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Preparation of chromium(III) complexes with a series of tetraazacycloalkanes, [12]aneN$_4$ to [16]aneN$_4$, and solid-state thermal isomerisation of *cis*-[CrCl$_2$([15]- or [16]aneN$_4$)]$^+$

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Abstract

A series of chromium(III) complexes of the forms *cis*- and/or *trans*-[CrX$_2$(mac)]$^+$ and [Cr(C$_2$O$_4$)(mac)]$^+$ were prepared, where X is F$^-$, Cl$^-$, or Br$^-$ ion, and mac is 1,4,7,10-tetraazacyclododecane ([12]aneN$_4$), 1,4,7,10-tetraazacyclotridecane ([13]aneN$_4$), 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$, cyclam), 1,4,7,11-tetraazacyclotetradecane ([14]aneN$_4$, isocyclam), 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$), or 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$).

When *trans*-[CrF$_2$(py)$_4$]$^+$ and [CrCl$_3$(thf)$_3$] were used as the starting materials for the preparation of [CrX$_2$(mac)]$^+$ complexes, only cis isomers were formed for [12]- and [13]aneN$_4$, whereas only trans isomers were formed for [15]- and [16]aneN$_4$, irrespective of halide ions. Both cis and trans isomers were isolated for [14]aneN$_4$ (cyclam and isocyclam); cis isomers were more easily obtained than trans isomers for cyclam, and vice versa for isocyclam. *cis*-[CrCl$_2$([15]- or [16]aneN$_4$)]$^+$ was derived from the reaction of the corresponding [Cr(C$_2$O$_4$)([15]- or [16]aneN$_4$)]$^+$ with sulphinyl chloride in methanol. [Cr(C$_2$O$_4$)(mac)]$^+$ complexes were prepared by the reaction of the respective dihalogeno complexes with NaHC$_2$O$_4$. Relative ligand field strengths of macs were estimated from D_q^{xy} values for trans-dihalogeno complexes, and D_q^{av} values for cis-dihalogeno and oxalato complexes as follows: cyclam > isocyclam > [15]aneN$_4$ > [16]aneN$_4$ for the trans isomers; cyclam > [15]aneN$_4$ > [16]aneN$_4$ ≈ isocyclam > [13]aneN$_4$ > [12]aneN$_4$ for the cis isomers; cyclam > [15]aneN$_4$ > [13]aneN$_4$ > [16]aneN$_4$ ≈ isocyclam > [12]aneN$_4$ for the oxalato complexes. *cis*-[CrCl$_2$([15]- or [16]aneN$_4$)]$^+$ were found to isomerise thermally to the corresponding trans isomers, even in the solid state.

INTRODUCTION

A number of metal complexes with tetraazacycloalkanes (hereinafter called mac) have been extensively studied because they are interesting as

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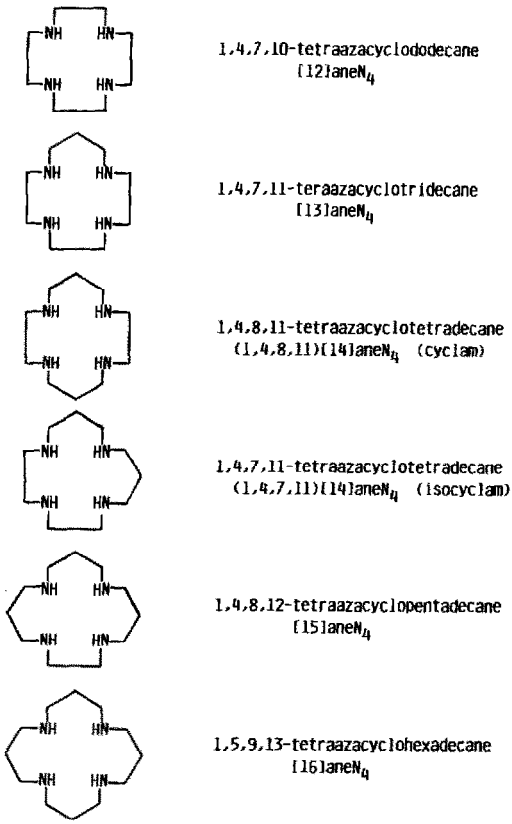

Fig. 1. Frameworks and abbreviations of a series of tetraazacycloalkanes (mac) used in the present study.

the structurally and functionally simplest models for investigating metalloproteins. However, only sporadic work has been carried out on chromium(III) complexes containing macs [1–7]. This may simply be due to the fact that the chromium(III) ion is so substitution-inert that its complexes are difficult to prepare. The primary purpose of the present study is therefore concerned with the preparation of a complete series of *cis*- and *trans*-$[CrX_2(mac)]^+$ and $[Cr(C_2O_4)(mac)]^+$, where X is F^-, Cl^-, or Br^- ion and mac is 1,4,7,10-tetraazacyclododecane ([12]aneN$_4$), 1,4,7,10-tetraazacyclotridecane ([13]aneN$_4$), 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$, cyclam), 1,4,7,11-tetraazacyclotetradecane ([14]aneN$_4$, isocyclam), 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$) or 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$). Figure 1 shows the frameworks and abbreviations of the tetraazacycloalkanes (mac) in the present study.

We have previously reported that coordinated ligands in metal complexes are unexpectedly movable even in the solid state: e.g. the complexes $[Cr(aa)(bb)(cc)]X_3$ easily lose a diamine (aa), which has the lowest boiling

point, to form either *cis*- or *trans*-[CrX_2(bb)(cc)]X depending upon the anion size (X^-), where aa, bb and cc are the same or different diamines among 1,2-diaminoethane (en), 1,2-diaminopropane (pn) and 1,3-diaminopropane (tn) [8]. In addition, the coordinated ligands in *cis*- and *trans*-[CrX_2(bb)(cc)]X must move for the complexes to isomerise [9]. It is thus informative to know whether or not the coordinated macs are movable in the solid state because they contain ring structures obtained by fusing together en and/or tn. Another purpose of the present study is therefore to gain information on the solid-state thermal isomerisation of the complexes obtained.

EXPERIMENTAL

Preparation of tetraazacycloalkanes

[13]aneN_4, cyclam, isocyclam, [15]aneN_4 and [16]aneN_4 were prepared by the same methods as those described in refs. 10–14, respectively. [12]aneN_4 was obtained in a manner similar to that of isocyclam, except that bis(2-aminoethyl)amine was used in place of bis(2-aminopropyl)amine.

Preparation of dihalogeno complexes

In general, the chloro and fluoro complexes were derived from [$CrCl_3$(thf)$_3$] [15] (thf = tetrahydrofuran) and/or *trans*-[CrF_2(py)$_4$]Br · H_2O [16] (py = pyridine), respectively, except for *cis*-[$CrCl_2$([15]aneN_4)]X (X = Cl, Br, I, SCN, BF_4 or $B(C_6H_5)_4$), *cis*-[$CrCl_2$([16]aneN_4)]Cl · 0.5H_2O, *trans*-[CrF_2(cyclam)]Br · H_2O and *cis*-[CrF_2(isocyclam)]Br · H_2O. *cis*-[$CrCl_2$([15]- or [16]aneN_4)]Cl was derived from the reaction of [$Cr(C_2O_4)$([15]- or [16]aneN_4)]ClO_4 with sulphinyl chloride in methanol. *trans*-[CrF_2(cyclam)]-Br · H_2O and *cis*-[CrF_2(isocyclam)]Br · H_2O were obtained by the reaction of the corresponding *trans*-dibromo(cyclam) and *cis*-dibromo(isocyclam) complexes with concentrated hydrofluoric acid, respectively. The bromo complexes were prepared by the reaction of the corresponding fluoro complexes with concentrated hydrobromic acid except for *trans*-[$CrBr_2$-(cyclam)]Br and *cis*-[$CrBr_2$(isocyclam)]Br, which were prepared by isomerisation of *cis*-[$CrBr_2$(cyclam)]Br and *trans*-[$CrBr_2$(isocycylam)]Br, respectively.

Chloro complexes

cis-*[$CrCl_2$([12]aneN_4)]Cl*, cis-*[$CrCl_2$([13]aneN_4)]Cl*, trans-*[$CrCl_2$([15]-aneN_4)]Cl and* trans-*[$CrCl_2$([16]ane N_4)]Cl.* These complexes were prepared by a modification of the method of Ferguson and Tobe [1]. [$CrCl_3$(thf)$_3$] [15] (5 mmol) and each tetraazacycloalkane (5 mmol) were dissolved in hot dimethylformamide (DMF, 45 cm^3). The solution was

refluxed for 20–30 min to give crude products. The crude cis and trans complexes were recrystallised from concentrated hydrochloric acid and from a mixture of water and acetone (1 : 1), respectively.

cis- *and* trans-*[$CrCl_2$(cyclam)]Cl.* A solution of [$CrCl_3(thf)_3$] (5 mmol) and cyclam (5 mmol) in DMF (45 cm^3) was refluxed for 20 min to produce crude cis complex with a small amount of trans isomer. The crude cis complex was suspended in boiling methanol (200 cm^3) for 5 min to give almost pure cis complex which was collected by filtration. The filtrate was used to obtain the trans isomer. Recrystallisation of the cis complex was carried out from concentrated hydrochloric acid.

The trans complex was obtained from the above filtrate by roto-evaporating to dryness. The trans complex thus obtained was purified by dissolving it in water and adding acetone to the solution.

cis- *and* trans-*[$CrCl_2$(isocyclam)]Cl.* A solution of [$CrCl_3(thf)_3$] (3.5 mmol) and isocyclam (3.5 mmol) in DMF was refluxed for 5 h to give a small amount of trans complex. The trans complex was collected by filtration, the filtrate being roto-evaporated to dryness. The products thus obtained were suspended in boiling methanol (100 cm^3) together with the above trans complex. The trans complex was generally more easily soluble in methanol than the cis complex. The insoluble cis isomer was collected by filtration, and recrystallised from a minimum amount of a mixture of water, acetone and concentrated hydrochloric acid (1 : 1 : 1). The above methanolic filtrate was evaporated to dryness to give crude trans complex, which was dissolved in a minimum amount of water; acetone was added to this solution to give green needles of pure trans complex.

cis-*[$CrCl_2$([15]aneN$_4$)]Cl · H_2O and* cis-*[$CrCl_2$([16]aneN$_4$)]Cl · 0.5H_2O.* Sulphinyl chloride (15 cm^3) was added dropwise to methanol (50 cm^3) at −10 °C; then [Cr(C_2O_4)([15]- or [16]aneN$_4$)]ClO_4 (10 mmol) was added (see below). The mixture was stirred at 0 °C for 6 h, during which time the mixture dissolved and changed from orange to purple. The purple cis products were then gradually precipitated, collected by filtration, and washed with cold ethanol and then ether. The *cis*-[15]aneN$_4$ complex could be recrystallised from hot methanol. However, attempts to purify the *cis*-[16]aneN$_4$ complex from methanol or acetone always failed because the cis form readily isomerised, so that the cis form was always contaminated to some extent with trans complex upon recrystallisation.

cis-[$CrCl_2$([15]aneN$_4$)]X (X = Br, I, SCN, BF_4 and $B(C_6H_5)_4$) were obtained by substitution of the chloride in methanol with NaBr, NaI, NaSCN, $NaBF_4$ and $NaB(C_6H_5)_4$, respectively.

Fluoro complexes

cis-*[CrF_2(cyclam)]Br.* *trans*-[$CrF_2(py)_4$]Br · 2H_2O [16] (10 mmol) dried at 100 °C for 2 h and cyclam (10 mmol) were dissolved in 2-methoxyethanol (10 cm^3). The solution was refluxed for 5 h to yield the desired complex.

Recrystallisation was carried out by dissolving it in water followed by gradual addition of acetone.

trans-*[CrF_2(cyclam)]Br · H_2O.* This was prepared from *trans*-[$CrBr_2$-(cyclam)]Br (see below) using a modification of the literature method [6]. *trans*-[$CrBr_2$(cyclam)]Br (10 mmol) was dissolved in a solution of NaOH (20 mmol) in water (20 cm^3). The resulting blue solution was cooled to room temperature and filtered to remove undissolved materials. The filtrate was acidified with an appropriate amount of 46% hydrofluoric acid and heated on a water bath until its volume was reduced to about 10 cm^3. After cooling, violet precipitates were obtained, which were collected by filtration and washed with acetone. Recrystallisation was carried out from a mixture of water and acetone (1 : 1).

cis- *and* trans-*[CrF_2(isocyclam)]Br · H_2O.* The cis complex was prepared by the same method as that described for *trans*-[CrF_2(cyclam)]Br except that *cis*-[$CrBr_2$(isocyclam)]Br (see below) was used in place of *trans*-[$CrBr_2$(cyclam)]Br. *trans*-[CrF_2(isocyclam)]Br was prepared in a similar way to that of *cis*-[CrF_2(cyclam)]Br, except that isocyclam was used in place of cyclam.

cis-*[CrF_2([12]aneN_4)]Br,* cis-*[CrF_2([13]aneN_4)]Br,* trans-*[CrF_2([15]-aneN_4)]Br and* trans-*[CrF_2([16]aneN_4)]Br.* These were prepared by a procedure similar to that described for *cis*-[CrF_2(cyclam)]Br · H_2O except that the respective tetraazacycloalkanes were used instead of cyclam.

Bromo complexes

cis-*[$CrBr_2$(cyclam)]Br.* The complex was prepared from the corresponding fluoro complex: a mixture of *cis*-[CrF_2(cyclam)]Br (3 mmol) and 48% HBr (10 cm^3) was stirred for one day in the dark under nitrogen atmosphere. Precipitates thus formed were collected by filtration and washed with acetone. Recrystallisation was carried out from dilute hydrobromic acid.

trans-*[$CrBr_2$(cyclam)]Br.* This was prepared by isomerisation of the above cis complex [2]. *cis*-[$CrBr_2$(cyclam)]Br (3 mmol) was dissolved in water (100 cm^3). The pH of the solution was adjusted to about 7 with $NaHCO_3$, and then the solution was refluxed for 8 h. The resulting solution was acidified with concentrated hydrobromic acid and then roto-evaporated to dryness. The residue thus obtained was heated in an air bath at 130 °C for 2 h. The solid was suspended in warm DMF (50 cm^3) for 10 min, and the insoluble trans isomer was collected by filtration and washed with a small amount of water and then acetone. The crude trans complex was recrystallised from dilute hydrobromic acid.

cis-*[$CrBr_2$([12]aneN_4)]Br · H_2O,* cis-*[$CrBr_2$([13]aneN_4)]Br,* trans-*[$CrBr_2$(isocyclam)]Br,* trans-*[$CrBr_2$([15]aneN_4)]Br and* trans-*[$CrBr_2$([16]-aneN_4)]Br.* These complexes were prepared by the same method as that for *cis*-[$CrBr_2$(cyclam)]Br except that the respective fluoro complexes were

TABLE 1

Analytical data for the cis-dihalogeno complexes

Mac	Complex	C (%)		H (%)		N (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
[12]aneN$_4$	[CrF$_2$([12]aneN$_4$)]Br	28.63	28.08	5.43	5.89	16.37	16.37
	[CrCl$_2$([12]aneN$_4$)]Cl [a]	28.70	29.06	5.80	6.10	16.49	16.95
	[CrBr$_2$([12]aneN$_4$)]Br·H$_2$O	19.87	19.94	4.92	4.60	11.81	11.62
[13]aneN$_4$	[CrF$_2$([13]aneN$_4$)]Br	30.10	30.34	6.10	6.22	15.44	15.73
	[CrCl$_2$([13]aneN$_4$)]Cl [a]	31.36	31.36	6.57	6.43	16.21	16.26
	[CrBr$_2$([13]aneN$_4$)]Br	22.96	22.61	4.41	4.64	11.58	11.72
Cyclam	[CrF$_2$(cyclam)]Br	31.34	32.44	6.65	6.53	14.68	15.13
	[CrCl$_2$(cyclam)]Cl [b]	33.38	33.49	6.81	6.74	15.55	15.62
	[CrBr$_2$(cyclam)]Br [b]	24.09	24.41	4.98	4.92	11.18	11.39
Isocyclam	[CrF$_2$(isocyclam)]Br·H$_2$O	30.49	30.94	7.14	6.75	14.40	14.43
	[CrCl$_2$(isocyclam)Cl [a]	33.38	33.49	6.70	6.74	15.21	15.62
	[CrBr$_2$(isocyclam)Br	24.23	24.41	4.89	4.92	11.27	11.39
[15]aneN$_4$	[CrCl$_2$([15]aneN$_4$)]Cl·H$_2$O	33.49	33.81	7.35	7.22	14.04	14.34
[16]aneN$_4$	[CrCl$_2$([16]aneN$_4$)]Cl·0.5H$_2$O	36.32	36.42	7.28	7.39	14.09	14.16

[a] Complexes reported in ref. 4.
[b] Complexes reported in ref. 1.

used in placed of *cis*-[CrF$_2$(cyclam)]Br. They were recrystallised from hot ethanol.

cis-*[CrBr$_2$(isocyclam)]Br.* The complex was obtained by isomerisation of *trans*-[CrBr$_2$(isocyclam)]Br: a solution of *trans*-[CrBr$_2$(isocyclam)]Br in

TABLE 2

Analytical data for the trans-dihalogeno complexes

Mac	Complex	C (%)		H (%)		N (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
Cyclam	[CrF$_2$(cyclam)]Br·H$_2$O	30.82	30.94	6.48	6.75	14.21	14.43
	[CrCl$_2$(cyclam)]Cl [a]	33.62	33.49	6.62	6.74	15.67	15.62
	[CrBr$_2$(cyclam)]Br [a]	24.46	24.41	4.59	4.92	11.52	11.39
Isocyclam	[CrF$_2$(isocyclam)]Br·H$_2$O	30.81	30.94	6.55	6.75	14.68	14.43
	[CrCl$_2$(isocyclam)]Cl [b]	33.74	33.49	6.77	6.74	15.20	15.62
	[CrBr$_2$(isocyclam)]Br	24.23	24.41	4.89	4.92	11.27	11.39
[15]aneN$_4$	[CrF$_2$([15]aneN$_4$)]Br	34.01	34.38	6.81	6.82	14.47	14.58
	[CrCl$_2$([15]aneN$_4$)]Cl [b]	35.02	35.45	7.03	7.03	14.70	15.03
	[CrBr$_2$([15]aneN$_4$)]Br	26.11	26.11	5.11	5.18	11.14	11.07
[16]aneN$_4$	[CrF$_2$([16]aneN$_4$)]Br	36.39	36.19	7.05	7.09	13.91	14.07
	[CrCl$_2$([16]aneN$_4$)]Cl	37.02	37.27	7.27	7.30	14.27	14.49
	[CrBr$_2$([16]aneN$_4$)]Br	27.58	27.72	5.39	5.43	10.73	10.77

[a] Complexes reported in ref. 1.
[b] Complexes reported in ref. 4.

TABLE 3

Analytical data for the oxalato complexes [a]

Complex	C (%)		H (%)		N (%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$[Cr(C_2O_4)([12]aneN_4)]ClO_4$	29.11	29.17	4.85	4.90	13.55	13.61
$[Cr(C_2O_4)([13]aneN_4)]ClO_4$	30.87	31.03	5.25	5.21	12.86	13.16
$[Cr(C_2O_4)(isocyclam)]ClO_4$ [b]	32.61	32.77	5.47	5.50	12.64	12.74
$[Cr(C_2O_4)(isocyclam)]ClO_4$ [c]	32.72	32.77	5.47	5.50	12.66	12.74
$[Cr(C_2O_4)([15]aneN_4)]ClO_4$	34.12	34.40	5.77	5.77	12.23	12.35
$[Cr(C_2O_4)([16]aneN_4)]ClO_4$	35.85	35.94	5.93	6.03	11.92	11.98

[a] The cyclam complex has already been reported in ref. 17.
[b] Complex derived from *cis*-$[CrCl_2(isocyclam)]Cl$.
[c] Complex derived from *trans*-$[CrCl_2(isocyclam)]Cl$.

48% HBr was stirred for one day to produce the cis isomer. Recrystallisation was carried out from dilute hydrobromic acid.

Preparation of oxalato complexes

The oxalato complexes were prepared by a modification of published procedures for the cyclam complex [17]. *cis*- or *trans*-$[CrCl_2(mac)]Cl$ (10 mmol) and $NaHC_2O_4$ (15 mmol) were dissolved in a minimum amount of water (around 15 cm^3), and the solution was heated at 80–90 ° C on a water bath for 3 or 24 h (3 h for the cis complex and 24 h for the trans complex). $NaClO_4$ (15 mmol) was then added to the hot solution, which was allowed to cool to yield the precipitates. The precipitates were collected by filtration, and washed with ethanol and then ether. Recrystallisation was carried out from water.

Tables 1–3 summarise the analytical data for the cis, trans and oxalato complexes obtained, respectively.

Measurements

Visible and ultraviolet absorption spectra were measured in 0.1 M HCl, 0.1 M $HClO_4$, water, methanol and acetone using a Jasco UVIDEC-505 UV/VIS recording digital spectrophotometer.

IR spectra were measured as KBr discs using a Jasco Model A-3 infrared spectrophotometer.

Cyclic voltamogramms were obtained with a Yanagimoto P-900 in a cell containing a glassy carbon working electrode, a platinum-coil auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. DMF was used as the solvent and tetrabutylammonium perchlorate

as the supporting electrolyte. Ferrocene was added as an internal check on the redox potential and reversibility.

TG and DTA measurements of the samples were carried out with a Seiko TA Station SSC 5000 system under flowing nitrogen (100 cm^3 min^{-1}), 10–20 mg of sample being used. The heating rate was 3.0 °C min^{-1}. The heating processes were also observed using a Chyo 100-L thermobalance.

RESULTS AND DISCUSSION

Preparation of cis- *and* trans-*[CrX_2(mac)]X*

For the preparation of *cis*- and *trans*-[CrX_2(mac)]X, [$CrCl_3(thf)_3$] [15] in DMF and/or *trans*-[$CrF_2(py)_4$]Br · H_2O [16] in 2-methoxyethanol were used as the starting materials because the macs barely reacted with other hydrated chromium(III) ions in aqueous media. Table 4 summarises the geometrical configuration of the $[CrX_2(mac)]^+$ complexes isolated, together with ideal metal–nitrogen (M–N) bond distances [19]. As seen from the table, when *trans*-$[CrF_2(py)_4]^+$ and [$CrCl_3(thf)_3$] were used as the starting materials for the preparation of $[CrX_2(mac)]^+$, only cis complexes were obtained for [12]- and [13]aneN_4 irrespective of halide ions. In marked contrast to this, only trans isomers were obtained for [15]- and [16]aneN_4. Both cis and trans isomers were obtained for cyclam and isocyclam; cyclam yielded mainly cis isomers, whereas isocyclam yielded mainly trans isomers. Such a selectivity in the formation of cis and trans isomers for macs is in accordance with the so-called ring size effects [18,19]: for [12]aneN_4 and [13]aneN_4, shorter ideal M–N distances (1.83 Å for [12]aneN_4 and 1.92 Å for [13]aneN_4) than the strain-free Cr–N distance

TABLE 4

Geometrical configuration of the complexes $[CrX_2(mac)]^+$ obtained when [$CrCl_3(thf)_3$] and/or *trans*-[$CrF_2(py)_4$]Br · H_2O were used as the starting materials [a]

Mac	[CrF_2(mac)]Br	[$CrCl_2$(mac)]Cl	[$CrBr_2$(mac)]Br	Ideal M–N bond distance (Å) [b]
[12]aneN_4	cis	cis	cis	1.83
[13]aneN_4	cis	cis	cis	1.92
Cyclam	cis and trans	cis and trans	cis and trans	2.07
Isocyclam	cis and trans	cis and trans	cis and trans	[c]
[15]aneN_4	trans	trans	trans	2.22
[16]aneN_4	trans	trans	trans	2.38

[a] Strain-free Cr–N bond distance was estimated as 2.05 Å from the empirical force-field calculation [7].

[b] Cited from ref. 19.

[c] Not estimated.

TABLE 5

Electronic spectral data for the cis-dihalogeno complexes obtained

Mac	Complex	$\tilde{\nu}(\times 10^3\ cm^{-1})$ (ϵ ($mol^{-1}\ dm^3\ cm^{-1}$)) [a]		D_q^{av} (cm^{-1}) [b]
		$\tilde{\nu}_I$	$\tilde{\nu}_{II}$	
[12]aneN$_4$	[CrF$_2$([12]aneN$_4$)]Br	17.5 (158)	27.6 (66)	1750
	[CrCl$_2$([12]aneN$_4$)]Cl	17.2 (150)	26.0 (93)	1720
	[CrBr$_2$([12]aneN$_4$)]Br·H$_2$O	16.7 (157)	25.6 (88)	1670
[13]aneN$_4$	[CrF$_2$([13]aneN$_4$)]Br	18.5 (159)	26.9 (59)	1850
	[CrCl$_2$([13]aneN$_4$)]Cl	17.9 (155)	24.6 (109)	1790
	[CrBr$_2$([13]aneN$_4$)]Br	17.7 (140)	23.7 (116)	1770
Cyclam	[CrF$_2$(cyclam)]Br	19.4 (127)	26.9 (59)	1940
	[CrCl$_2$(cyclam)]Cl	18.6 (128)	24.6 (140)	1860
	[CrBr$_2$(cyclam)]Br	18.3 (110)	23.7 (129)	1830
Isocyclam	[CrF$_2$(isocyclam)]Br·H$_2$O	18.7 (133)	25.8 (54)	1870
	[CrCl$_2$(isocyclam)]Cl	18.0 (115)	23.0 (96)	1800
	[CrBr$_2$(isocyclam)]Br	17.9 (110)	22.3 (102)	1790
[15]aneN$_4$	[CrCl$_2$([15]aneN$_4$)]Cl·H$_2$O	18.5 (70)	23.8 (71)	1850
[16]aneN$_4$	[CrCl$_2$([15]aneN$_4$)]Cl·0.5H$_2$O	18.0 (52)	23.7 (54)	1800

[a] Measured in methanol.

[b] Estimated from the lower energy band maxima.

(2.05 Å) [7] prevent chromium(III) ion from incorporating into small ligand holes in a coplanar manner; hence only cis complexes were obtained. However, [15]aneN$_4$ and [16]aneN$_4$ which have greater ideal M–N distances (2.22 Å for [15]aneN$_4$ and 2.38 Å for [16]aneN$_4$) than the strain-free Cr–N distance preferentially produced trans isomers. Thus some thought was required in the preparation of *cis*-[15]- and [16]aneN$_4$ complexes. Fortunately, we successfully prepared *cis*-[CrCl$_2$([15]- and [16]aneN$_4$)]Cl using the reaction of [Cr(C$_2$O$_4$)([15]- and [16]aneN$_4$)]ClO$_4$ with sulphinyl chloride in methanol at 0 °C. The *cis*-[16]aneN$_4$ complex thus obtained was isomerised to trans isomer in water, acetone and methanol in a short period of time (about 2 h). Both the [15]- and [16]aneN$_4$ complexes were found to isomerise thermally even in the solid state (see below).

Relative ligand field strengths of the macrocyclic ligands

Tables 5–7 summarise the electronic spectral data for *cis*- and *trans*-[CrX$_2$(mac)]X, and [Cr(C$_2$O$_4$)(mac)]ClO$_4$. The octahedral complexes of a d^3 ion usually exhibit the absorption band due to two spin-allowed d–d transitions from $^4A_{2g}$ ground state to $^4T_{2g}$ and $^4T_{1g}$ excited states. The two excited states are expected to split into more than two levels in descending

TABLE 6

Electronic spectral data for the trans-dihalogeno complexes obtained

Mac	Complex	$\tilde{\nu}(\times 10^3\ cm^{-1})$ (ϵ ($mol^{-1}\ dm^3\ cm^{-1}$)) [a]				D_q^{xy} (cm^{-1}) [b]
		$\tilde{\nu}_I$		$\tilde{\nu}_{II}$		
Cyclam	$[CrF_2(cyclam)]Br \cdot H_2O$	19.5 (16)	23.9 (22)	27.0 (sh)	28.9 (20)	2360
	$[CrCl_2(cyclam)]Cl$	17.6 (20)	24.6 (sh)	27.2 (33)		2380
	$[CrBr_2(cyclam)]Br$	16.6 (30)	22.7 (sh)	25.0 (sh)	27.5 (40)	2310
Isocyclam	$[CrF_2(isocyclam)]Br \cdot H_2O$	18.8 (41)	22.3 (85)	23.4 (sh)	28.4 (60)	2200
	$[CrCl_2(isocyclam)]Cl$	17.0 (20)	21.5 (sh)	22.3 (58)	26.3 (sh)	2170
	$[CrBr_2(isocyclam)]Br$	16.2 (42)	21.3 (97)	22.7 (sh)	26.4 (69)	2090
[15]aneN$_4$	$[CrF_2([15]aneN_4)]Br$	18.6 (24)	21.2 (44)	24.6 (sh)	28.4 (33)	2120
	$[CrCl_2([15]aneN_4)]Cl$	16.9 (26)	21.5 (63)	24.1 (67)		2110
	$[CrBr_2([15]aneN_4)]Br$	16.1 (36)	20.8 (sh)	22.0 (64)	24.7 (sh)	2080
[16]aneN$_4$	$[CrF_2([16]aneN_4)]Br$	18.2 (22)	22.3 (33)	24.2 (13)	28.6 (15)	2040
	$[CrCl_2([16]aneN_4)]Cl$	16.2 (35)	20.0 (33)	23.8 (66)		1980
	$[CrBr_2([16]aneN_4)]Br$	15.5 (45)	20.0 (sh)	22.9 (67)		1930

[a] Measured in methanol; sh stands for shoulder.
[b] Estimated from the results of Gaussian analyses of the spectra by the method of ref. 19.

in symmetry from O_h to D_{4h} and C_{2v}. Thus, the present complexes are expected to give more than two absorption bands. However, as seen from Tables 5 and 7, *cis*-$[CrX_2(mac)]X$ and $[Cr(C_2O_4)(mac)]ClO_4$ gave only two

TABLE 7

Electronic spectral data and cyclic voltammetric data for the oxalato complexes

Complex	$\tilde{\nu}(\times 10^3\ cm^{-1})$ (ϵ ($mol^{-1}\ dm^3\ cm^{-1}$)) [a]		D_q^{av} (cm^{-1}) [b]	Cr(III)/Cr(II) reduction potential (V vs. SCE)
	$\tilde{\nu}_I$	$\tilde{\nu}_{II}$		
$[Cr(C_2O_4)([12]aneN_4)]ClO_4$	18.6 (181)	26.8 (93)	1860	−1.64 [f]
$[Cr(C_2O_4)([13]aneN_4)]ClO_4$	19.9 (167)	26.9 (116)	1990	−1.76 [f]
$[Cr(C_2O_4)(cyclam)]ClO_4$ [c]	20.3 (149)	27.0 (117)	2030	−1.87 [g]
$[Cr(C_2O_4)(isocyclam)]ClO_4$ [d]	19.9 (173)	26.3 (127)	1990	−1.75 [f]
$[Cr(C_2O_4)(isocyclam)]ClO_4$ [e]	19.9 (200)	26.3 (168)	1990	−1.75 [f]
$[Cr(C_2O_4)([15]aneN_4)]ClO_4$	20.1 (101)	26.5 (106)	2010	−1.66 [g]
$[Cr(C_2O_4)([16]aneN_4)]ClO_4$	19.9 (76)	26.2 (101)	1990	−1.59 [g]

[a] Measured in 0.1 M hydrochloric acid.
[b] Estimated from the lower energy band maxima.
[c] Cited from ref. 17.
[d] Prepared from the cis-dichloro complex.
[e] Prepared from the trans-dichloro complex.
[f] Reversible.
[g] Irreversible.

absorption maxima due to the spin-allowed transitions. In this case, the average ligand field parameters (D_q^{av}) for the cis complexes were estimated from the lower energy first-band maxima (ν_1). However, *trans*-$[CrX_2(mac)]X$ gave three or four bands. For the better estimation of ligand field parameters (D_q^{xy}), Gaussian analyses were carried out for the spectra of the trans complexes using the method of Schwartz [20].

The D_q^{av} and D_q^{xy} values thus obtained may reflect the relative ligand field strengths of the macrocyclic ligands. From the comparison of the D_q^{av} values for the cis-dichloro and oxalato complexes, and the D_q^{xy} values for the trans-dichloro complexes, the order of the ligand field strengths of the macrocyclic ligands can be evaluated as follows.

(1) For the cis-dichloro complexes, cyclam > [15]aneN$_4$ > [16]aneN$_4$ ≈ isocyclam > [13]aneN$_4$ > [12]aneN$_4$;

(2) For the oxalato complexes, cyclam > [15]aneN$_4$ > [13]aneN$_4$ > [16]aneN$_4$ ≈ isocyclam > [12]aneN$_4$;

(3) For the trans-dichloro complexes, cyclam > isocyclam > [15]aneN$_4$ > [16]aneN$_4$.

In every case, cyclam is in the highest position, implying that cyclam best fits to chromium(III) ion.

It should be mentioned that we derived two oxalato complexes of cyclam and isocyclam from the corresponding cis- and trans-dichloro complexes, respectively. The electronic spectra of the two cyclam complexes prepared from the cis- and trans-dichloro complexes were identical, whereas those of isocyclam were not: as seen from Table 7, the ϵ values (173 and 127 mol^{-1} dm^3 cm^{-1}) for the oxalato complex prepared from the cis-dichloro complex are smaller than those (200 and 168 mol^{-1} dm^3 cm^{-1}) prepared from the trans-dichloro complex, although their absorption maxima appear at the same wave numbers (19.9 and 26.1 cm^{-1}). This suggests the presence of two isomers in the isocyclam complexes, but unfortunately characterisation of the two isomers could not be made.

Cyclic voltammetry

The cyclic voltammetric data for the oxalato complexes are listed in the last column of Table 7. The Cr(III)/Cr(II) reduction waves of the cyclam, [15]aneN$_4$ and [16]aneN$_4$ complexes were irreversible, while those of the [12]aneN$_4$, [13]aneN$_4$ and isocyclam complexes were reversible. Inspection of the Cr(III)/Cr(II) reduction potentials tells us that the order of resistance to reduction is cyclam > [13]aneN$_4$ ≈ isocyclam > [15]aneN$_4$ > [12]aneN$_4$ > [16]aneN$_4$. This indicates that the macrocyclic ligands of intermediate ring size such as cyclam, isocyclam and [13]aneN$_4$ stabilise the chromium(III) oxidation state more than those of smaller or greater ring size; cyclam stabilises the oxidation state most.

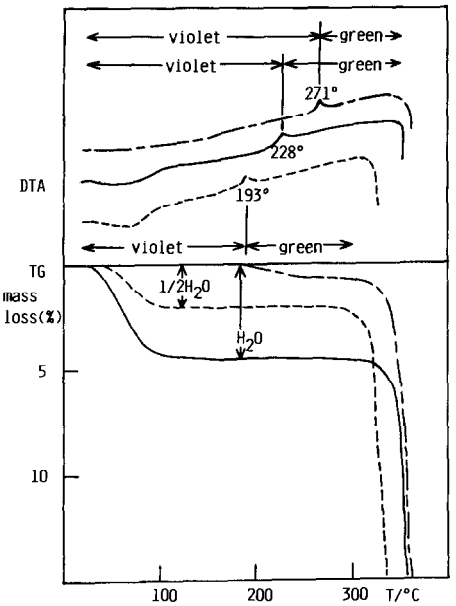

Fig. 2. TG and DTA curves of *cis*-$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$ (——), *cis*-$[CrCl_2([15]aneN_4)]BF_4$ (— - —) and *cis*-$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$ (- - - - -).

Isomerisation of cis-*$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$,* cis-*$[CrCl_2([15]aneN_4)]BF_4$ and* cis-*$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$ in the solid state*

The solid state thermal isomerisation of the complexes were investigated using TG and DTA methods.

Figure 2 illustrates the TG and DTA curves of *cis*-$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$, *cis*-$[CrCl_2([15]aneN_4)]BF_4$ and *cis*-$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$. The TG curve of *cis*-$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$ shows a mass loss at 30–100 °C, which corresponds to one mole of lattice water (found, 4.6%; calcd., 4.6%). *cis*-$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$ evolved a half mole of lattice water (found, 2.1%; calcd., 2.3%) at 30–100 °C. *cis*-$[CrCl_2([15]aneN_4)]BF_4$ has no lattice water. No change in the TG curves is found until the complexes decompose at about 310 °C (*cis*-$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$), 290 °C (*cis*-$[CrCl_2([15]aneN_4)]BF_4$) and 300 °C (*cis*-$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$). However, small but clear exothermic DTA peaks appear with no weight loss at 228 °C (*cis*-$[CrCl_2([15]aneN_4)]Cl \cdot H_2O$), 271 °C (*cis*-$[CrCl_2([15]aneN_4)]BF_4$) and 193 °C (*cis*-$[CrCl_2([16]aneN_4)]Cl \cdot 0.5H_2O$), when all the complexes changed in colour from the original violet to green. The electronic spectra of the green products thus obtained were identical to those of *trans*-$[CrCl_2([15]aneN_4)]^+$ and *trans*-$[CrCl_2([16]aneN_4)]^+$, indicating that all the cis complexes isomerise exothermically to the corresponding trans forms.

Such an exothermic isomerisation has also been found in the solid state isomerisation of the bis(diamine) complexes *cis*-$[CrX_2(aa)_2]Y$ where X and Y are chloride and/or bromide ions and aa is a diamine [9]. During the isomerisation of the bis(diamine) complexes, the intermediate $[CrX_2Y(aa)_2]$ was isolated, in which one of the diamines acts as a monodentate ligand. However, such an intermediate could not be obtained in the course of the isomerisation of the present macrocyclic complexes. It may be considered that the isomerisation takes place in such a way that one of the four nitrogen atoms in the macrocyclic ligand migrates to the position of one of the coordinated chloride ions. The details of the isomerisation are under investigation.

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REFERENCES

1 J. Ferguson and M.L. Tobe, Inorg. Chim. Acta, 4 (1970) 109.
2 C.K. Poon and K.C. Pun, Inorg. Chem., 19 (1980) 568.
3 G.J. Samuels and J.H. Espenson, Inorg. Chem., 19 (1980) 233.
4 R.G. Swisher, G.A. Brown, R.C. Smierciak and E.L. Blinn, Inorg. Chem., 20 (1981) 3941.
5 D.A. House, R.W. Hay and M.A. Ali, Inorg. Chim. Acta, 72 (1983) 239.
6 J. Eriksen and O. Mønsted, Acta Chem. Scand., A37 (1983) 579.
7 J. Thom, J.C. Boeyens, G.J. MacDougal and R.D. Hancock, J. Am. Chem. Soc., 106 (1984) 3198.
8 A. Uehara, Y. Nishiyama and R. Tsuchiya, Inorg. Chem., 21 (1982) 2422.
9 R. Tsuchiya, A. Uehara and T. Yoshikuni, Inorg. Chem., 21 (1982) 590.
10 Y. Hung, Inorg. Synth., 20 (1980) 106.
11 E.K. Barefield, F. Wagner, A.W. Herlinger and A.R. Dahl, Inorg. Synth., 16 (1976) 220.
12 L. Sabatini and L. Fabbrizzi, Inorg. Chem., 18 (1979) 438.
13 E.K. Barefield and G. Freeman, Inorg. Synth., 20 (1980) 108.
14 W.L. Smith and K.N. Raymond, Inorg. Synth., 20 (1980) 109.
15 J.P. Collman, E.T. Kittleman, W.S. Hunt and N.A. Moore, Inorg. Synth., 8 (1966) 150.
16 J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen and C.E. Schäffer, Acta Chem. Scand., 24 (1970) 247.
17 D.A. House and V. McKee, Inorg. Chem., 23 (1984) 4237.
18 Y. Hung, L.Y. Martin, S.C. Jackels, A.M. Tait and D.H. Busch, J. Am. Chem. Soc., 99 (1977) 4029.
19 L.Y. Martin, L.J. DeHayes, L.J. Zompa and D.H. Busch, J. Am. Chem. Soc., 96 (1974) 4046.
20 L.M. Schwartz, Anal. Chem., 43 (1971) 1336.