a variety of nonaqueous solvents. Unfortunately the data for DMA, DMF, and DMSO are incomplete and complete correction curves cannot be established. Table VII summarizes the data for a range of protic and aprotic solvents, and Figure 3 shows the form of the Robinson and Stokes' correction factor curves for these solvents. The curves for the protic solvents water and formamide follow the expected parabolic form. The limited data for methanol (Table VII) and the correction curves for aprotic solvents suggest that the tetramethylammonium ion is anomalous and that its solvation is such in these solvents that solvent molecules are carried with the cations in the transport process.

The inadequate number of results for the solvents of this study, particularly for ions of Stokes' radii of about

(39) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, **10**, 127 (1960).

(40) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworth & Co., Ltd., London, 124 (1959).

(41) R. Gopal and M. M. Husain, *J. Indian Chem. Soc.*, **40**, 981 (1963).

Table VII. Stokes' Radii (Å) for Protic and Dipolar Aprotic Solvents at 25°

Solvent	Me ₄ N ⁺	Et ₄ N ⁺	Pr ₄ N ⁺	Bu ₄ N ⁺	Am ₄ N ⁺	Ref
^a	3.47	4.00	4.52	4.94	5.29	41 ^b
Water	2.07	2.86	3.97	4.77	5.27	^c
Formamide	1.99	2.48	...	3.66	...	^d
Methanol	2.19	2.49	3.27	3.87	4.33	21
Nitromethane	2.40	2.74	3.33	3.83	...	^e
Acetonitrile	2.50	2.80	3.35	3.79	4.21	^f
Nitrobenzene	2.64	2.78	3.39	3.87	...	^f
Acetone	2.76	2.96	3.47	4.02	4.61	^f
DMF	2.67	2.93	3.58	4.06	...	27
DMA	...	2.72	3.41	3.90	...	28

^a Radii estimated from molecular volumes or models. ^b Page 125 of this reference. ^c D. F. Evans and R. L. Kay, *J. Phys. Chem.*, **70**, 366 (1966). ^d J. M. Notley and M. Spiro, *ibid.*, **70**, 1502 (1966). ^e R. L. Kay, S. C. Blum, and H. I. Schiff, *ibid.*, **67**, 1223 (1963). ^f D. F. Evans, C. Zawoyski, and R. L. Kay, *ibid.*, **69**, 387 (1965).

4.5 Å, necessitates caution. However, it seems certain that correction factors will account for a 10–15% increase in the Stokes' radius for all of the cations considered. If the tetramethylammonium ion is taken as anomalous, an extrapolation of the parabolic section

of the curves suggests that corrections of 50–60% to the Stokes' radii of chloride and bromide are not unreasonable.

It is clear that the complex cations have solvent molecules associated with them in the transport process and, contrary to Prue and Sherrington,³⁷ who made no correction to Stokes' radii, that both chloride and bromide ions carry DMSO, DMF, and DMA solvent molecules with them.

Since all three solvents have electronegative groups in accessible positions, it is logical to assume that the solvation of the cation, like the interaction in the formation of an ion pair, involves the nitrogen protons of the ethylenediamine ligands. In the parlance of Parker,¹⁰ the cations through the nitrogen protons act as hydrogen-bond donors and the solvents as hydrogen-bond acceptors.

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Studies of Iron Tricarbonyl Cyclooctatetraene Complexes

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Abstract: Two new 1,2-disubstituted cyclooctatetraene (COT) iron tricarbonyl complexes have been prepared and structurally characterized both in solution and in the solid state. Using proton nmr spectroscopy, we have established that the substituted COT ligands are bonded to the Fe(CO)₃ fragment in the manner of a 1,3-diene. Unlike the parent compound, COTFe(CO)₃, the new complexes do not undergo rapid intramolecular rearrangements in solution. A reexamination of previous work on the parent compound in the light of the present results on the substituted complexes strongly suggests that COTFe(CO)₃ has the analogous 1,3-diene type structure at low temperatures in solution. The results of Mössbauer spectroscopic investigations are reported which further corroborate this conclusion. In addition, some comments concerning the possible mechanism of rearrangement of COTFe(CO)₃ in solution are presented.

In 1959, the compound C₈H₈Fe(CO)₃ (I) was reported.^{3–5} From its nmr spectrum,^{3,4} which consists of a single, sharp proton resonance at room temperature, it was concluded^{3,4,6} that the complex was an open-faced sandwich, with the C₈H₈ group being approximately planar and symmetrically bound to the iron atom. An X-ray crystallographic investigation showed,⁷ however, that in the solid state at least, the cyclooctatetraene (COT) molecule is bound to the iron atom through only four of its carbon atoms, in the

manner of a 1,3-diene (structure Ia, Figure 1). This result led to the further speculation⁷ that perhaps, in solution, the molecule was stereochemically dynamic, with the COT moiety rotating eccentrically with respect to the remaining Fe(CO)₃ fragment. If such a rotation were sufficiently rapid, all eight COT protons could become equivalent on the nmr time scale.

That COTFe(CO)₃ is stereochemically dynamic was firmly established last year when its proton nmr spectrum as a function of temperature was investigated.^{8–10} As the temperature is lowered, the sharp singlet is broadened until, at –155°, two well-separated resonances result. These are due to (1) protons on carbon atoms involved in π bonding to the iron atom, and (2) olefinic protons attached to the remaining four

(1) Columbia University, New York, N. Y. 10027.

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(3) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 336 (1960).

(4) M. D. Rausch and G. N. Schrauzer, *Chem. Ind. (London)*, 957 (1959).

(5) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(6) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

(7) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 489 (1961).

(8) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

(9) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966).

(10) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).