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Octahedral Chromium(III) Complexes in Dipolar Aprotic Solvents. V.[*] Isomerisation and Anation Reaction of *trans*-$[CrCl(DMSO)(en)_2]^{2+}$, and *cis* and *trans*-$[Cr(DMSO)_2(en)_2]^{3+}$ in Anhydrous Dimethyl Sulphoxide

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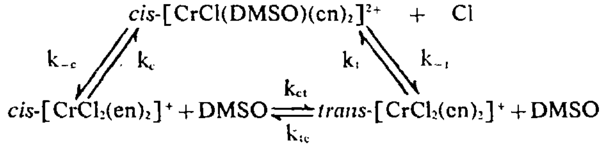
The isomerisation and anation reactions of complexes of the type trans–$[CrCl(DMSO)(en)_2]^{2+}$ *and* cis *and* trans–$[Cr(DMSO)_2(en)_2]^{3+}$ *have been studied in dimethyl sulphoxide (DMSO) over a wide range of chloride concentration and temperature. This work supplements an earlier study*[1] *of the reactions of* cis *and* trans–$[CrCl_2(en)_2]^+$ *in DMSO. Following the isolation of the* trans–$[CrCl(DMSO)(en)_2](ClO_4)_2$ *complex a reappraisal of the previously suggested mechanism for the reactions of* trans–$[CrCl_2(en)_2]^+$ *has been made. The kinetics were interpreted in terms of a dissociative mechanism with the characteristic effects of ion association. For* trans–$[CrCl(DMSO)(en)_2]^{2+}$ *in the presence of chloride ion loss of ethylenediamine dominated the kinetics. However no significant loss of ethylenediamine was detected in any of the other reactions.*

Introduction

The kinetics and equilibria for the $[CrCl_2(en)_2]^+$ system in DMSO were previously studied[1] and were represented as follows:



The reactions were found to be dissociative interchange reactions with pronounced effects due to ion association. More recently the analogous $[CrBr_2(en)_2]^+$ system has been studied in DMSO[2] where the complete range of solvent-containing complexes were isolated, namely *cis* and *trans*–$[CrBr(DMSO)(en)_2](ClO_4)_2$, and *cis* and *trans*–$[Cr(DMSO)_2(en)_2](ClO_4)_3$. The present work was undertaken to allow a more direct comparison to be made with the $[CrBr_2(en)_2]^+$ system and to attempt to elucidate further the steric courses of the reactions given above. Furthermore in these systems where the strength of the Cr–O bond is clearly illustrated by the stability of the solvent-containing complexes a far more direct comparison exists with the much studied aquation reactions[3-5] than was possible for the corresponding cobalt(III) systems[6-9] in dipolar aprotic solvents.

Experimental Section

(a) *Preparation of Compounds.* The preparations and analyses have been previously published[1,2] for the complexes: *cis* and *trans*–$[CrCl_2(en)_2]ClO_4$, *cis*–$[CrCl(DMSO)(en)_2](ClO_4)_2$, *cis* and *trans*–$[Cr(DMSO)_2(en)_2](ClO_4)_3$.

Trans-chloro(dimethyl sulphoxide)bisethylenediaminechromium(III)perchlorate was prepared and recrystallized after the method of Fee, Harrowfield and Jackson.[10] (Found: C, 20.0; H, 5.8; N, 11.6; Cl, 7.4. *Trans*–$[CrCl(DMSO)(en)_2](ClO_4)_2$ required: C, 19.8; H, 5.8; N, 11.6; Cl, 7.3%).

Recrystallization of tetraethylammonium chloride and the distillation procedure for the purification of the solvent have been described previously.[11]

(b) *Kinetic Technique.* The reactions were followed spectrophotometrically using both a Beckman DU or a Perkin Elmer 450 double beam spectrophotometer. All runs were conducted "in situ" and thermostatted by circulating water through the cell housing from an external thermostat. The temperature was controlled to wihin 0.1° and was monitored by means of a copper-constantin thermocouple. Rate constants

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(*) Part IV, *Inorg. Chim. Acta*, 6, 197 (972).

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(1) D.A. Palmer and D.W. Watts, *Aust. J. Chem.*, *21*, 2895 (1968).

(2) D.A. Palmer and D.W. Watts, *Inorg. Chim. Acta*, 6, 197 (1972).

(3) C.S. Garner and D.J. MacDonald, « Advances in the Chemistry of Coordination Compounds », (S. Kirschner Jr. Ed.) p. 266 (Macmillan Co., N.Y., 1961).

(4) L.P. Quinn and C.S. Garner, *Inorg. Chem.*, 3, 1348 (1964).

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(6) M.L. Tobe D.W. Watts, *J. Chem. Soc.*, 2991 (1964).

(7) W.R. Fitzerald and D.W. Watts, *Aust. J. Chem.*, *19*, 1411 (1966).

(8) I.R. Lantzke and D.W. Watts, *Aust. J. Chem.*, *19*, 949 (1966).

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(10) W.W. Fee, J.N.M.B. Harrowfield, and W.G. Jackson, *J. Chem. Soc.*, (*A*), 2613 (1970).

(11) W.A. Millen and D.W. Watts, *Aust. J. Chem.*, *19*, 43 (1966).

were measured over a temperature range of 24° to 70°.

The visible absorption spectra of the *cis* and *trans*–$[CrCl_2(en)_2]^+$ ions and related solvent-containing species in DMSO are shown in Figure 1. These spectra were recorded on the Perkin Elmer spectrophotometer at 22° and differ slightly in wavelength values above 500 nm from the spectra previously published[1] for the *cis* and *trans*–$[CrCl_2(en)_2]^+$ and *cis*–$[CrCl(DMSO)(en)_2]^{2+}$ ions. The difference is due to a systematic error in the monochromator of the instrument used to record the earlier results.

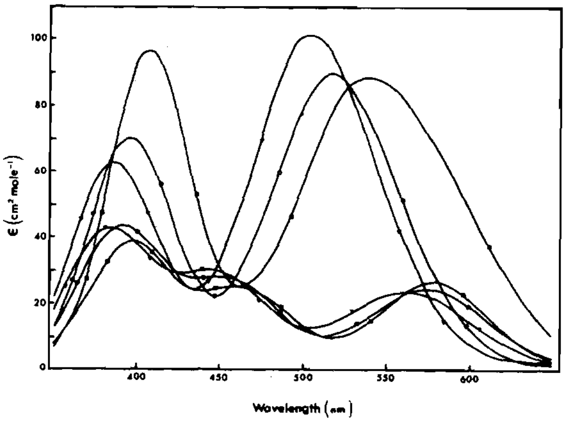

Figure 1. Spectra of Component Complex Ions.
□ *cis*-$[CrCl_2(en)_2]^+$, ■ *trans*-$[CrCl_2(en)_2]^+$,
○ *cis*-$[CrCl(DMSO)(en)_2]^{2+}$, ● *trans*-$[CrCl(DMSO)(en)_2]^{2+}$,
▽ *cis*-$[Cr(DMSO)_2(en)_2]^{3+}$ ▼ *trans*-$[Cr(DMSO)_2(en)_2]^{3+}$

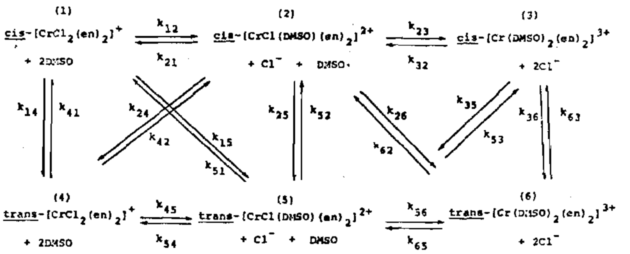

Figure 2. Complex Reaction Sequence

All rate constants presented here are initial first order rate constants calculated as previously,[2] on the assumption that in each reaction all of the reactant is consumed.

Results

The complete reaction scheme for the $[CrCl_2(en)_2]^+$ system showing only the kinetically observed paths is shown in Figure 2.

Rate constants for the solvolysis of *cis*–$[CrCl_2(en)_2]^+$, k_{12}, and the anation of *cis*–$[Cr(DMSO)(en)_2]^{2+}$, k_{21}, chloride ion have been published.[1] Similarly the rate constants for the reaction of *trans*–$[CrCl_2(en)_2]^{2+}$, k_{41} and k_{42}, were obtained previously.[1] However, the latter values were measured prior to the detection of the *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ ion and as this species may well provide the major reaction path for the solvolysis of *trans*–$[CrCl_2(en)]^+$, the values of k_{41} and k_{42} should be reexamined. Unfortunately, due to the small differences between the spectra of the *trans*–$[CrCl_2(en)_2]^+$ and *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ species and to the further complicating effect of a relatively rapid secondary reaction (*i.e.* $k_{52} > k_{45}$), k_{45} can not be measured by available techniques.

Table I. Rate Constants for the Removal of *trans*-$[CrCl(DMSO)(en)_2]^{2+}$ in DMSO.
Complex Concentration: 4.94 - 5.09×10^{-3} *M*

$10^3[Cl^-]$ *M*	$10^3(k_{52}+k_{51})$ min^{-1}	Temperature °C
0	2.20	49.75
0	6.23	59.2
0	13.7	66.4
2.09	1.40	50.1
2.09	3.69	58.25
2.09	8.73	67.0
5.89	0.975	58.55
5.89	2.50	67.3
5.89	3.35	70.0

Table I gives the rate constants for the reaction of trans–$[CrCl(DMSO)(en)_2]^{2+}$ ($k_{51}+k_{52}$), at various chloride concentrations. In the absence of added chloride ion the reaction observed was isomerization, k_{52}. As the chloride concentration was increased k_{52} decreased significantly and a side reaction appeared to be occuring simultaneously. At chloride concentrations greater than equimolar with respect to complex a rapid initial reaction was observed with isosbestic points at 469 nm, 421 nm, and 397 nm which were not compatible with any of the known species shown in Figure 1. However the final spectrum recorded under these conditions compared closely with the spectrum obtained by allowing a solution of $[CrCl_2(OH_2)(en)_2]^+$ in DMSO to stand for several hours at room temperature.[12] Therefore it is apparent that the presence of free chloride ion promotes loss of ethylenediamine from the *trans*–$[CrCl(DMSO)(en)_2]^+$ ion in DMSO.

Anation of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ by chloride ion resulted in complete retention of configuration and the rate constants for this reaction, k_{32}, are shown in Figure 3 as a function of the initial chloride concentration at 30°.

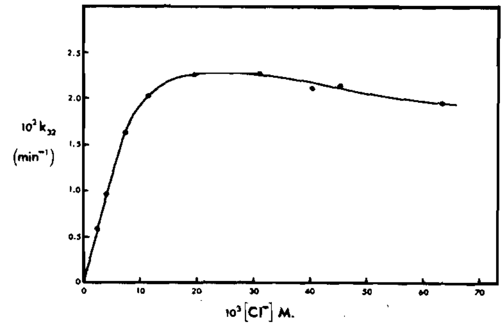

Figure 3. Variation of k_{32} with Uncomplexed Chloride Ion Concentration.

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[12] D.A. House and C.S. Garner, *Inorg. Chem.*, 5, 840 (1966).

Table II. Activation Parameters.
Enthalpy of activation, ΔH*, is given in kJ mol⁻¹ and the enthopy of activation, ΔS*, in JK⁻¹ mol⁻¹.

Complex	Rate Constant	10^3[Cl⁻] *M*	ΔH* at 70°	ΔS* at 70°
trans-$[CrCl(DMSO)(en)_2]^{2+}$	k_{52}	0	97 ±1.5	12±4
	k_{52}	2.09	97 ±2.5	25±12
	k_{52}	5.89	97 ±3.0	33±12
cis-$[Cr(DMSO)_2(en)_2]^{3+}$	k_{32}	31.2	81 ±4 [a]	8±8 [a]
trans-$[Cr(DMSO)_2(en)]^{3+}$	k_{63}	0	91.5±1.5 [a]	4±4 [a]
	$k_{63}+k_{62}$	27.1	93 ±1.0 [a]	25±4 [a]

[a] These values are for 30°

Rate constants for the anation and isomerization of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$, k_{62} and k_{63} respectively, were measured at 30° and are presented in Figure 4 as a function of the initial chloride concentration.

Activation energy parameters for all reactions are given in Table II.

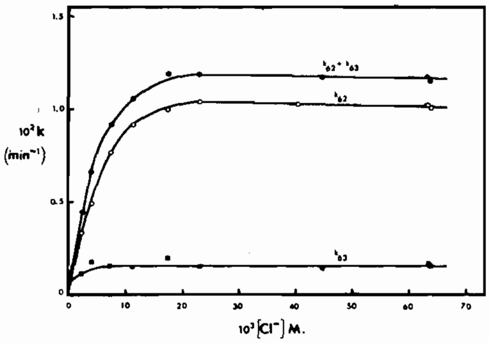

Figure 4. Variation of k_{62}, k_{63}, and $k_{62}+k_{63}$ with Uncomplexed Chloride Ion Concentration.

Discussion

The preliminary investigation of this system[1] indicated that solvolysis of *cis*–$[CrCl_2(en)_2]^+$ and chloride entry into *cis*–$[CrCl(DMSO)(en)_2]^{2+}$ proceeded by dissociative mechanisms with the kinetics influenced by ion association of the substrate and the transition state.

Before attempting further discussion of the reaction of *trans*–$[CrCl_2(en)_2]^+$ it is convenient to examine the apparent anomolus behaviour of the *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ ion. At chloride concentrations less than equimolar with complex the dominant initial reaction was isomerization with some coincident loss of ethylenediamine. As was observed for the corresponding *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ no solvolysis or anation occurred.[2] Loss of ethylenediamine dominates the reaction at chloride concentrations greater than equimolar with respect to *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ concentration. It is interesting to note that loss of ethylenediamine was not observed in preliminary runs with *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ in DMSO in the presence of chloride or bromide ions. However loss of ethylenediamine was found to be the major path for reaction of *trans*–$[CrCl(OH_2)(en)_2]^{2+}$ in 0.1 *M* HNO_3 solution as well as for the reactions of a number of other analogous *trans* complexes in aqueous solution.[4] Kraus and Taube[13] studied the isomerization and water exchange of *cis* and *trans*–$[Co(OH_2)_2(en)_2]^{3+}$ and suggested that a path existed in which cleavage of the Co–N bond of the ethylenediamine ligand occurred. It is possible that a path exists for the isomerization of *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ in which the Cr–N bond is broken. Loss of the monodentate ethylenediamine may then occur when the concentration of chloride ion, or hydrogen ion in the case of aqueous systems, is sufficient to cause them to interact with the "free end" of the ethylenediamine preventing it from recoordinating. Thus when no anion is present in the inner solvation sphere, that is when the anion concentration is not high enough to cause ion association of the substrate, the "free end" of the ethylenediamine recoordinates, which at least in some cases, leads to isomerization.[*] Photochemical studies[14] of reactions of similar complexes indicated that once the Cr–N bond is broken it is not always reformed, but rather solvolysis occurs to give free ethylenediamine.

In the reactions of *trans*–$[CrCl_2(en)_2]^+$ loss of ethylenediamine was insignificant which suggests that *trans*–$[CrCl(DMSO)(en)_2]^{2+}$ is not an intermediate in the solvolysis. Thus *trans*–$[CrCl_2(en)_2]^{2+}$ behaves similarly to *trans*–$[CoCl_2(en)_2]^+$ in DMSO[5] with solvolysis giving *cis*–$[CrCl(DMSO)(en)_2]^{2+}$ directly with some isomerization, k_{41}, occuring at higher chloride concentrations. From chloride exchange data[1] at chloride concentrations of c.a. 30×10^{-3} *M* it was shown that approximately 86% of the total chloride dissociations of the *trans*–$[CrCl_2(en)_2]^+$ substrate lead to retention of configuration. This value compares closely with the results of Bosnich, Ferguson, and Tobe[15] who found a minimum of 87% of chloride exchange of *trans*–$[CoCl_2(en)_2]^+$ in methanol gave retention.

The rate of stereospecific anation of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ shows a dependence on chloride concentration, Figure 3, which is characteristic of an S_N1IP mechanism and closely resembles the anation of this complex by bromide ion.[2] Related equilibrium studies[16] at comparable complex concentrations showed that for triply-charged, polar cations such as *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ ion pairing would be virtually com-

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(*) After the preparation of this manuscript one of us (DWW) had the plaesure of examining a thesis by Mr. W.G. Jackson submitted for a Ph.D. degree at the University of Melbourne. The work was supervised by Dr. Warren W. Fee. In this work the ideas expressed above have been confirmed and some monoethylenediamine complexes prepared.

(13) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, *83*, 1280 (1961)

(14) A.W. Adamson and D.W. Watts, unpublished results.

(15) B. Bosnich, J. Ferguson, and M.L. Tobe, *J. Chem. Soc.*, (A), 1636 (1966).

(16) I.R. Lantzke and D.W. Watts, *Aust. J. Chem.*, *19*, 969 (1966).

plete at equimolar concentrations of chloride and complex. Here the maximum value of k_{32} must correspond to the substrate being completely in the form of an ion triplet.

The rate of chloride entry into *cis*–[Cr(DMSO)$_2$(en)$_2$]$^{3+}$ is approximately 30 times faster than the rate of bromide entry[2] which corresponds to a 17kJ lower value of ΔG° (84kJ mol^{-1} compared to 101kJ mol^{-1}). Ion association studies[17,18] have shown that in dipolar aprotic solvents chloride ion is more strongly associated with complex cations than is bromide ion. This leads to the interesting conclusion that the chloride ions has a substantially stronger interaction in the intermediate than does the bromide ion. This difference being substantially greater than that which exists in the ion association interaction of the reacting ion. This is further illustrated by the entropies of activation for chloride entry (–8JK^{-1}) and for bromide entry (75K^{-1}) emphasising the higher degree of ordering in the transition state of the chloride reaction.

The dependence of k_{63} and k_{62} on chloride concentration is shown in Figure 4. As in the case of bromide anation,[2] chloride entry into *trans*–[Cr(DMSO)$_2$(en)$_2$]$^{3+}$ resulted in the formation of 100% *cis* product (*i.e.* $k_{65} = 0$) indicating that anion entry into the intermediate is sterically restricted. In this system $k_{32} > k_{63}$ and thus *cis*–[CrCl(DMSO)(en)$_2$]$^{2+}$ is formed, at least in part, by the secondary anation reaction k_{32}. Analysis of the contribution of this path by a conventional consecutive reaction technique is difficult because of the uncertainty in k_{32} which may have any value from 0 to 2.5×10^{-2} min^{-1} depending upon the extent to which the *cis*–[Cr(DMSO)$_2$(en)$_2$]$^{3+}$ ion is ion paired. Finally it is noteworthy that loss of ethylenediamine was not observed at the working temperature of 30° indicating that isomerization occurs via solvent exchange. However recent work by Fee and Jackson[19] has shown that loss of ethylenediamine does accompany isomerization of *trans*–[Cr(DMSO)$_2$(en)$_2$]$^{3+}$ at higher temperatures. This observation indicating that the reaction involving ethylenediamine loss has the greater activation energy.

It is apparent that there is now a need for solvent exchange data to complement the existing kinetic data. This would provide a more complete understanding of the mechanisms of reaction of both *trans* solvent-containing complexes, and in particular would lead to an understanding of the role of the single end dissociation of ethylenediamine in the isomerization of these species.

Acknowledgments. One of us (DWW) wishes to acknowledge the financial support of the Australian Research Grants Committee.

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[17] D.A. Palmer and D.W. Watts, *Inorg. Chem.*, *10*, 281 (1971).

[18] W.A. Millen and D.W. Watts, *J. Am. Chem. Soc.*, *89*, 6858 (1967).

[19] W.W. Fee and W.G. Jackson, private communication.