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The Preparation and Characterisation of Chromium(III) Complexes of C-*Meso*- and C-*Racemic*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *a* and tet *b*)

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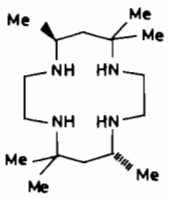
A variety of chromium(III) complexes of C-meso- *and* C-racemic-*5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet* a *and tet* b *respectively) have been characterised. Tet* a *gives the* trans-*complexes [$CrCl_2$(tet a)]Cl·HCl·$2H_2O$, [$CrCl_2$(tet a)]ClO_4, [Cr(tet a)(OH_2)$_2$]Br_3·H_2O, [Cr(tet a)-($NCS)_2$]NCS·$2H_2O$, [Cr(tet a)Br_2]Br, [Cr(tet a)Br_2]-ClO_4 and [Cr(tet a)(H_2O)$_2$](ClO_4)$_3$·H_2O. However, the* cis-*complexes [$CrCl_2$(tet b)]Cl, [Cr(tet b)-($NCS)_2$]NCS·$0.5H_2O$, [Cr(tet b)Br_2]Br, [Cr(tet b)-NO_3](NO_3)$_2$, [Cr(tet b)ox]ClO_4·$0.5H_2O$, [Cr(tet b)-(acac)](ClO_4)$_2$ and [Cr(tet b)(N_3)$_2$]N_3 are formed with the* C-racemic *ligand. Tet* b *is known to readily fold to give* cis-*octahedral complexes with the (RRRR, SSSS)* sec-*NH configuration and two equatorial methyls and one axial methyl substituent on each six-membered chelate ring. Tet* a *only folds with difficulty because of the unfavourable interaction of axial methyl substituents in the six-membered chelate rings with ligands in the axial position of the coordination sphere.*

Introduction

Currently only limited synthetic work has been carried out on chromium(III) complexes of macrocyclic ligands. Ferguson and Tobe [1] have described the preparation of a number of *cis*- and *trans*-complexes of the type $[Cr(cyclam)X_2]^+$ where cyclam = 1,4,8,11-tetraazacyclotetradecane and X = Cl^-, Br^-, NCS^-, NO_2^- and N_3^-). With cyclam, chromium(III) gives predominantly *cis*-complexes, and the *trans*-isomers rarely comprised more than 10% of the total product. Isomerisation of *cis*-[$CrCl_2$-(cyclam)]Cl by refluxing at pH 7 for *ca.* 8 hour gives *ca.* 50% yields of the *trans*-isomer [2].

Sperati [3] has reported the preparation of a number of Cr(III) complexes of macrocyclic tetraaza ligands by oxidation of the appropriate Cr(II) complexes. The oxidation route currently appears to be the only useful method for the prepration of Cr(III) complexes of unsaturated macrocylces. Chromium(III) complexes of [12]aneN$_4$ (cyclen) and [15]aneN$_4$ have also recently been characterised [4].

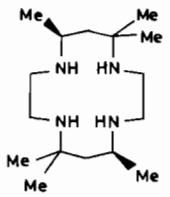
The present paper discusses the preparation of a variety of Cr(III) complexes of tet *a* (I) and tet *b* (II) which are C-*meso* and C-*racemic* diastereoisomers respectively.



tet a

(C - meso)

(I)



tet b

(C - racemic)

(II)

Tet *b* readily folds to give *cis*-complexes with the (RRRR, SSSS) *sec*-NH configuration [5] and two equatorial and one axial methyl substituent on each six-membered chelate ring. Tet *a* only folds with difficulty and normally occupies the equatorial plane in octahedral complexes giving rise to *trans*-isomers. Using these two ligands it should be possible to prepare a number of *cis*- and *trans*-$[CrX_2L]^{n+}$ complexes.

Experimental

The macrocyclic ligands tet *a* and tet *b* were prepared as described by Hay, Lawrence and Curtis [6].

Trans-[$CrCl_2$(tet a)]$^+$ Salts

$CrCl_3$·$6H_2O$ (4.3 g, 0.016 mol) and tet *a*·$2H_2O$ (5 g, 0.016 mol) were separately dissolved in DMF (25 cm^3). The solutions were boiled for 15 min (for dehydration), cooled to *ca.* 100 °C and the ligand added to the Cr(III) solution. The solution colour

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changed from violet to green and the volume of DMF was reduced to *ca.* 10 cm^3 by boiling. Green crystals of *trans*-$[CrCl_2(tet\ a)]Cl$ (4.5 g) slowly deposited from the hot solution as the volume was reduced (bumping was prevented by magnetic stirring). The complex was removed by filtration and washed with acetone. The mother liquor was added to water (300 cm^3), followed by conc. HCl (20 cm^3) and 10 cm^3 of conc. $HClO_4$ (60%). The precipitated perchlorate salt (1.5 g) was digested on a steam bath for 30 min and then filtered from the cooled solution and washed with 2-propanol then ether.

Recrystallisation

The chloride salt (1.0 g) was dissolved in hot HCl (20 cm^3, 0.1 M) and an equal volume of conc. HCl added. Green crystals of *trans*-$[CrCl_2(tet\ a)]Cl \cdot HCl \cdot 2H_2O$ (0.7 g) deposited overnight. Addition of $HClO_4$ (3 cm^3, 60%) to the mother liquor gave a small amount of the less water soluble perchlorate salt.

The perchlorate salt (1.0 g) was dissolved in hot sodium hydroxide solution (20 cm^3, 0.2 *M*) to give an orange solution which was filtered. An equal volume of conc. HCl was added and the solution reheated (60 °C) for 10 min, when $HClO_4$ (5 cm^3, 60%) was added. The resulting green microcrystalline precipitate was digested at 60 °C for a further 10 min and filtered off after cooling and washed with methanol (yield almost quantitative).

Analytical data for the various complexes obtained are summarised in Table I.

Cis-*[CrCl$_2$(tet b)]Cl*

A solution of $CrCl_3 \cdot 6H_2O$ (2.7 g, 0.01 mol) in DMF (25 cm^3) was boiled for *ca.* 0.5 hr to give $CrCl_3(DMF)_3$. The ligand (2.8 g, 0.01 mol) in DMF (25 cm^3) was added to the deep violet solution to give a deep green solution, followed by the deposition of sea-green crystals. The reaction was completed by boiling for 15 min, using a magnetic stirrer to prevent 'bumping'. The product (4.5 g) was collected from the cooled solution by filtration and washed with isopropanol then ether.

The complex was recrystallised by suspending 0.5 g of the chloride salt in NaOH solution (50 cm^3, 0.1 *M*) and heating at 60 °C till it all dissolved to give a sky blue solution. The solution was filtered and conc. HCl (25 cm^3) added to give a magenta solution from which crystals slowly deposited. Yield almost quantitative.

Due to the considerable differences in the solubility of the $[CrCl_2L]Cl$ complexes it is not necessary to isolate pure samples of tet *a* and tet *b*. Thus using 7.65 g of a tet *a*/tet *b* mixture obtained directly by $NaBH_4$ reduction of *trans*-[14]dieneN$_4$, and 6.56 g of $CrCl_3 \cdot 6H_2O$ in DMF solution gave 2.5 g of $[CrCl_2(tet\ b)]Cl$ from the hot solutions and 4 g of $[CrCl_2(tet\ a)]Cl$ by evaporation of the mother liquor.

Tet a *Complexes*

trans-*[CrBr$_2$(tet a)]Br*

The complex $[CrCl_2(tet\ a)]Cl$ (0.20 g) was dissolved in sodium hydroxide solution (15 cm^3, 0.2 *M*)

TABLE I. Analytical Data.

Complex	C (%)	H (%)	N (%)	Formula
cis-$[CrCl_2(tet\ b)Cl]Cl$*	43.5 (43.4)	8.1 (8.2)	12.8 (12.65)	$C_{16}H_{36}N_4Cl_3Cr$
trans-$[CrCl_2(tet\ a)]ClO_4$*	37.71 (37.92)	7.41 (7.16)	11.20 (11.05)	$C_{16}H_{36}N_4CrCl_3O_4$
trans-$[CrCl_2(tet\ a)]Cl \cdot HCl \cdot 2H_2O$	37.27 (37.29)	8.21 (8.02)	10.87 (10.87)	$C_{16}H_{41}N_4CrCl_4O_2$
trans-$[Cr(tet\ a)(OH_2)_2]Br_3 \cdot H_2O$	30.03 (30.49)	6.39 (6.72)	8.79 (8.89)	$C_{16}H_{42}Br_3CrN_4O_3$
trans-$[Cr(tet\ a)(NCS)_2]NCS \cdot 2H_2O$	42.30 (41.73)	7.36 (7.34)	17.66 (17.93)	$C_{19}H_{40}CrN_7O_2S_3$
trans-$[Cr(tet\ a)Br_2]Br$	33.21 (33.35)	6.80 (6.30)	9.45 (9.72)	$C_{16}H_{36}Br_3N_4Cr$
trans-$[Cr(tet\ a)Br_2]ClO_4$	32.35 (32.26)	6.11 (6.09)	9.49 (9.40)	$C_{16}H_{36}Br_2ClCrN_4O_4$
trans-$[Cr(tet\ a)(H_2O)_2](ClO_4)_3 \cdot H_2O$	27.64 (7.89)	6.44 (6.15)	7.97 (8.13)	$C_{16}H_{42}Cl_3CrN_4O_{15}$
cis-$[Cr(tet\ b)(NCS)_2]NCS \cdot 0.5H_2O$	44.13 (43.90)	6.97 (7.18)	18.65 (18.86)	$C_{19}H_{37}CrN_7O_{0.5}S_3$
cis-$[Cr(tet\ b)Br_2]Br$	33.22 (33.35)	6.45 (6.30)	9.66 (9.72)	$C_{16}H_{36}Br_3CrN_4$
cis-$[Cr(tet\ b)(NO_3)](NO_3)_2$	36.70 (36.78)	7.00 (6.94)	18.34 (18.76)	$C_{16}H_{36}CrN_7O_9$
cis-$[Cr(tet\ b)ox]ClO_4 \cdot 0.5H_2O$	40.79 (40.56)	7.15 (7.00)	10.75 (10.51)	$C_{18}H_{37}ClCrN_4O_{8.5}$
cis-$[Cr(tet\ b)ox]Br \cdot 1.5H_2O$	40.41 (40.68)	6.86 (7.39)	10.44 (10.54)	$C_{18}H_{39}BrCrN_4O_{5.5}$
cis-$[Cr(tet\ b)(acac)](ClO_4)_2$	39.75 (39.75)	7.20 (6.83)	10.73 (8.82)	$C_{21}H_{44}CrCl_2N_4O_{10}$
cis-$[Cr(tet\ b)(N_3)_2]N_3$	41.37 (41.55)	7.92 (7.84)	39.25 (39.36)	$C_{16}H_{36}CrN_{13}$

*For *cis*-$[CrCl_2(tet\ b)Cl]Cl$; % Cr (calc) = 11.75, found 11.6. *For *trans*-$[CrCl_2(tet\ a)]ClO_4$; % Cr (calc) = 10.3, found 10.5.
*For *trans*-$[CrCl_2(tet\ a)]Cl \cdot HCl \cdot 2H_2O$; % Cr (calc) = 10.09, found 10.26.

by heating gently to give an orange solution. Conc. HBr (4–5 cm^3) was added and the mixture slowly evaporated on a water bath to a volume of *ca.* 10 cm^3. Green crystals deposited on standing overnight in a refrigerator, these were filtered off and purified by dissolving in the minimum volume of methanol followed by precipitation with diethyl ether.

trans-*[CrBr$_2$(tet* a*)]ClO$_4$*

The complex [$CrCl_2$(tet *a*)]ClO_4 (0.20 g) was dissolved in hot sodium hydroxide solution (10 cm^3, 0.2 *M*) and conc. HBr (5 cm^3) and conc. $HClO_4$ (3 cm^3) added. The mixture was heated on a water for *ca.* 5 min and then left to cool. The green crystalline product which deposited was filtered off, washed with cold 2-propanol then diethyl ether.

trans-*[Cr(tet* a*)(NCS)$_2$]NCS·2H$_2$O*

A solution of potassium thiocyanate (0.50 g) in water (10 cm^3) was added to a filtered solution of [$CrCl_2$(tet *a*)]Cl (0.20 g) in hot acetic acid (20 cm^3, 0.1 *M*). The resulting mixture was heated on a water bath (*ca.* 30 min) during which time the colour of the solution changed from blue to orange. On standing overnight in a refrigerator, the solution deposited well formed orange crystals, which were filtered off, washed with water, followed by ethanol and diethyl ether. The yield is near quantitative. The complex is soluble in DMF and sparingly soluble in acetone.

trans-*[Cr(tet* a*)(H$_2$O)$_2$](ClO$_4$)$_3$·H$_2$O*

The complex [$CrCl_2$(tet *a*)]ClO_4 (0.20 g) was dissolved in sodium hydroxide solution (10 cm^3, 0.2 *M*) to give an orange solution. This solution was cooled in an ice bath, and concentrated perchloric acid added dropwise with constant stirring until the solution was acidic to litmus. Additional concentrated $HClO_4$ (2 cm^3) was then added. The solution was cooled in an ice bath when the pale pink product crystallised. The complex was filtered off, and washed with cold isopropanol then ether and dried.

trans-*[Cr(tet* a*)(H$_2$O)$_2$]Br$_3$·H$_2$O*

The complex [$CrCl_2$(tet *a*)]ClO_4 (0.25 g) was dissolved in sodium hydroxide solution (5 cm^3, 0.2 *M*) to give an orange solution, which was then cooled in an ice bath. Conc. HBr (5 cm^3) was added and orange crystals deposited on refrigeration overnight. The crystals were washed with absolute ethanol then ether and dried. This complex has a tendency to form green [$CrBr_2$(tet *a*)]Br in the solid state.

Tet b *Complexes*

cis-*[Cr(tet* b*)(NCS)$_2$]NCS·0.5H$_2$O*

The complex *cis*-[$CrCl_2$(tet *b*)]Cl (0.20 g) in water (50 cm^3) was heated almost to boiling, and a solution of potassium thiocyanate (excess, 0.50 g) in water (5 cm^3) added. The reaction mixture was heated on a water bath for *ca.* 1 hr. On cooling, the beautifully crystalline maroon complex formed, and was filtered off, washed with water then diethyl ether. The complex is very soluble in acetone.

cis-*[Cr(tet* b*)Br$_2$]Br*

The complex *cis*-[$CrCl_2$(tet *b*)]Cl (0.20 g) was dissolved in sodium hydroxide solution (50 cm^3, 0.5 *M*) by gentle heating on a water bath to give a blue solution. Concentrated hydrobromic acid was added dropwise until the colour of the solution changed from blue to magenta. The solution was filtered and the filtrate slowly evaporated on a water-bath to a volume of *ca.* 15 cm^3, during which time green crystals of the complex slowly formed. The complex was filtered off and washed with water followed by ethanol and diethyl ether.

cis-*[Cr(tet* b*)(NO$_3$)$_2$]NO$_3$*

The complex *cis*-[$CrCl_2$(tet *b*)]Cl (0.20 g) was dissolved in sodium hydroxide solution (50 cm^3, 0.5 *M*) by warming on a water bath to give a blue solution. The solution was filtered hot and nitric acid (60 cm^3, 0.5 *M*) was added dropwise until the colour changed to magenta. The solution volume was then reduced to *ca.* 20 cm^3 by rotary evaporation. Standing in a refrigerator overnight gave the pink microcrystalline complex which was filtered off, washed with cold water, followed by ethanol and diethyl ether.

cis-*[Cr(tet* b*)ox]ClO$_4$·0.5H$_2$O*

A mixture of *cis*-[$CrCl_2$(tet *b*)]Cl (0.15 g) and oxalic acid (0.20 g) in water (20 cm^3) was heated on a water bath for *ca.* 3 min, then diethylamine (*ca.* 1 cm^3) was added. Heating of the reaction mixture was continued for a further 10 min during which time the solution changed in colour from blue to cherry-red. The solution was filtered hot, and a concentrated aqueous solution of sodium perchlorate (*ca.* 2 cm^3 was added), giving the pink microcrystalline complex. The complex was filtered off after cooling then washed with water, followed by ethanol and finally diethyl ether.

cis-*[Cr(tet* b*)ox]Br·1.5H$_2$O*

Thix complex was prepared in a similar manner to that used for the preparation of *cis*-[Cr(tet *b*)ox]-ClO_4·0.5H_2O except that a concentrated aqueous solution of sodium bromide was used for precipitation instead of sodium perchlorate.

cis-*[Cr(tet* b*)(acac)](ClO$_4$)$_2$*

Acetylacetone (0.30 g, excess) was added to a solution obtained by dissolving *cis*-[$CrCl_2$(tet *b*)]Cl (0.20 g) in sodium hydroxide solution (50 cm^3, 0.5 *M*). The mixture was heated on a water bath for *ca.*

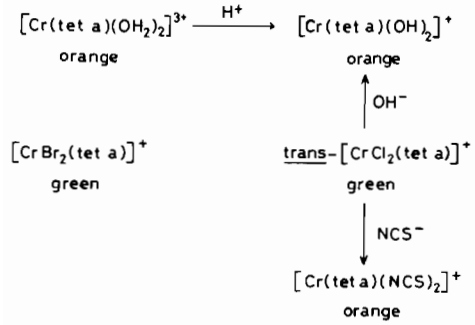
5 min and filtered hot. A solution of sodium perchlorate (0.5 g) in water (5 cm^3) was added to the filtrate. On standing overnight, the blue solution yielded well-formed red crystals, which were filtered off, washed thoroughly with water, followed by ethanol then diethyl ether.

cis-[Cr(tet b)(N$_3$)$_2$]N$_3$

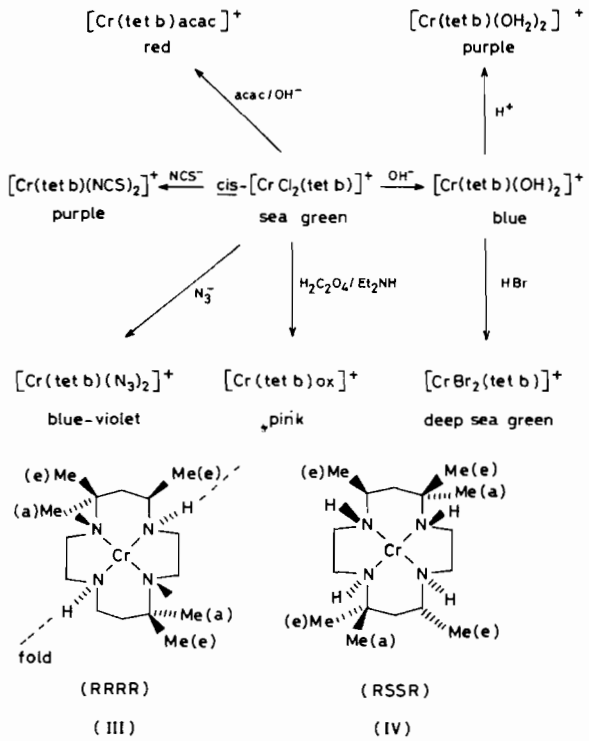
The complex [$CrCl_2$(tet *b*)]Cl (0.20 g) was suspended in water (50 cm^3) and the suspension heated on a water-bath for *ca.* 1 hr. A solution of sodium azide (0.50 g) in water (10 cm^3) was added and the reaction mixture was heated for *ca.* 1 hr with stirring, during which time the mixture changed in colour from blue to blue-violet. On standing the blue-violet microcrystalline complex deposited. The complex was filtered off then washed with water, followed by ethanol then diethyl ether.

Results and Discussion

The reaction of [$CrCl_3(DMF)_3$], prepared *in situ* by dehydration of $CrCl_3 \cdot 6H_2O$ in DMF solution, with tet *a* gives a good yield of *trans*-[$CrCl_2$(tet *a*)]$^+$ which can be readily characterised as the perchlorate salt, or as *trans*-[$CrCl_2$(tet *a*)]Cl·HCl·2H_2O from hydrochloric acid solution. A similar reaction with tet *b* gives *cis*-[$CrCl_2$(tet *b*)]Cl. These complexes can be used to prepare a large variety of other complexes by the routes shown in Schemes 1 and 2. The reaction of [$CrCl_3(DMF)_3$] with saturated macrocyclic ligands provides an excellent route to their Cr(III) Complexes.



The complex *trans*-[$CrCl_2$(tet *a*)]Cl·HCl·2H_2O presumably contains $H_5O_2^+Cl^-$ [7] also found in *trans*-[$CoCl_2(en)_2$]$^+H_5O_2^+2Cl^-$ and *trans*-[Co((−)pn)$_2$Cl$_2$]$^+$-$H_5O_2^+2Cl^-$ [8]. Tet *b* is known to readily fold to give *cis*-complexes with the (RRRR, SSSS) *sec*-NH configuration and two equatorial methyl groups and one axial methyl group in each six-membered chelate ring (III). Where ligand folding can occur, 14-membered tetra-aza ligands appear to favour a *cis*-configuration on chromium(III). A preliminary report [9] on the single crystal X-ray structure and kinetics of decarboxylation of *cis*-(RRRR), (SSSS)-[Cr(O$_2$CO)tet *b*]-ClO_4 has appeared. A *trans*-configuration is normally favoured on cobalt(III), and *cis*-complexes generally only form when chelating bidentate ligands are present. The tet *a* ligand is known to fold with difficulty due to unfavourable interactions between the substituent methyl groups and the ligands in the axial sites of the coordination octahedron. Although the *sec*-NH proton stereochemistry in *trans*-[$CrCl_2$-(tet *a*)]$^+$ has not yet been established, preliminary X-ray work [10] on *trans*-[CrCl(tet *a*)(OH_2)][$(NO_3)_2$ (an hydrolysis product) suggests the most thermodynamically stable RSSR (*meso*) configuration (IV) with two equatorial groups and one axial methyl group in the chair six-membered rings.



Base hydrolysis of *trans*-[$CrCl_2$(tet *a*)]$^+$ has recently been studied [11]. Approximately two mol of OH^- are consumed per mol of complex in the pH range 7.8–9.4, and the final visible absorption spectrum is identical to that obtained from *trans*-[Cr(tet *a*)(OH_2)$_2$][$(ClO_4)_3$ dissolved in 0.01 *M* NaOH. The rate constant k_{OH} for reaction (1) is 145 M^{-1} s^{-1} at 25 °C and I = 0.1 *M* with $\Delta H^{\ddagger}$ = 114 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 179 J K^{-1} mol^{-1}:

$$\textit{trans}\text{-}[CrCl_2(\text{tet } a)]^+ + OH^- \xrightarrow{k_{OH}} \textit{trans}\text{-}[CrCl(\text{tet } a)OH]^+ + Cl^- \quad (1)$$

Base hydrolysis of the tet *a* complex is some 112 fold faster than base hydrolysis of *trans*-[$CrCl_2$(cyclam)]$^+$ at 25 °C where k_{OH} = 1.3 M^{-1} s^{-1} [1]. These reac-

TABLE II. Infrared Spectra.

Compound	Bands (cm^{-1})
cis-[Cr(tet *b*)$(N_3)_2$]N_3	2080, 2050(sh) coord N_3^- (ν_a NNN) 2041 (ν_a NNN) ionic N_3^- 1341 ν_s(NNN) ionic, 1275 ν_s(NNN) coord. 3070 cm^{-1} ν(NH)
cis-[Cr(tet *b*)ox]ClO_4	1700, 1682 ν_a(C=O) 1380, 1370 ν_s(CO) + ν(CC) *ca.* 1100 and 620 (ionic ClO_4) 3130, 3207 ν(NH)
cis-[Cr(tet *b*)Br_2]Br	3030, 3140 ν(NH)
cis-[Cr(tet *b*)$(NCS)_2$]NCS·$2H_2O$	2050–2020 νCN (N-bonded and ionic NCS^-) 817 ν(CS) N-bonded (weak) 476 δ NCS N-bonded (weak) 3100 νNH
cis-[Cr(tet *b*)(NO_3)]$(NO_3)_2$	1515 $\nu_a(NO_2)$ 1290 $\nu_s(NO_2)$ 1000 ν(NO) 3090, 3205 νNH
cis-[Cr(tet *b*)(acac)]$(ClO_4)_2$	1600 ν(C···O) + ν(C···C) νNH 3115, 3090 ClO_4 *ca.* 1100 and 620
trans-[Cr(tet *a*)$(H_2O)_2$]$(ClO_4)_3$·H_2O	3450 (br) νOH ClO_4 1100 and 622 νNH 3025, 3100, 3200
trans-[Cr(tet *a*)Br_2]ClO_4	νNH 3190, 3210(sh), 3220(sh) ClO_4 *ca.* 1100 and 620
trans-[Cr(tet *a*)$(NCS)_2$]NCS	2020–2060(br) νCN (N-bonded and ionic NCS^-) νNH 3140, 3180(sh)

tions appear to occur by an S_N1CB mechanism, as (a) a large positive entropy of activation is observed, as expected for a dissociative process [12], and (b) steric acceleration due to alkyl ring substitution occurs. The aquation reactions (2) have also been investigated [13, 14] using 0.05 *M* H_2SO_4 as solvent.

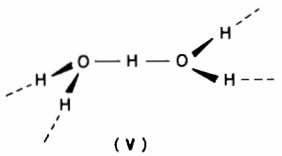
$$\textit{trans}\text{-}[CrX_2(\text{tet } a)]^+ + H_2O \xrightarrow{k_{aq}} \textit{trans}\text{-}[CrX(\text{tet } a)(OH_2)]^{2+} + X^- \quad (2)$$

At 25 °C $k_{aq}(Cl) = 1.26 \times 10^{-5}$ s^{-1} with $\Delta H^{\ddagger} = 90.1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -37$ J K^{-1} mol^{-1} and $k_{aq}(Br) = 1.70 \times 10^{-3}$ s^{-1} with $\Delta H^{\ddagger} = 71.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -58$ J K^{-1} mol^{-1}.

Infrared Spectra

The infrared spectral data for the various complexes is summarised in Table II. In a number of cases this data provides confirmatory evidence for the various structures. Thus in *cis*-[Cr(tet *b*)$(N_3)_2$]N_3 bands due to ν_a(NNN) of coordinated azide occur at 2080 and 2050 (sh) cm^{-1} with ionic azide at 2041 cm^{-1}. The complex *cis*-Cr(tet *b*)$(NO_3)_3$ could be formulated as *cis*-[Cr(tet *b*)NO_3^-]$(NO_3)_2$ with bidentate nitrate or as *cis*-[Cr(tet *b*)$(NO_3)_2$]NO_3 containing monodentate nitrate. The complex has limited solubility in DMSO giving $\Lambda_M = 85$ ohm^{-1} cm^2 mol^{-1} at 25 °C consistent with a 1:1 electrolyte and two monodentate nitrate ligands. Gatehouse *et al.* [15] noted that the unidentate NO_3 group exhibits three NO stretching bands, as expected for its C_{2v} symmetry. For example, [Ni(en)$_2$$(NO_3)_2$] containing unidentate nitrate has $\nu_a(NO_2)$ at 1420 cm^{-1}, $\nu_s(NO_2)$ 1305 cm^{-1} and ν(NO) at 1008 cm^{-1}. The present complex has bands at 1515, 1290 and 1000 cm^{-1}. However, i.r. data of this type must be treated with caution [16].

The i.r. data supports an isothiocyanato (N-bonded) structure for *cis*-[Cr(tet *b*)$(NCS)_2$]NCS·$2H_2O$ and *trans*-[Cr(tet *a*)$(NCS)_2$]NCS, as expected with the hard Cr(III) metal centre. The complex [$CrCl_2$(tet *a*)]Cl·$H_5O_2^+Cl^-$ has a series of very broad absorption bands at *ca.* 1670, 2100 and 2460 cm^{-1}. The species $H_5O^+Cl^-$ can occur in *cis, trans*(V) and *gauche* conformations [8].



(V)

Electronic Spectra

In O_h symmetry, three ligand field bands are expected for a d^3 ion $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and the two electron transition $^4A_{2g} \rightarrow {}^4T_1(P)$. The assignment of geometric configuration is confirmed by the d–d spectra. For example, the more symmetrical *trans*-isomers of $[CrN_4Cl_2]^+$ chromophores normally have extinction coefficients of <30 and the lowest energy d–d band ($^4A_{2g} \rightarrow {}^4T_{2g}$) occurs in the range 570–580 nm, Table III. The less symmetrical *cis*-isomers have much higher extinction coefficients (*ca.* 70–120 M^{-1} cm^{-1}) and the lowest energy d–d band occurs in the region 530–560 nm. For the *cis*-$[Cr(tet\ b)X_2]^{n+}$ compounds all the λ_{max} values appear shifted 20–50 nm towards the i.r. when compared with normal *cis*-$[CrN_4X_2]^{n+}$ chromophores.

The electronic spectra of the various complexes prepared are summarised in Table IV, and are consistent with a *trans*-configuration for the tet *a* derivatives and a *cis*-configuration for the tet *b* derivatives. Thus *trans*-$[CrCl_2(tet\ a)]ClO_4$ has the lowest energy ligand field band at 574 nm ($\epsilon = 25\ M^{-1}\ cm^{-1}$) while *cis*-$[CrCl_2(tet\ b)]Cl$ has λ_{max} 598 nm (this latter complex is insoluble in all the common solvents). A number of the complexes were insufficiently soluble in the common solvents for their solution spectra to be determined, and in these cases the λ_{max} values were obtained using Nujol mulls on filter paper.

TABLE III. Electronic Spectra of *Cis*- and *Trans*-$[CrN_4X_2]^{n+}$ Chromophores.

Complex	λ_{max} (ϵ) nm (M^{-1} cm^{-1})	Ref.
trans-$[CrCl_2(en)_2]^+$	578 (24.5) 453 (23) 396 (34)	17
trans-$[CrCl_2(cyclam)]^+$	572 (19.9) 407 (sh) (35) 365 (41)	1
cis-$[CrCl_2(en)_2]^+$	528 (71) 402 (69)	17
cis-$[CrCl_2(cyclam)]^+$	529 (111) 404 (106)	1
cis-$[Cr(en)_2(H_2O)_2]^{3+}$	484 (67) 366 (43)	18
cis-$[Cr(cyclam)(H_2O)_2]^{3+}$	483 (126) 370 (38)	1
cis-$[Cr(Me_2cyclam)(H_2O)_2]^{3+}$	506 (75) 380 (53)	19
trans-$[CrCl_2(Me_2cyclam)]^+$	571 (20) 386 (31)	19
cis-$[CrCl_2(Me_2cyclam)]^+$	559 (123) 412 (97)	19

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TABLE IV. Electronic Spectra of the Complexes.

Complex	Solvent	λ_{max} (ϵ) (nm) (M^{-1} cm^{-1})
trans-$[CrCl_2(tet\ a)]ClO_4$	DMF	574 (25), 440sh (27), 387 (47)[b]
trans-$[Cr(tet\ a)(NCS)_2]NCS \cdot 2H_2O$	Nujol[c]	500, 420, 322, *ca.* 238
trans-$[Cr(tet\ a)(H_2O)_2]Br_3 \cdot H_2O$[a]	Nujol[c]	530, 408, 340, 250
trans-$[Cr(tet\ a)(H_2O)_2](ClO_4)_2 \cdot H_2O$	MeOH	535 (65), 423 (96), 205 (1.05×10^4)
trans-$[Cr(tet\ a)Br_2]ClO_4$	DMF	602 (30), 410sh, 374 (47)
trans-$[Cr(tet\ a)Br_2]Br$	MeOH	600 (33), 410sh (38), 382 (43)
cis-$[CrCl_2(tet\ b)]Cl$	Nujol[c]	598, 430
cis-$[Cr(tet\ b)ox)]Br \cdot 1.5H_2O$	Nujol[c]	522, 390, 280sh, 232
cis-$[Cr(tet\ b)Br_2]Br$	Nujol[c]	595, 438, 250
cis-$[Cr(tet\ b)(NO_3)_2]NO_3$	Nujol[c]	525, 392, 230
cis-$[Cr(tet\ b)(N_3)_2]N_3$	Nujol[c]	570, 420, 280sh, 230
cis-$[Cr(tet\ b)(acac)](ClO_4)_2$	Nujol[c]	512, 385, 325
cis-$[Cr(tet\ b)(NO_3)_2]NO_3$	DMF	524 (202), 390 (116)
cis-$[Cr(tet\ b)(NCS)_2]NCS \cdot 0.5H_2O$	CH_3CN	526 (210), 390 (99), 322 (7.8×10^3), 235 (2.2×10^4)
cis-$[Cr(tet\ b)ox]ClO_4 \cdot 0.5H_2O$	DMF	528 (139), 380 (69)

[a]This is not a stable compound in water as it anates to the green bromo-complex. [b]Sperati (ref. 3) reports 578 (29), 420sh (31), 385 (42). [c]Nujol = nujol mull spectrum.

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