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Complexes of Chromium(III) with a Cyclic Tetradentate Secondary Amine

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A series of cationic octahedral chromium(III) complexes of the type cis$[Cr\,cyclamX_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; X = Cl, Br, NCS, ONO and N_3) have been isolated as crystalline salts. In addition, the trans*–$[Cr\,cyclamCl_2]^+$ cation has been isolated as its chloride and perchlorate. The* cis *and* trans*–$[Cr\,cyclam(H_2O)_2]^{3+}$ cations, together with the corresponding hydroxoaquo and dihydroxo derivatives have also been characterised, either as solids or else in solution and the various acid dissociation constants determined. In general, the geometric configuration has been assigned by comparison of the visible absorption spectra with those of the analogous bis(ethylenediamine) complexes. All the substitution reactions appear to take place with full retention of geometric configuration.*

Introduction

The cyclic tetramine, 1,4,8,11-tetraazacyclotetradecane (cyclam) forms complexes with a variety of transition metal ions.[1,2,3,4] The ligand can be found in the flat[1,2] or folded[4] configuration, leading to *trans* and *cis* octahedral complexes respectively, but the different stereochemical requirements of the two forms[1] prevent steric change during substitution and make these complexes valuable substances in any study of the mechanism and steric course of octahedral substitution.[4,5] Furthermore, the difficulty of removing such a macrocyclic ligand from the complex makes it particularly useful for the study of the aquation of the acido group in the acido-amine complexes of chromium(III) where it has been reported[6] that, in the aquation of *trans*–$[Cren_2Cl_2]^+$ two parallel reactions occur, one leading to the displacement of the chloride and the other leading to displacement of ethylenediamine. In order to avoid this complication we have prepared a number of complexes of the type, $[Cr\,cyclamXY]^{n+}$. The kinetics and mechanism of their acid and base hydrolysis will be reported elsewhere.

Results and Discussion

On refluxing a solution of $CrCl_3 . 3THF$ (THF = tetrahydrofuran) with excess 1,4,8,11-tetraazacyclotetradecane in dimethylformamide, a mixture of *cis* and *trans*–$[Cr\ cyclam\ Cl_2]Cl$ was obtained. The *trans* isomer rarely comprised more than 10% of the total product and occasionally was not present at all. Attempts to prepare this isomer in good yield by other methods, for example, by oxidising a mixture of chromium(II) chloride, sodium chloride and the ligand, were unsuccessful and, in every case, only the *cis* isomer was obtained. This apparent preference for the Cr^{III} complexes to adopt a *cis* configuration is in marked contrast to the behaviour observed with Co^{III} where the *trans* isomers are usually obtained and *cis* isomers can be isomerised to the *trans* form under the appropriate conditions.[7] Until now we have been unable to cause any of the chromium(III) complexes to undergo isomerisation or any other stereochemical change and so we cannot say whether the preponderence of the *cis* configuration is a thermodynamic as well as a kinetic effect. The two dichloro complexes served as starting materials for all the other complexes examined. All the substitution reactions took place with complete retention of configuration and the lack of crystalline *trans*-derivatives other than the dichloro complex reflects a shortage of the starting material, which was used preferentially for the kinetic studies, rather than any inherent instability of the *trans* configuration.

The assignment of geometric configuration is based entirely upon the comparison of the visible absorption spectra with those of known bis(ethylenediamine) analogues. This comparison is most valid when the difference between the spectra of the *cis* and *trans* isomers is greatest, as for example, in the case of the dichloro, dibromo, and diaquo species; but, in general, the *cis* isomers have higher extinction coefficients. The characteristic features of the visible and near U.V. spectra are collected in Table I where they are compared with published data for the corresponding characterised bis(ethylenediamine)-chromium(III) complexes.

The coordinated chloride of the *cis*-dichloro-complex can be readily removed by warming with a slight excess of acidified silver nitrate solution. Two orange complexes, analysing as $Cr(NO_3)_3$ cyclam . $2H_2O$ and $Cr(NO_3)_3$ cyclam . H_2O, can be isolated from the reac-

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Table I. Characteristic Features of the Electronic Absorption Spectra of *cis*— and *trans*—[Cr cyclam XY]$^{n+}$ and the corresponding [Cren$_2$XY]$^{n+}$ Complexes

XY	amine	λ_{max} mμ	ε_{max}	λ_{min} mμ	ε_{min}	λ_{max} mμ	ε_{max}	λ_{min} mμ	ε_{min}	λ_{max} mμ	ε_{max}	Ref.
trans—Cl_2	en	578	24.5	514	8	453	23	439	22	396	34	6
trans—Cl_2	cyclam	572	19.9	485	4	~407 sh	35			365	41	this work
cis—Cl_2	en	528	71	456	21	402	69					6
cis—Cl_2	cyclam	529	111	468	26	404	106					this work
trans—Br_2	en	607	35	530	5	460 sh	24					9
cis—Br_2	en	544	89	468	29	415	83					9
cis—Br_2	cyclam	527	94	455	48	408	72	356	38			this work
trans—$(OH)_2$	en	502	32			396	29					10
trans—$(OH)_2$	cyclam	482	31			388	36					this work
cis—$(OH)_2$	en	526	64			377	66					10
cis—$(OH)_2$	cyclam	547	84			370	66					this work
trans—$(NCS)_2$	en	486	95	416	31	~365 sh	67					11
cis—$(NCS)_2$	en	490	148	417	40	370	91	360	87			11
cis—$(NCS)_2$	cyclam	486	189	418	35	368	101					this work
trans—$(ONO)_2$	en	477	44			328	185					12
cis—$(ONO)_2$	en	481	90			357	152					12
cis—(ONO_2)	cyclam	481	134	415	29	355	211					this work
cis—$(N_3)_2$	en	515	224	447	69	398	148	352	38			13
cis—$(N_3)_2$	cyclam	517	276	445	60	400	144					this work
trans—$(H_2O)_2$	en	507	23			445	29					10
trans—$(H_2O)_2$	cyclam	510	24	462	12	405	39	390	38	350	53	this work
cis—$(H_2O)_2$	en	484	67			366	43					10
cis—$(H_2O)_2$	cyclam	483	126	417	26	370	38					this work
trans—$(H_2O)Cl$	en	545	21	495	16	445	25	427	24	380	46	6
trans—$(H_2O)Cl$	cyclam	550	16									this work
cis—$(H_2O)Cl$	en	508	72	437	20	385	56					6

sh = shoulder.

Table II. pK$_a$ values for some *cis*- and *trans* diaquo complexes of chromium(III) and cobalt(III)

Complex	Conditions	pK$_1$	pK$_2$	Ref.
cis—[Cr cyclam$(H_2O)_2$]$^{3+}$	20°, ionic	3.8 [a]	7.0 [a]	this work
	strength *ca.* 0.1	3.8 [b]	7.0 [b]	this work
trans—[Cr cyclam$(H_2O)_2$]$^{3+}$	20°, $\mu = 0.1$	3.05 [a]	6.6 [a]	this work
cis—[Co cyclam$(H_2O)_2$]$^{3+}$	25° 0.5 *M* $NaClO_4$	4.9	8.0	7
trans—[Co cyclam$(H_2O)_2$]$^{3+}$	25° 0.5 *M* $NaClO_4$	2.82	7.22	7
cis—[Cr en$_2(H_2O)_2$]$^{3+}$	25° 1.0 *M* $NaNO_3$	4.80	7.17	10
trans—[Cr en$_2(H_2O)_2$]$^{3+}$	25° 1.0 *M* $NaNO_3$	4.08	7.49	10
cis—[Co en$_2(H_2O)_2$]$^{3+}$	25° 1.0 *M* $NaNO_3$	6.06	8.19	15
trans—[Co en$_2(H_2O)_2$]$^{3+}$	25° 1.0 *M* $NaNO_3$	4.45	7.94	15

[a] From the acid back titration of the product of base hydrolysis of the dichloro complex. [b] Complex supplied as *cis*—Cr cyclam$(NO_3)_3 2H_2O$.

tion mixture. The analysis would suggest coordinated nitrate in at least one of the two cases and the infra-red spectrum of a Nujol mull of the monohydrate contains a number of very strong bands associated with coordinated nitrate.[8] Two very strong multiplet bands at 1508, 1518 (sh), 1523 (sh), 1528 cm^{-1} and 1268, 1275 (sh), 1283 and 1304 cm^{-1} have been assigned to the asymmetric and symmetric NO_2 stretch of coordinated nitrate and a strong broad band at 1000 cm^{-1} has been assigned to the N—O stretch. The other bands expected for coordinated and ionic nitrate are present but not readily distinguishable from Nujol and cyclam absorptions. Nevertheless, the spectrum of a freshly prepared aqueous solution is identical to that of the *cis*-diaquo complex indicating that these complexes are extremely labile. The nitrato complex serves as the starting material for the preparation of all the other *cis* diacido species.

The *cis* hydroxoaquo complex can be obtained as its crystalline dithionate trihydrate and a solution of this salt is in rapid acid-base equilibrium with the diaquo and the dihydroxo complexes. However, on heating this material for three hours at 120° a product is obtained that analyses as [Cr cyclam $OHH_2OS_2O_6$]. This compound, although soluble in dilute acid, is only slowly converted to the *cis* diaquo complex and it seems likely that the dehydrated species is either polynuclear with hydroxide bridges, or else the dithionate group is coordinated.

The visible absorption spectrum of *cis*—[Cr cyclam$(ONO)_2$]$^+$ closely resembles that of the corresponding

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bis(ethylenediamine) complex which has been assigned an O-bonded nitrito arrangement.[12] The spectrum of its acidified aqueous solution changes slowly to that of the *cis* diaquo complex suggesting an acid catalysed aquation similar to that reported by Matts and Moore[14] for $[Cr(NH_3)_5ONO]^{2+}$ At first sight the reaction appears to be somewhat slower but further comment should be reserved until after a detailed kinetic study has been carried out.

The first and second acid dissociation constants of *cis*- and *trans*- $[Cr\,cyclam(H_2O)_2]^{3+}$ were determined by recording the pH at half neutralisation in the course of titrating either the diaquo complex with standard alkaly or else the dihydroxo complex with standard acid. The dihydroxo complexes were obtained in solution by reacting the corresponding dichloro complexes with excess alkali. Although it has not been possible to isolate the *trans*–$[Cr\,cyclam(H_2O)_2]^{3+}$ catio nor either of its conjugate bases as pure solids it can be shown that the act of base hydrolysis of the *trans*-dichloro complex takes place with complete retention of configuration. For example, at 600 mμ the molar extinction coefficient of the product of the base hydrolysis of the *trans*–$[Cr\,cyclamCl_2]^+$ is 1.9 M^{-1} cm^{-1} (c.f. 53 for the *cis* dihydroxo complex). The pK$_a$ values are reported in Table II, where they are compared with data for the analogous Co^{III} cyclam complexes as well as the ethylenediamine complexes. The acidities are consistent with previously noticed trends. Thus the replacement of two ethylenediamine ligands by one cyclam considerably enhances the acidity of the aquo group in both the Cr^{III} and Co^{III} analogues. This effect is most apparent for the first dissociation. The differences in the acidity of the *cis* and *trans* diaquo complexes is reduced on going from Co^{III} to Cr^{III} and this, in great part, is due to a marked enhancement of the acidity of the *cis* diaquo chromium(III) species. It is not immediately apparent why this should be so.

Experimental Section[16]

cis-*dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III)chloride.* Trichlorotris(tetrahydrofuran)-chromium(III) (1.8 g) and 1,4,8,11-tetraazacyclotetradecane (1.0 g) were dissolved in hot, dry dimethylformamide and the solution refluxed for ten minutes. The precipitated complex was filtered, off, washed with warm dimethylformamide and then with acetone. The product was suspended in boiling methanol (200 ml) for five minutes and the insoluble *cis* isomer was filtered off from the methanol solution of the *trans* complex and recrystallised as dark-red needles from a H_2O/HCl/acetone mixture. *Anal.* Calcd. for $C_{10}H_{24}N_4Cl_3Cr$: C, 33.6; H, 6.7; N, 15.6; Cl, 29.6; ionic Cl, 9.9. Found: C, 33.6; H, 7.2; N, 15.5; Cl, 30.05; ionic Cl, 10.05.

The *cis-perchlorate* was prepared by adding a few drops of concentrated perchloric acid to a cold saturated aqueous solution of the chloride. The salt, which precipitated immediately, was filtered off, washed with a little cold water and then acetone and air dried. *Anal.* Calcd. for $C_{10}H_{24}N_4O_4Cl_3Cr$: C, 28.4; H, 5.7; N, 13.3; Cl, 25.2. Found: C, 28.2; H, 5.8; N, 13.0; Cl, 24.9.

trans-*dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride.* The methanolic extract from the preparation of the *cis* isomer was evaporated to small bulk and acetone added to precipitate the complex. This was filtered off and recrystallised from water-acetone mixture from which it was obtained as grey-pink (tungsten light), grey-green (daylight) needles. *Anal.* Calcd. for $C_{10}H_{24}N_4Cl_3Cr$: C, 33.6; H, 6.7; N, 15.6; Cl, 29.6; ionic Cl, 9.9. Found: C, 34.2; H, 6.8; N, 15.8; Cl, 30.2; ionic Cl, 9.9.

The very slightly soluble *trans* perchlorate was prepared in the same way as the *cis* isomer. *Anal.* Calcd. for $C_{10}H_{24}N_4O_4Cl_3Cr$: C, 28.4; H, 5.7; N, 13.3; Cl, 25.2. Found: C, 28.5; H, 5.7; N, 13.1; Cl, 25.1.

cis-*nitratoaquo(1,4,8,11-tetraazacyclotetradecane)-chromium(III) nitrate.* A solution *cis*–$[Cr\,cyclamCl_2]Cl$ (3.6 g, 0.01 moles) in water (50 ml) was treated with silver nitrate (5.27 g, 0.031 moles) in water (50 ml) containing a few drops of concentrated nitric acid. The mixture was refluxed in subdued light for 15 minutes, cooled to room temperature and the precipitated AgCl was filtered off. The filtrate was evaporated on a hot plate until the volume was reduced to 5-10 ml and then refiltered through a porosity 4 filter. A saturated solution of lithium nitrate in acetone (100 ml) was added and, on cooling and scratching the walls of the beaker, an orange crystalline powder was obtained. On various occasions samples containing one or two moles of water were obtained but these did not differ significantly either in their properties or their colour. *Anal.* (monohydrate) Calcd. for $C_{10}H_{26}N_7O_{10}Cr$: C, 26.2; H, 5.7; N, 21.4. Found: C, 26.2; H, 6.0; N, 21.3. (dihydrate) Calcd. for $C_{10}H_{28}N_7O_{11}Cr$: C, 25.3; H, 5.95; N, 20.7. Found: C, 25.5; H, 5.7; N, 20.6.

cis-*hydroxoaquo(1,4,8,11-tetraazacyclotetradecane)-chromium(III) dithionate trihydrate.* A solution of *cis*–$[Cr\,cyclam(NO_3)(H_2O)](NO_3)_2(H_2O)$(0.5 g) in water (5 ml) was treated with pyridine (5 ml) and then a saturated aqueous solution of lithium dithionate (1-2 ml). Acetone (50 ml) was added and the hydrated complex precipitated as a violet-pink powder which was filtered off, washed with acetone and dried over silica gel. *Anal.* Calcd. for $C_{10}H_{33}N_4O_{11}CrS_2$: H, 6.3; C, 23.9; H, 6.6; N, 11.2; S, 12.8. Found: C, 24.0; N, 11.0; S, 12.6.

On heating in an oven at 120° the complex loses three moles of water and the colour deepens to violet. *Anal.* Calcd. for $C_{10}H_{27}N_4O_8CrS_2$: C, 26.8; H, 6.0; N, 12.5; S, 14.3. Found: C, 27.1; H, 6.0; N, 12.6; S, 14.3.

cis-*diaquo(1,4,8,11-tetraazacyclotetradecane)chromium(III)bromide-trihydrate.* Excess bromine-free concentrated hydrobromic acid was added to solid *cis*–$[Cr\,cyclamOH(H_2O)]S_2O_6 2H_2O$ and the complex

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(16) Although we have been fortunate so far and have had no trouble with these compounds it should be pointed out that many perchlorates and nitrates of transition metal amine complexes have been known to explode violently, especially when dried. Care should always be taken when preparing and handling such compounds.

was precipitated on addition of a large volume of acetone. The orange powder (which is slightly light sensitive) was filtered off, washed with acetone and air dried. *Anal.* Calcd. for $C_{10}H_{32}N_4O_4Br_3Cr$: C, 21.3; H, 5.7; N, 9.9; Br, 42.5. Found: C, 21.4; H, 5.8; N, 10.1; Br, 42.1.

cis-*dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide.* A solution of *cis*–[Cr cyclam-$(H_2O)(NO_3)](NO_3)_2H_2O$ (0.5 g) in water (10 ml) was heated for 5-10 minutes with excess hydrobromic acid (10 ml of 60% HBr). The complex crystallised out on cooling as grey-violet crystals, which could be recrystallised from dilute HBr. *Anal.* Calcd. for $C_{10}H_{24}N_4Br_3Cr$: C, 24.4; H, 4.9; N, 11.4; Br, 48.6. Found: C, 24.6; H, 5.1; N, 11.0; Br, 48.6.

The following *cis*-diacido salts were prepared by slowly adding a saturated solution of the sodium salt of the required anionic ligand to a boiling solution of the aquo-nitrato complex (0.5 g) in water (10 ml). The mixture was then refluxed for 5-10 minutes and the required complex crystallised from the cooled and evaporated solution.

cis-*diazido(1,4,8,11-tetraazacyclotetradecane)chromium(III) azide.* Red violet crystals (0.3 g). *Anal.* Calcd. for $C_{10}H_{24}N_{13}Cr$: C, 31.7; H, 6.4; N, 48.2. Found: C, 31.9; H, 6.5; N, 48.1.

cis-*dinitrito(1,4,8,11-tetraazacyclotetradecane)chromium(III) nitrate.* Red brown crystals (0.3 g). *Anal.* Calcd. for $C_{10}H_{24}N_7O_6Cr$: C, 30.8; H, 6.2; N, 25.1. Found: C, 30.7; H, 6.4; N, 25.0.

cis-*diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III)thiocyanate.* Orange-red crystals (0.4 g). *Anal.* Calcd. for $C_{13}H_{24}N_7CrS_3$: C, 36.6; H, 5.7; N, 23.0; S, 22.5. Found: C, 36.9; H, 5.7; N, 22.8; S. 22.4.

Visible and ultraviolet spectra were measured with Unicam SP500 and SP800 spectrophotometers, the infra-red spectra were measured with a Perkin-Elmer P.E. 225 spectrophotometer.