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Preparation and Kinetic Studies of New Ammine Complexes of Chromium(III) with Ligands Dimethylformamide (DMF) and Dimethylsulfoxide (Me_2SO). Kinetics of the Solvolysis Reaction of $[CrH_2O(NH_3)_5]^{3+}$ in Me_2SO and Aquation of $[CrMe_2SO(NH_3)_5]^{3+}$

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The following new complexes have been prepared: trans$[Cr(Me_2SO)_2(NH_3)_4](ClO_4)_3$; cis$[Cr(dmf)_2(NH_3)_4](ClO_4)_3$; cis$[Cr(Me_2SO)(dmf)(NH_3)_4](ClO_4)_3\cdot 2H_2O$; $[CrMe_2SO(NH_3)_5](ClO_4)_3\cdot H_2O$ *and* $[CrMe_2SO(NH_3)_5]I_3$. *Furthermore, the following new cations have been characterized only in solution:* cis$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$, trans$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$ *and* cis$[CrH_2O(dmf)(NH_3)_4]^{3+}$. *The electronic spectra are recorded for all of these complexes and standard analyses lead to the sequences* $Cl < dmf < Me_2SO < H_2O$ *in the spectrochemical series, and* $H_2O < dmf < Me_2SO < Cl$ *in the nepheleuxetic series for Cr(III). The aquation kinetics of* $[CrMe_2SO(NH_3)_5]^{3+}$ *and solvolysis kinetics of* $[CrH_2O(NH_3)_5]^{3+}$ *in anhydrous* Me_2SO *have been studied. With the* $[CrMe_2SO(NH_3)_5]^{3+}$ *complex a single process corresponding to aquation of* Me_2SO *is observed. Kinetics studies give* $k_{aq} = 3.2 \times 10^{-4}\ s^{-1}$ *at 49.5 °C* $[I = 0.10\ M\ (HClO_4)]$, *with activation parameters* $\Delta H^{\ddagger} = 20.30$ *Kcal mol*$^{-1}$ *and* $\Delta S^{\ddagger} = -11.92$ *cal mol*$^{-1}$ *K*$^{-1}$. *With the* $[CrH_2O(NH_3)_5]^{3+}$ *complex a single process corresponding to solvolysis of* H_2O *is observed in anhydrous* Me_2SO. *Kinetic studies give* $k = 6.10 \times 10^{-4}\ s^{-1}$ *at 50 °C, with activation parameters* $\Delta H^{\ddagger} = 22.74$ *Kcal mol*$^{-1}$ *and* $\Delta S^{\ddagger} = -2.98$ *cal mol*$^{-1}$ *K*$^{-1}$.

Introduction

In the last few years there has been considerable interest in the preparation and kinetic studies of Cr(III) ammines in both aqueous solution and polar, aprotic solvents, although less extensively studied in the latter case. Continuing our interest on Cr(III) ammines we undertook to prepare and study complexes of the above type in the non aqueous solvents dmf and Me_2SO.

During the course of this work Jackson and Fee [1] published a kinetic study on several ammine complexes of Cr(III) with included these ligands. Some of the complexes studied by these authors have also been prepared by us. Where different procedures were used, they have been included in the *Experimental Section.*

Experimental

Preparative Methods

New complexes

trans$[Cr(Me_2SO)_2(NH_3)_4](ClO_4)_3$. *trans*$[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ (2 g) [4] was dissolved in 3 ml of anhydrous Me_2SO and the solution warmed at 60° for 1 h 15 min with constant stirring. After cooling in ice the desired product was precipitated with 60% $HClO_4$ *(CAUTION: using more concentrated acid or carrying out the precipitation from hot solution may result in violent explosions).* The crystalline solid was filtered, washed with alcohol and dried with ether. It may be recrystallized from water by adding concentrated $HClO_4$.

The gray-blue solid changes slowly to red. The conversion is much faster in aqueous solution (*i.e.* one observes a marked change in the visible spectrum after *ca.* 24 hours). *Anal.* Found: Cr, 8.9; NH_3, 11.8. Calc: Cr, 9.1; NH_3, 11.8.

cis$[Cr(dmf)_2(NH_3)_4](ClO_4)_3$. *cis*$[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ (1 g) [4] was dissolved in anhydrous dmf (2 ml) and the solution heated to 60–65 °C for 30 minutes after which time it was poured onto three volumes of ice-cold ethanol. It can be recrys-

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tallized by dissolving it rapidly in the minimum amount of water–$NaClO_4$ at 50 °C and cooling. *Anal.* Found: Cr, 9.2; N, 14.8; H, 4.6. Calc: Cr, 9.21; N, 14.88; H, 4.64.

cis*$[Cr(Me_2SO)(dfm)(NH_3)_4](ClO_4)_3\cdot 2H_2O$.* One gram of *cis*$[CrCl(Me_2SO)(NH_3)_4](ClO_4)_2$ [1] was dissolved in 2 ml of dmf and the equivalent amount of $Hg_2(NO_3)_2$ was added. The mixture was warmed to 40 °C for 10 min, the Hg_2Cl_2 formed separated by centrifugation and 70% $HClO_4$ added dropwise until incipient precipitation. The product was filtered and recrystallized as above. *Anal.* Found: Cr, 8.6; N, 11.4. Calc: Cr, 8.58; N, 11.56. The complex loses water of crystallization on heating in a vacuum at 100 °C for 6–7 hours.

Complexes previously reported

$[CrMe_2SO(NH_3)_5](ClO_4)_3\cdot H_2O$ [*2*]. $[CrH_2O(NH_3)_5](ClO_4)_3$ (10 g) [3] was dissolved in anhydrous Me_2SO (60 ml) and the mixture was warmed at 55–60 °C with constant stirring for 90 min. After cooling in ice the desired product was precipitated with 60% $HClO_4$. The red crystalline solid was filtered, washed with alcohol and dried with ether. It may be recrystallized from water, by adding concentrated $HClO_4$. *Anal.* Found: Cr, 9.7; NH_3, 15.8. Calc: Cr, 9.78; NH_3, 16.00.

The anhydrous salt may be obtained by heating the monohydrate at 100 °C in a vacuum for 5 hours. *Anal.* Found: Cr, 10.1; NH_3, 16.4. Calc: Cr, 10.12; NH_3, 16.58.

$[Cr(Me_2SO)(NH_3)_5]I_3\cdot H_2O$. This was prepared from a solution of $[Cr(Me_2SO)(NH_3)_5](ClO_4)_3H_2O$ (3 g) in water (25 ml) by adding concentrated HI (3.5 ml). The red crystalline precipitate was washed with a small amount of ice-cold water and dried with ether. *Anal.* Found: Cr, 8.4; NH_3, 13.8; I, 61.3. Calc: Cr, 8.47; NH_3, 13.87; I, 62.0.

cis*$[Cr(Me_2SO)_2(NH_3)_4](ClO_4)_3$* [*1*]. One gram of *cis*$[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ [4] was dissolved in 5 ml of anhydrous Me_2SO and the solution heated at 55–60 °C for 1 h 30 min after which time it was cooled in ice and the desired product precipitated with 60% $HClO_4$. The red solid was filtered and washed as above. *Anal.* Found: Cr, 9.1; NH_3, 11.8. Calc: Cr, 9.1; NH_3, 11.8.

trans*$[CrCl(Me_2SO)(NH_3)_4](ClO_4)_2$* [*1*]. One gram of *trans*$[CrCl(H_2O)(NH_3)_4](ClO_4)_2$ [4] was dissolved in 2 ml of anhydrous Me_2SO, heated at 55 °C for 1 hour and the solution poured onto four volumes of ice cold ethanol. The resulting precipitate was collected and washed as above. The blue crystals slowly change to red on standing. *Anal.* Found: Cr, 11.8; NH_3, 15.6. Calc: Cr, 12.0; NH_3, 15.7.

Complexes characterized only in solution

cis*$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$*. A ten fold molar excess of Hg^{2+} was added to a *ca.* 10^{-2} *M* solution of *cis*$[CrCl(Me_2SO)(NH_3)_4]^{2+}$ in 10^{-3} *M* $HClO_4$ and the resulting mixture was allowed to stand at room temperature for one hour. A twofold excess of HCl (with regard to that required to complex all Hg^{2+}) was added and the solution passed through a Dowex 50 W-X2 (100–200 mesh) cation exchanger thereby separating cationic species from $[HgCl_4]^{2-}$. The column was eluted with increasingly concentrated $HClO_4$. Dipositive species (probably unreacted *cis*$[CrCl(Me_2SO)(NH_3)_4]^{2+}$) were eluted with 2.5 *M* $HClO_4$. The desired species, as shown by its electronic spectrum, was eluted with 3.5 *M* $HClO_4$. Cr/NH_3 molar ratio found: 1/4.05.

trans*$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$ and* cis*$[CrH_2O(dmf)(NH_3)_4]^{3+}$*. These were made as above but starting from *trans*$[CrCl(Me_2SO)(NH_3)_4](ClO_4)_2$ and *cis*$[CrCl(dmf)(NH_3)_4](ClO_4)_2$ respectively.

Characterization

Chromium was determined spectrophotometrically as CrO_4^{2-} after oxidation of the complexes with H_2O_2 in alkaline solution [5]. Ammonia was determined by distillation using the boric acid procedure [6]; iodine was determined volumetrically [6]. All experiments were carried out with freshly distilled and dried solvents and freshly prepared products. Visible spectra were obtained with Beckman DB-GT recording and DU-2 manual spectrophotometers. Infrared spectra were recorded on a Beckman IR 20A spectrophotometer purged with dry air. Samples were prepared as KBr disks.

Kinetic Measurements

Kinetic runs were followed spectrophotometrically on a Beckman DB-GT recording or a Beckman DU-2 manual spectrophotometer, fitted with a thermostatted (±0.1°) cell compartment. $Ln(A_\infty - A_t)$ was plotted against time and the best straight line was found using a least squares fit. Initial sample concentrations were determined spectrophotometrically. A_∞ were determined assuming the reaction to be complete. Most experiments were carried out at 530 nm. Rate constants were found to be independent of the wavelength. A reproducibility better than 3% was found in all cases. Most values are averages of at least two determinations.

TABLE I. Electronic Spectra of *cis*-$[Cr(NH_3)_4]$ Complexes (wavelength in nm). $[HClO_4]$ = 0.1 *M.*

	Max.	Min.	Max.	10Dq	B	$x/\beta = \gamma$	3rd Max. (calc)
$[CrMe_2SO(NH_3)_5]^{3+}$	497	416	367	20120	646	0.74	230–5
	$\epsilon = 40.1$	$\epsilon = 9.9$	$\epsilon = 32.8$				
$[Cr(Me_2SO)_2(NH_3)_4]^{3+}$	512	433	380	19531	625	0.71	240–5
	$\epsilon = 50.6$	$\epsilon = 9.6$	$\epsilon = 32.1$				
$[Cr(dmf)_2(NH_3)_4]^{3+}$	502/3	425	372/3	19900	637	0.73	230–5
	$\epsilon = 71.8$	$\epsilon = 17.4$	ϵ 52.3				
$[Cr(Me_2SO)(dmf)(NH_3)_4]^{3+}$	510	430	378	19608	627	0.73	235–0
	$\epsilon = 60.9$	$\epsilon = 15.9$	ϵ 41.6				
$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$	507	430	374	19724	647	0.74	235–0
	$\epsilon = 40.0$	$\epsilon = 12$	$\epsilon = 33$				
$[CrH_2O(dmf)(NH_3)_4]^{3+}$	500/1	426	368/9	19980	666	0.75	230–5
	$\epsilon = 45.7$	$\epsilon = 16.5$	$\epsilon = 35.0$				
$[CrCl(Me_2SO)(NH_3)_4]^{3+}$	523	445	390	19048	600	0.69	245–0
	$\epsilon = 43.1$	$\epsilon = 9.3$	$\epsilon = 32.1$				
$[CrCl(dmf)(NH_3)_4]^{3+}$	522	440	385	19157	639	0.73	240–5
	$\epsilon = 41.7$	$\epsilon = 13$	$\epsilon = 37.4$				

TABLE II. Electronic Spectra of *trans*-$[Cr(NH_3)_4]$ Complexes (wavelength in nm), $[HClO_4]$ = 0.1 *M.*

	Max.	Min.	Max.	Min.	Max.
$[Cr(Me_2SO)_2(NH_3)_4]^{3+}$	557	499	465	433	384
	$\epsilon = 24.7$	$\epsilon = 13.2$	$\epsilon = 16.7$	$\epsilon = 14.4$	$\epsilon = 34.7$
$[CrCl(Me_2SO)(NH_3)_4]^{2+}$	576	513	470	442	390
	$\epsilon = 23.2$	$\epsilon = 10.5$	$\epsilon = 15.3$	$\epsilon = 13.7$	$\epsilon = 34.8$
$[CrH_2O(Me_2SO)(NH_3)_4]^{3+}$	552	503	472	434	384
	$\epsilon = 21.5$	$\epsilon = 17.5$	$\epsilon = 18.9$	$\epsilon = 14.0$	$\epsilon = 33$

Results and Discussion

It is apparent from Table I that the electronic spectra of the penta- and *cis*tetraammine complexes can be interpreted assuming an ideal symmetry O_h. As is usual in this type of complexes no significant distortion due to asymmetry of the ligand field is observed. For the *trans* complexes (Table II) some splitting of the first maximum due to low symmetry components of the ligand field is observed as found in most complexes of this type [8]. Values of B (Racah's interelectronic parameter) and values of the third transition energy allowed by the spin selection rule but completely masked by intense charge transfer bands have been calculated for the *cis* complexes by interpolation in the Tanabe–Sugano diagram for a d^3 ion [7]. The value of parameter *x* (energy difference between the central ion terms ^4F and ^4P in the limit of zero crystal field) and parameter x/β (β being the same value in the free ion) have been calculated from the corresponding weak field equation for a d^3 ion [8]. From the above results, the ligands Me_2SO and dmf may be placed in the spectrochemical series for Cr(III) ammines as follows

$$Cl < dmf < Me_2SO < H_2O$$

and in the analogous nephelauxetic series as follows

$$H_2O < dmf < Me_2SO < Cl$$

Infrared Spectra

The infrared spectra of the new compounds prepared show in addition to the bands of NH_3, H_2O and ClO_4^- those of the ligands dmf and Me_2SO (Table III). These ligands are coordinated through the oxygen atom as confirmed by the shift to lower frequencies [9–11] of the bands attributable to S=O and C=O stretching frequencies, in the region 960–990 cm^{-1} and 1610–1670 cm^{-1} respectively. Jackson and Fee [1] suggested such a coordination mode on the basis of close similarities of the electronic spectra to their aqua counterparts.

Solvolysis Reaction of $[CrH_2O(NH_3)_5]^{3+}$ *in Anhydrous* Me_2SO *and Aquation Reaction of* $[CrMe_2SO(NH_3)_5]^{3+}$

The solvolysis reaction of $[CrH_2O(NH_3)_5]^{3+}$ in anhydrous Me_2SO and the aquation of $[CrMe_2SO$-

TABLE III. Selected IR band Frequencies (cm^{-1}).

Complex	ν(S=O)	ν(C=O)	Ref.
$[CrMe_2SO(NH_3)_5]^{3+}$	960	–	a
cis$[Cr(Me_2SO)_2(NH_3)_4]^{3+}$	960	–	a, [1]
cis$[Cr(dmf)_2(NH_3)_4]^{3+}$	–	1675	a
cis$[Cr(dmf)(Me_2SO)(NH_3)_4]^{3+}$	955	1660	a
cis$[CrCl(Me_2SO)(NH_3)_4]^{2+}$	940	–	a, [1]
cis$[CrCl(dmf)(NH_3)_4]^{2+}$	–	1666	[1]
trans$[Cr(Me_2SO)_2(NH_3)_4]^{3+}$	955	–	a
trans$[CrCl(Me_2SO)(NH_3)_4]^{2+}$	950	–	a, [1]
Me_2SO	1055	–	[15]
dmf	–	1714	[16]

[a]This work, KBr disk.

TABLE IV. Observed and Predicted Isosbestic Points for the Reactions.

$$[CrH_2O(NH_3)_5]^{3+} + Me_2SO \rightarrow [CrMe_2SO(NH_3)_5]^{3+} + H_2O$$

Observed	*Predicted*
472 (ϵ = 41.2)	472 (ϵ = 41.3)
417 (ϵ = 13.1)	418 (ϵ = 13.0)
358 (ϵ = 37.0)	358 (ϵ = 37.0)

$$[CrMe_2SO(NH_3)_5]^{3+} + H_2O \xrightarrow{HClO_4\ 0.1\ M} [CrH_2O(NH_3)_5]^{3+} + Me_2SO$$

Observed	*Predicted*
475 (ϵ = 36.1)	473 (ϵ = 36.0)
418 (ϵ = 10.3)	418 (ϵ = 11.5)
360 (ϵ = 31.8)	358 (ϵ = 32.0)

TABLE V. Rate Data for the Reaction $[CrH_2O(NH_3)_5]^{3+}$ + Me_2SO.

T °C	C_o[a]	k × 10^4 s^{-1}
30	0.1058	0.50
30	0.0069	0.49
30	0.0038	0.49
35	0.0101	1.12
40	0.0153	2.31
40	0.0534	2.31
40	0.0244	2.30
50	0.0142	6.10
50	0.0046	6.04

[a]C_o = initial concentration. λ = 530 nm.

TABLE VI. Rate Data for the Reaction $[CrMe_2SO(NH_3)_5]^{3+}$ + H_2O.

T °C	C_o[a]	k × 10^4 s^{-1}
33.4	0.0436	0.45
33.4	0.0218	0.51
35.5	0.0362	0.69
37.6	0.0372	0.83
40.8	0.0382	1.2
41.4	0.0387	1.3
44.8	0.0387	1.9
49.5	0.0364	3.2
49.5	0.0225	3.2
49.5	0.0497	3.3
49.5	0.0261	3.1[b]
53.5	0.0369	4.1
57.2	0.0389	5.9

[a]C_o = initial concentration of $[CrMe_2SO(NH_3)_5]^{3+}$. $[HClO_4]$ = 0.1 *M*; I = 0.1; λ = 530 nm. [b]In this experiment $[H_3^+O]$ = 0.05 *M*; I = 0.1 ($LiClO_4$).

$(NH_3)_5]^{3+}$ lead, in the conditions studied, to only one product in each case: $[CrMe_2SO(NH_3)_5]^{3+}$ and $[CrH_2O(NH_3)_5]^{3+}$ respectively, as found from ion exchange separations and isosbestic point studies [12, 13].

In a typical isosbestic point experiment $[CrH_2O(NH_3)_5](ClO_4)_3$ (0.459 g) was dissolved in anhydrous Me_2SO (100 ml) or a concentration of *ca.* 2.5 × 10^{-2} *M* was used starting from $[CrMe_2SO(NH_3)_5](ClO_4)_3$ in $HClO_4$ 0.1 *M*. The visible spectra of the solutions were determined in the temperature range of 30–55 °C at 20 minutes intervals over a period of 140 minutes. The agreement between the calculated and observed values (Table IV) and their non-variation with temperature imply, under the conditions studied, the absence of other reactions (*e.g.* loss of NH_3).

The final spectra obtained (at high temperature) are in both cases in very good agreement with those of authentic samples of $[CrMe_2SO(NH_3)_5]^{3+}$ and $[CrH_2O(NH_3)_5]^{3+}$ *i.e.*, the reactions go to essential completion.

Values of the rate constants for the solvolysis and aquation reaction at different temperatures are given in Tables V and VI. No variation of the rate constants with either initial concentration of complex, acidity, ionic strength (I = 0.1 *M* in $HClO_4$ was routinely used), or wavelength (530 nm was routinely used) was found in each case. Activation parameters for both reactions were calculated from Arrehnius' equation: $\Delta H^{\ddagger}_{solv.}$ = 22.74 Kcal mol^{-1} and $\Delta S^{\neq}_{solv.}$ = −2.98 cal mol^{-1} K^{-1}; and $\Delta H^{\neq}_{aq.}$ = 20.30 Kcal mol^{-1} and $\Delta S^{\neq}_{aq.}$ = −11.92 cal mol^{-1} K^{-1}.

The values found for both rate constants and activation parameters are in good agreement with those found in similar systems [1, 14, 17].

It is interesting that $[CrMe_2SO(NH_3)_5]^{3+}$ behaves differently from other complexes of the type [CrX-

$(NH_3)_5]^{(3-n)^+}$ (X^{n-} = CH_3COO^-, CH_2ClCOO^-, $CHCl_2COO^-$, $HC_2O_4^-$, SO_4^{2-}, NO_3^-) when X is bonded via oxygen. This behaviour is in agreement with that found by A. G. Sykes [17] with the complex $[Crdmf(NH_3)_5]^{3+}$. Both undergo aquation without ammonia loss. On the other hand, the complex $[CrH_2O(NH_3)_5]^{3+}$ also undergoes solvolysis in anhydrous Me_2SO without ammonia loss.

References

1 W. G. Jackson, P. D. Nowles, W. W. Fee, *Inorg. Chim. Acta, 22,* 111 (1977).
2 F. G. Kosel, N. V. Duffy, *J. Inorg. Nucl. Chem., 39,* 1708 (1977).
3 E. Kyuno, M. Kamada, W. Tanaka, *Bull. Chem. Soc. Japan, 40,* 1848 (1967).
4 D. W. Hoppenjans, J. B. Hunt, *Inorg. Chem., 8,* 506 (1969).
5 G. W. Haupt, *J. Res. Natl. Bur. Std., 48,* 414 (1952).
6 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis', 3rd. ed., Longmans, London (1961).
7 B. W. Figgis, 'Introduction to Ligand Field', Wiley, New York (1966).
8 C. J. Ballhausen, 'Introduction to Ligand Field Theory', McGraw–Hill, New York (1962).
9 C. V. Borney, J. H. Weber, *Inorg. Chem., 7,* 283 (1968).
10 M. Farona, J. Craselli, M. Grossman, W. Ritchey, *Inorg. Chim. Acta, 3,* 495 (1969).
11 B. B. Weyland, R. F. Schram, *Inorg. Chem., 8,* 971 (1969).
12 W. G. Jackson, W. W. Fee, *Inorg. Chem., 14,* 1174 (1975).
13 W. G. Jackson, W. W. Fee, *Inorg. Chem., 14,* 1154 (1975).
14 J. V. Edwards, F. Monacelli, G. Ortaggi, *Inorg. Chim. Acta Rev., 11,* 47 (1974).
15 W. D. Horrocks, F. A. Cotton, *Spectroch. Acta, 17,* 134 (1961).
16 C. V. Berney, J. H. Weber, *Inorg. Chem., 7,* 283 (1968).
17 N. Al-Shatti, T. Ramasani, A. G. Sykes, *J. Chem. Soc. Dalton, 74* (1977).