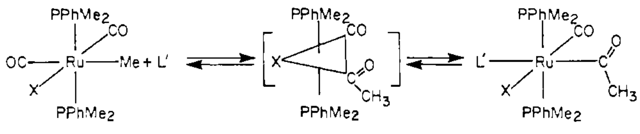
produces *fac*-**3**. In spite of the general preference of π acceptors for the basal site,[32] even a small concentration of **12a** will provide **3**. We also note here that **16** may be obtained from **14** via the more conventional methyl migration route *provided* that the sp intermediate is stereochemically labile.[22]

Alternatively the reaction can proceed through a trigonal-bipyramidal (tbp) intermediate (Scheme III). If acyl is equatorial, the question of alkyl or CO migration obviously does not apply since some movement of *both* groups is likely. Intermediate **13** can conceivably lead to *fac* or *mer* products depending on whether movement of $-CH_3$ is toward or away from the equatorial As. Mawby has recently presented strong evidence[17] derived from the stereochemistry of Lewis base induced insertion reactions on Ru(II) that supports a tbp intermediate. Unless we assume that the anticipated greater thermodynamic stability of 18-e *fac* complexes compared to their *mer* isomers[38] leads to a significantly lower energy barrier for the formation of *fac*-**3**, it is difficult to reconcile the stereospecificity with which **13** proceeds along the reaction coordinate. The possibility of rapid *mer*-**3** $\rightarrow$ *fac*-**3** isomerization is ruled out by the observation that *fac*/*mer* mixtures of **3** prepared by oxidative addition of CH_3OSO_2F to **1** are geometrically stable in solution.

Halide-Promoted Migratory Insertion Reactions. Although we cannot rule out the possibility of a second-order (first order in **3** and halide) or a solvent-assisted[1] reaction at this time,[39] halide-promoted migratory insertion can be considered to occur via the reverse of Scheme III. Many kinetic studies of Mn(I) systems have in fact found that the insertion rate is independent of incoming ligand and proceeds via a rate-determining formation of a coordinatively unsaturated 16-e acyl. Theoretical studies agree and show that interaction of nucleophile and OC–M–R substrate prior to acyl formation is in fact destabilizing.[22]

It is notable that the stereochemistry of the CO migratory insertions studied in this paper is strongly solvent and ligand dependent (Table IV). Thus far *all* insertions of Mn(I) have given products where the incoming ligand and acyl are mutually cis in agreement with a rigid sp intermediate formed by alkyl migration. Ru(II)[17] and Ir(III)[40] as well as the Fe(II) complexes studied in this paper appear to be quite different in this respect giving kinetic products with acyl trans to the incoming ligand. In the case of Ru(II) a tbp intermediate is assumed. Trans geometry in the acyl kinetic product **19** results from preferential attack trans to acyl. It should be pointed out that the mechanism described above may not be general since complex **14** (M = Ru) is reported to give a kinetic product **16** with cis $L-M-C(O)CH_3$ geometry.[37]



17 **18** **19**

L' = CO, PPhMe$_2$

It is premature to further speculate on the mechanism of the halide-promoted insertions at this point, but it is apparent that attack of iodide in the equatorial plane of **13** can give three (**2a**, **2c**, and **2d**) of the four possible acetyl iodo isomers described in this study.

Acknowledgment. The author thanks the Natural Sciences and Engineering Research Council of Canada for financial support as well as Mr. T. Button and Mr. J. Doull for their assistance with the preparation of some of the compounds described in this study. We also thank Bruker Spectrospin (Toronto) for providing the 62.83-MHz ^{13}C spectra.

Registry No. **1**, 56760-75-9; **2a**, 78764-22-4; **2c**, 78821-61-1; **2d**, 78821-62-2; *fac*-**3**, BF_4^- salt, 78764-24-6; *fac*-**3**, PF_6^- salt, 78764-25-7; *fac*-**3**, OSO_2F^- salt, 78764-26-8; *mer*-**3**, OSO_2F^- salt, 78821-64-4; *mer*-**3**, PF_6^- salt, 78821-65-5; **4a**, 78822-13-6; **4c** or **4d**, 78764-27-9; *mer*-**5**, I^- salt, 78764-28-0; *mer*-**5**, ClO_4^- salt, 78764-30-4; *fac*-**6**, BF_4^- salt, 78764-32-6; $Fe(CO)_5$, 13463-40-6; CH_3I, 74-88-4; CH_3OSO_2F, 421-20-5; CF_3I, 2314-97-8; $CF_3C(O)I$, 354-36-9; Br^-, 24959-67-9; Cl^-, 16887-00-6; NCS^-, 302-04-5.

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Chromium(III) Complexes Containing Macrocyclic Ligands

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Received August 21, 1980

Five chromium(III) compounds, *cis*-$[Cr([12]aneN_4)Cl_2]Cl\cdot H_2O$, *cis*-$[Cr([12]aneN_4)(NCS)_2]NCS\cdot 2H_2O$, *cis*- and *trans*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$, and *trans*-$[Cr([15]aneN_4)Cl_2]Cl\cdot 2H_2O$ ($[12]aneN_4$ = 1,4,7,10-tetraazacyclododecane, $1,4,7,11[14]aneN_4$ = 1,4,7,11-tetraazacyclotetradecane, $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane), were synthesized and characterized. For the chromium(III) complexes containing the 12-membered macrocycle, only the cis isomer was isolated, while for the chromium(III) complex containing the 15-membered ring, only the trans isomer was isolated. The chromium(III) complexes containing the unsymmetrical 14-membered ring, $1,4,7,11[14]aneN_4$, were isolated in equal amounts of cis and trans forms. The ranking of the Dq^{xy} for various trans complexes is $1,4,8,11[14]aneN_4 > 1,4,7,10[14]aneN_4 > [15]aneN_4$. $[12]aneN_4$ appears to be a relatively weak-field ligand. Conductivity and spectral data indicate that the first- and second-aquation rates for $[Cr([12]aneN_4)Cl_2]Cl\cdot H_2O$ are unusually fast.

Introduction

We have prepared cobalt(II), nickel(II), and copper(II) complexes that contain strained metal-to-nitrogen bonds.[1-7] Ligands include the 12-membered 1,4,7,10-tetraazacyclododecane ($[12]aneN_4$)[1-3] and 1,4,7,10-tetrabenzyl-1,4,7,10-tet-

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Table I. Electronic Spectral Data for Chromium(III) Complexes (Wavelength, nm)

	I	II	III
	Solid		
[Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O	585	405	
[Cr([12]aneN$_4$)(NCS)$_2$]NCS·2H$_2$O	550	335	
cis-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	550	435	
trans-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	585	445	370
[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O	580 sh	407 sh	405
	Aqueous Solution		
[Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O	520 (153)	368 (20)[a]	
[Cr([12]aneN$_4$)(NCS)$_2$]NCS·2H$_2$O	527 (197)	365 sh (84)[a]	
cis-[Cr(1,4,8,11[14]aneN$_4$)Cl$_2$]$^+$ [b]	529 (111)	404 (106)	
trans-[Cr(1,4,8,11[14]aneN$_4$)Cl$_2$]$^+$ [b]	572 (19.9)	407 sh (35)	365 (41)
cis-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	532 (116)	420 (90)	
cis-[Cr(1,4,8,11[14]aneN$_4$)Cl$_2$]$^+$ [b]	529 (111)	404 (106)	
cis-[Cr(1,4,8,11[14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$ [b]	483 (126)	370 (38)	
trans-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	585 (43)	448 (112)	380 (82)
trans-[Cr(1,4,8,11[14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$ [b]	510 (24)	405 (39)	350 (53)
[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O	592 (24)	470 (57)	417 (61)
	Methanol Solution		
[Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O	585 (92)	400 (59)	
cis-[Cr(1,4,7,11)[14]aneN$_4$)Cl$_2$]Cl	555 (124)	435 (95)	
trans-[Cr(1,4,7,11)[14]aneN$_4$)Cl$_2$]Cl	575 (27)	447 (69)	400 sh (50)
[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O	586 (24)	476 (48)	410 (63)
	Acetonitrile Solution		
[Cr([12]aneN$_4$)(NCS)$_2$]NCS·2H$_2$O	548 (187)		

[a] In 0.1 N HNO$_3$. [b] Reference 18.

raazacyclododecane (tb[12]aneN$_4$)[2–6] and the unsymmetrical 14-membered ring, 1,4,7,11-tetraazacyclotetradecane (1,4,7,11[14]aneN$_4$).[7] We have extended our study to include some chromium(III) complexes.

Results

Blue [Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O was synthesized by refluxing CrCl$_3$·6H$_2$O with [12]aneN$_4$ in absolute ethanol in the presence of activated zinc. Violet [Cr([12]aneN$_4$)(NCS)$_2$]NCS·2H$_2$O was prepared by adding aqueous NH$_4$SCN to an aqueous solution of [Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O, and green [Cr([15]aneN$_4$)Cl$_2$]Cl·H$_2$O was prepared from the reaction of CrCl$_3$·3THF with [15]aneN$_4$ in DMF. Only one product was isolated in high yield from each of these reactions. A mixture of *cis*- and *trans*-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl was synthesized by refluxing CrCl$_3$·3THF with 1,4,7,11[14]aneN$_4$ in DMF under nitrogen, and the cis and trans isomers were separated by fractional crystallization from methanol. Thin-layer chromatography was performed on either alumina or silica gel plates to confirm the purity and to determine whether conformational isomers could be isolated. The largest difference in the R_f factor for the isomers was obtained in methanol. The red cis isomer complex had an R_f value of 0.33, and the green trans isomer had an R_f value of 0.72 on silica gel. There was no evidence of contamination of one isomer by the other after recrystallization and no evidence of separable conformational isomers.

The chromium oxidation state was confirmed from the 3:1 analytical ratio of anion to metal. The magnetic moments for all these complexes, 3.8–3.9 μ_B, are near the spin-only value for three unpaired electrons. Such magnetic moments are characteristic of chromium(III) complexes. Finally, the electronic spectra of these complexes (Table I) are consistent with those of other chromium(III) complexes.[8–12]

Table II. Molar Conductivity Data

complex	H$_2$O	CH$_3$OH	CH$_3$CN
[Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O	460	85	
[Cr([12]aneN$_4$)(NCS)$_2$]NCS·2H$_2$O	210		118
cis-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	111[a] 205	60	
trans-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl	260	156	90
trans-[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O	144[a] 184	77	

[a] Initially.

In methanol and acetonitrile, the molar conductivity of [Cr([12]aneN$_4$)X$_2$]X·nH$_2$O (X = Cl and SCN) indicates that these complexes are 1:1 electrolytes.[13] The complexes *cis*-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl and *trans*-[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O in methanol and *trans*-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl in nitromethane are also 1:1 electrolytes.[13] These data confirm that two anions are coordinated to the chromium(III) in these solvents, and it is likely that the anions are also coordinated in the solid state. In water, the molar conductivity of [Cr([12]aneN$_4$)Cl$_2$]Cl·H$_2$O lies above the range of a 3:1 electrolyte, indicating that chlorides are rapidly displaced by water. The coordinated water or amine may further ionize in water, thereby increasing the conductivity above what is usually expected of a 3:1 electrolyte. The molar conductivity of [Cr([12]aneN$_4$)(SCN)$_2$]SCN·2H$_2$O in water approaches that of a 2:1 electrolyte. We conclude, therefore, that the SCN$^-$ is only partially displaced by water. The complex *cis*-[Cr(1,4,7,11[14]aneN$_4$)Cl$_2$]Cl is initially a 1:1 electrolyte in water; after 1 h the conductivity increases to that of a 2:1 electrolyte. A similar phenomenon occurs for *trans*-[Cr([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O, which is initially a 1:1

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electrolyte but becomes a 2:1 electrolyte within 3 days. These data suggest that the aquation reaction occurs most slowly for *trans*-$[Cr([15]aneN_4)Cl_2]Cl \cdot 2H_2O$ and *cis*-$[Cr(1,4,7,11\text{-}[14]aneN_4)Cl_2]Cl$ but more rapidly for the chromium(III) complex containing the ligand $[12]aneN_4$.

$$CrLCl_2^+ + H_2O \rightarrow CrLCl(H_2O)^{2+} + Cl^-$$

In contrast to that of *cis*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$, the initial conductivity of the trans isomer in water is typical of a 2:1 electrolyte. We conclude, therefore, that the first aquation of the trans isomer occurs rapidly but the second aquation occurs more slowly than that of the $[12]aneN_4$ complex. We are currently conducting a complete kinetic investigation of these reactions.

Infrared spectra provided information about the nature of the bonding and the geometries of these complexes. Both Cr^{III}–$[12]aneN_4$ complexes exhibit broad bands at 3420 cm^{-1} in Nujol, which are assigned to the hydrogen-bonded O–H stretches of lattice water. All of the complexes prepared in this study show medium-to-strong absorptions in the 3245–3070-cm^{-1} range, assigned to N–H stretches of the coordinated amine. The N–H stretches of the coordinated ligand have been shifted to lower energies than those of the free ligand. The N–H stretch of $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$ is observed as a broad band, which lies at 3070 cm^{-1}. These data suggest that the amine protons of $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$ are more hydrogen bonded than those of $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$.

The $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$ complex exhibits bands at 2070 and 2040 cm^{-1}, which are attributed to thiocyanate since these bands are not present in $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$. The band at 2070 cm^{-1} is assigned to thiocyanate coordinated through the nitrogen, and the band at 2040 cm^{-1} is assigned to ionic thiocyanate.[14] The C–S stretching frequencies and the N–C–S bending frequencies, which are commonly used to determine the mode of coordination to the thiocyanate, are masked by ligand vibrations.

The geometries of $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$, $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$, and the red isomer of $[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$ are all assigned as cis-octahedral partially on the basis of the N–H stretching region. The N–H stretching region of a cis-octahedral complex will be more highly split and much broader than a trans-octahedral complex.[3,15,16] In addition, Poon[15] has shown that the number and positions of the bands in the CH_2 rocking region (800–910 cm^{-1}) can be used to differentiate the cis and trans isomers of $[Co([14]aneN_4)X_2]^+$ complexes. The trans isomers show two bands near 900 cm^{-1} and one near 810 cm^{-1}, while the *cis* isomers have at least five bands between 800 and 910 cm^{-1}. The complex $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ exhibits six bands at 800, 810, 825, 860, 870, and 910 cm^{-1}. These data support a cis-octahedral geometry for the $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ complex. The CH_2 rocking region (800–910 cm^{-1}) of the $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$ complex is complicated by thiocyanate absorptions. As a result, this region cannot be used to confirm the geometry of $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$. Unfortunately, the 800–900-cm^{-1} region of the infrared spectrum is not useful in differentiating the cis and trans isomers of chromium(III) complexes of $1,4,7,11[14]aneN_4$. Both complexes have approximately the same number of bands in that region of the spectrum. The N–H stretching vibrations for $[Cr([15]aneN_4)Cl_2]Cl \cdot 2H_2O$ are consistent with the trans geometry; however, CH_2 vibrations cannot be used to assign geometry.

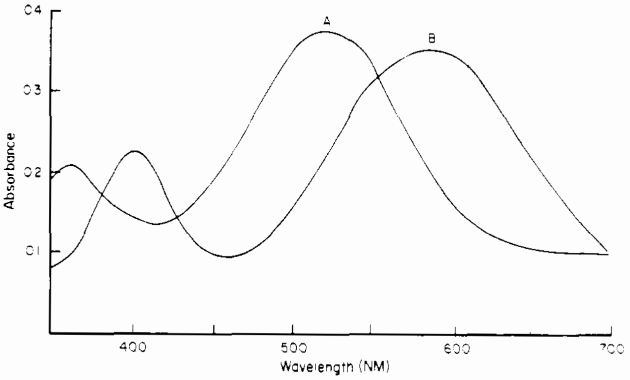

Figure 1. Visible absorption spectra of *cis*-$[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ in (A) aqueous solution and (B) methanol solution.

The position of the transitions in the electronic spectra, the number of bands, and their extinction coefficients are usually reliable indicators for distinguishing chromium(III) cis and trans isomers.[8-12] Cis chromium(III) complexes usually have two bands in the visible region, and these bands are at lower energies and have higher extinction coefficients than those of the corresponding trans isomers. All the complexes listed as cis in Table I have two bands in the visible region, and trans complexes display three bands. The complex $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ has an extinction coefficient of 153 at 520 nm in 0.1 N HNO_3, and red *cis*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$ has an extinction coefficient of 116 at 532 nm. These extinction coefficients are comparable to those of *cis*-$[Cr(en)_2Cl_2]^+$ and *cis*-$[Cr(1,4,8,11[14]aneN_4)Cl_2]^+$, 70.6 and 111, respectively.[9,17] The extinction coefficient for the complex $[Cr([12]aneN_4)(NCS)_2]NCS \cdot 2H_2O$ is 197 at 527 nm in 0.1 N HNO_3 solution. The analogous ethylenediamine complexes, *cis*- and *trans*-$[Cr(en)_2(NCS)_2]^+$, have extinction coefficients of 157 and 95, respectively.[10,18] In contrast, the extinction coefficients for *trans*-$[Cr(en)_2Cl_2]^+$ and *trans*-$[Cr(1,4,8,11\text{-}[14]aneN_4)Cl_2]^+$ [16] are less than 25 within the same spectral range. The complex assigned as *trans*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$ has an absorbance maximum at 582 nm in aqueous solution with an extinction coefficient of 43, and $[Cr([15]aneN_4)Cl_2]Cl \cdot 2H_2O$ has an absorbance maximum in water at 592 nm with an extinction coefficient of 24. We have assigned the trans geometry to this complex because of both the electronic spectrum and the similar appearance of the N–H stretching region for $[Cr([15]aneN_4)Cl_2]Cl \cdot 2H_2O$ to that of *trans*-$[(1,4,7,11[14]aneN_4)Cl_2]Cl$ compared to that of its cis isomer.

The electronic spectrum of $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ in 0.1 N HNO_3 has absorption maxima at 520 and 368 nm and was shown to be the diaquo complex by the following series of experiments. An aqueous solution of $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ was passed through a column of Amberlite IRC-50 cation exchange resin in the Na^+ form. The column was washed free of all chloride, and the effluent was titrated potentiometrically, yielding 3.08 chloride ions per molecule. The complex was then eluted from the resin with 2 N $HClO_4$. The eluate, $Cr([12]aneN_4)(H_2O)_2^{3+}$, has an electronic spectrum that is identical with that of $[Cr([12]aneN_4)Cl_2]Cl \cdot H_2O$ in 0.1 N HNO_3 (Figure 1) but different from that of $[Cr([12]aneN_4)Cl_2]Cl$ in methanol, where the chlorides are believed to be coordinated to the Cr^{III} (Figure 1).

The relative ligand field strength of the macrocyclic ligands can be estimated from the electronic spectra of their complexes.[19] The lowest energy band expected for the trans

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chromium(III) complexes, ν_1, corresponds to the ${}^4E_g \leftarrow {}^4B_1g$ electronic transition. This transition is sensitive to the axial ligand field strength. The next band, ν_2, is assigned the ${}^4B_{2g} \leftarrow {}^4B_{1g}$ transition and reflects only the in-plane ligand field. The highest energy band maximum in the visible region, ν_3, is assigned the ${}^4A_{2g} \leftarrow {}^4B_{1g}$ transition. Since ν_2 is a function of only the in-plane ligand, its energy should be independent of the axial ligand. For all of the trans complexes prepared in this study, the energy of the second band is nearly the same in methanol as it is in water. (Recall that the conductivity data indicated that the chloride ions are coordinated to the chromium(III) in methanol, while in water, water molecules are coordinated to chromium(III).) We have used ν_2 to obtain a Dq^{xy} value for various macrocycles in *trans*-diacido complexes. The average Dq^{xy} values for 1,4,7,11[14]aneN_4, 1,4,8,11[14]aneN_4, and [15]aneN_4 are 2238, 2450, and 2123 cm^{-1}, respectively. In contrast to that of the trans complexes, the lowest energy band for cis chromium(III) complexes is usually considered a measure of the average Dq of the complex. The Dq values for the cis complex were obtained from band I, Table I.

The pH measurements confirm the ionization of the coordinated water in the complex $[Cr([12]aneN_4)Cl_2]Cl{\cdot}H_2O$ in water and are consistent with aqueous conductivity measurements. The pH of a 2×10^{-3} M solution of $[Cr([12]aneN_4)Cl_2]Cl{\cdot}H_2O$ is 3.36. In comparison, a 1.48×10^{-3} M aqueous solution of $[Ni([12]aneN_4)](NO_3)_2$ increased the pH of distilled water to a value of 7.77. The pK_1 and pK_2 values of $[Cr([12]aneN_4)Cl_2]Cl{\cdot}H_2O$ were estimated by titration with standardized NaOH in 0.5 M $NaClO_4$ solution. The values of pK_1 and pK_2 are 4 and 6.2, respectively, and are consistent with other $CrN_4(H_2O)_2{}^{3+}$ complexes.[17,20] The other chromium(III) complexes involved in this study also produce acidic aqueous solutions; the most acidic solution is produced by the Cr(III) complex of [12]aneN_4, and the least acidic solution by the chromium(III) complex of [15]aneN_4. Since these pH measurements were made on freshly prepared solutions, the results are consistent qualitatively with the rates of formation of aquo–chromium complexes as determined via the conductivity data. Since the acidity of these solutions originates with only a $CrL(H_2O)_2{}^{3+}$ or $CrL(H_2O)Cl^{2+}$ complex, the concentration of these ions is indirectly proportional to the pH of the solution.

Discussion

The average Dq^{xy} value for 1,4,7,11[14]aneN_4 is smaller than for 1,4,8,11[14]aneN_4. A similar trend was observed for the nickel(II) complexes containing these ligands.[7,21] For the *trans*-bis(ethylenediamine)chromium(III) complex, which is assumed to be relatively strain free, the Dq^{xy} is 2200 cm^{-1}.[18] Since the Dq^{xy} value for 1,4,7,11[14]aneN_4 most closely approaches the Dq^{xy} value for the unstrained *trans*-bis(ethylenediamine)chromium(III) complex, we assumed that the Cr^{3+} complex of 1,4,7,11[14]aneN_4 is also relatively strain-free. The stronger field 1,4,8,11[14]aneN_4 has a constrictive effect on the Cr(III) ion as does the 14-membered macrocyclic ligand 1,7-CTH (Dq^{xy} = 2385 cm^{-1}),[22] while the [15]aneN_4 has a dilative effect on the Cr(III). The best fit found so far for Co(III) is for the 1,4,8,11[14]aneN_4 ligand[23] (the 1,4,7,11-[14]aneN_4–Co^{III} complex has not yet been prepared), and the best fit for Ni(II) is for [15]aneN_4.[24] A spectrochemical series for *trans*-$Cr^{III}N_4$ systems is [15]aneN_4 < (en)$_2$ < 1,4,7,11-[14]aneN_4 < 1,7-CTH < 1,4,8,11[14]aneN_4.

Since chromium(III) has an effective ionic radius between those of Ni(II) and low-spin Co(III),[29] we would expect the "best fit" for a planar tetraaza cyclic ligand to have a ring size between 14 and 15 atoms. The symmetrical 14-membered ring can only coordinate to the chromium(III) in such a manner as to form four equivalent chromium to nitrogen bonds. In contrast, the unsymmetrical 14-membered ring has more available options in the manner in which it can coordinate to the metal ion. As a result, the unsymmetrical 14-membered macrocycle can coordinate coplanar with the chromium(III) with less strain energy than can the symmetrical 14-membered ring.

We cannot adequately explain why the lowest energy band maximum in the electronic spectrum does not increase in energy as the axial field strength increases. The opposite effect is observed for both the [15]aneN_4 and 1,4,7,11[14]aneN_4 complexes.

By comparing the Dq values for cis chromium(III) complexes, we can conclude that [12]aneN_4 is a relatively weak-field ligand. Thus, *cis*-$Cr(en)_2Cl_2{}^+$, *cis*-$[Cr(1,4,8,11[14]aneN_4)Cl_2]^+$, *cis*-$\alpha$-$Cr(trien)Cl_2{}^+$, and *cis*-$\beta$-$Cr(trien)Cl_2{}^+$ all have higher average Dq values than the *cis*-$Cr([12]aneN_4)Cl_2{}^+$ complex.[10,16,25] The relative order of ligand field strength in the cis configuration is *cis*-[12]aneN_4 < *cis*-trien < *cis*-(en)$_2$ < *cis*-1,4,8,11[14]aneN_4. These data suggest that [12]aneN_4 is bonded to chromium(III) in a highly strained manner. Although [12]aneN_4 is also bonded to nickel(II), copper(II), cobalt(II), and cobalt(III) in a strained manner,[2,6,26] the effects are more pronounced for the chromium(III) complexes.

The stereochemistry of the complexes prepared in this study is a function of the size and nature of the macrocyclic ligand. Only the cis isomer is formed with the [12]aneN_4 ligand. The nickel(II), cobalt(II), and cobalt(III) complexes also formed only cis complexes. It was suggested that Ni^{II}–[12]aneN_4 complexes could rearrange to the trans geometry at high temperatures and high ionic strengths in water.[21] However, there is no evidence that such a geometry can occur with the chromium(III) complexes containing a 12-membered ring nor is there evidence for any cis–trans rearrangement reactions occurring with these complexes.

In marked contrast to the [12]aneN_4 ligands in which only the cis isomer was isolated, the [15]aneN_4 ligand formed only the trans chromium(III) complex. Samuels and Espenson[27] reference unpublished crystal data which states that $[Cr([15]aneN_4)Cl_2]Cl$ is in a trans geometry. However, for the chromium(III) complexes containing the 14-membered macrocycles 1,4,7,11[14]aneN_4 and 1,4,8,11[14]aneN_4, both the cis and trans isomers have been isolated.[15] It appears that [15]aneN_4 is large enough to coordinate in a coplanar manner with chromium(III), but the [12]aneN_4 ring is too small.

It was reported that *cis*-$[Cr(1,4,8,11[14]aneN_4)Cl_2]Cl$ was isolated in a 9 times higher yield than the trans isomer.[15] (The opposite is true for the cobalt complexes with this ligand.) However, the cis and trans isomers of Cr(III) complexes with 1,4,7,11[14]aneN_4 were isolated in equal amounts. Both Poon and Pun[28] and Ferguson and Tobe[17] noted that the isomerization of *cis*-$[Cr(1,4,8,11[14]aneN_4)Cl_2]^+$ to the trans isomer did not occur at low pH. However, Poon and Pun[28] were successful in causing the above isomerization to occur at higher pH values under refluxing conditions. We were not able to isomerize any of our cis complexes at room temperature under either acidic or basic conditions. The ratio of the cis to trans

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isomers that were isolated for each chromium(III) macrocycle system may be kinetically controlled; it is likely that the macrocycle originally coordinates with chromium(II) and that this intermediate complex is oxidized to the final product. Since the ionic radius of chromium(II) is considerably larger than that of nickel(II),[29] it is quite likely that all the ligands discussed in this paper are originally coordinated to chromium(II) in a cis manner and then rearrange to the stable product. Such isomerization is more likely with larger or more flexible macrocycles than 1,4,8,11[14]aneN_4.

Experimental Section

Preparation of Complexes. Synthesis of Dichloro(1,4,7,10-tetraazacyclododecane)chromium(III) Chloride Monohydrate. A solution of 1.0 g (0.0038 mol) of chromium trichloride hexahydrate and 100 mL of absolute ethanol was prepared in a 200-mL round-bottom flask. One gram of mossy zinc, which had been activated by washing with 3 N HCl and rinsed with absolute ethanol, was added. Next, 0.5 g (0.0029 mol) of [12]aneN_4[30] was added to the green solution, and the mixture was refluxed for 1 h with stirring. As the reaction proceeded, a blue precipitate formed. After the mixture was cooled to room temperature, the blue precipitate was centrifuged from solution, washed with absolute ethanol, and recrystallized from a mixture of concentrated hydrochloric acid and ethanol; yield 0.71 g (70%). Anal. Calcd for $[Cr(C_8H_{20}N_4)Cl_2]Cl\cdot H_2O$: C, 27.56; H, 6.36; N, 16.07; Cr, 14.91. Found: C, 27.44; H, 6.22; N, 16.24; Cr, 14.67.

Synthesis of Bis(isothiocyanato)(1,4,7,10-tetraazacyclododecane)chromium(III) Thiocyanate Dihydrate. Five-tenths of a gram of $[Cr([12]aneN_4)Cl_2]Cl\cdot H_2O$ was dissolved in 25 mL of water, and a solution of 2.5 g of NH_4SCN in 5 mL of water was added. This mixture was warmed for 45 min at 80 °C on a water bath and then allowed to cool to room temperature. The violet precipitate that formed upon cooling was centrifuged from solution and dissolved in a minimum amount of hot water. Refrigeration of this solution for 1 h yielded violet crystals, which were filtered, air-dried, and stored over P_2O_5. Anal. Calcd for $[Cr(C_8H_{20}N_4)(NCS)_2]NCS\cdot 2H_2O$: C, 30.40; H, 5.57; N, 22.56. Found: C, 30.02; H, 5.28; N, 22.84.

Synthesis of *cis*-Dichloro(1,4,7,11-tetraazacyclotetradecane)chromium(III) Chloride. A solution of 0.35 g (0.001 mol) of $CrCl_3\cdot 3THF$ and 0.20 g (0.001 mol) of 1,4,7,11[14]aneN_4 in 50 mL of dry DMF was refluxed under nitrogen for 1 h and then rotoevaporated to dryness. The dark product was washed with acetone and dried. Next, the product was suspended in 50 mL of boiling methanol for 10 min. The insoluble dark red cis isomer was centrifuged from the solvent and dissolved in a minimum amount of a 1:1:1 mixture of water, acetone, and HCl. Refrigeration overnight yielded a fine precipitate of the cis isomer, yield 0.14 g (38%). Anal. Calcd for $[Cr(C_{10}H_{24}N_4)Cl_2]Cl$: C, 33.48; H, 6.74; N, 15.62. Found: C, 33.36; H, 6.82; N, 15.62.

Synthesis of *trans*-Dichloro(1,4,7,11-tetraazacyclotetradecane)chromium(III) Chloride. The dark methanolic solution from the synthesis of the cis isomer was evaporated to a 10-mL volume. Ten milliliters of acetone was then added to precipitate the green trans isomer. The precipitate was centrifuged from the solvent and recrystallized by using a minimum amount of a 50% water–50% acetone mixture; yield 0.12 g (33%). Anal. Calcd for $[Cr(C_{10}H_{24}N_4)Cl_2]Cl$: C, 33.48; H, 6.74; N, 15.62. Found: C, 33.61; H, 6.88; N, 15.41.

Synthesis of *trans*-Dichloro(1,4,8,12-tetraazacyclopentadecane)chromium(III) Chloride Dihydrate. In a 250-mL round-bottom flask, 0.75 g (0.0035 mol) of 1,4,8,12-tetraazacyclopentadecane was dissolved in 100 mL of dry DMF. To this was added 1.3 g (0.0035 mol) of $CrCl_3\cdot 3THF$. A reflux condenser and nitrogen inlet/outlet were attached to the flask, and the solution was refluxed under nitrogen for 20 min. The solution color changed from violet to olive green with refluxing. Filtration yielded 60 mg of red-violet compound. The infrared spectrum of this compound indicated that no organics were present. Rotoevaporation of the filtrate to dryness yielded a green solid. The solid was suspended in acetone and heated with stirring for 15 min. During this time the acetone took on a red color. The green precipitate was filtered off and dried. Recrystallization from a 50% methanol–50% HCl mixture yielded dark green crystals, yield 0.30 g (23%). Anal. Calcd for $[Cr(C_{11}H_{26}N_4)Cl_2]Cl\cdot 2H_2O$: C, 32.32; H, 7.39; N, 13.71. Found: C, 32.46; H, 6.66; N, 13.65.

Physical Measurements. The equivalent molar conductance measurements were made with an American Instrument Co. Model 5-2050 conductivity bridge in conjunction with a Beckman Model BB1 conductivity cell. The cell constant was 1.00/cm. The solvents used for making measurements were water, methanol, acetonitrile, and nitromethane. The mass susceptibilities were determined by the Evans method using a Varian A-60 NMR instrument with coaxial NMR tubes. The solvent used was water or chloroform with 2% *tert*-butyl alcohol added as an inert reference. The complex dissolved in the solvent was placed in the outer tube, and the solvent alone was placed in the inner tube. Concentrations of 4.15–18.93 mg/mL were used. Diamagnetic corrections were made by using Pascal's constants. A Perkin-Elmer Model 337 spectrophotometer was used to record all infrared spectra. The spectra of complexes were obtained in both Nujol mulls and KBr pressed pellets. The spectra were calibrated with polystyrene standards. A Beckman Acta MIV UV-visible–near-IR spectrophotometer with 1- or 10-cm matched quartz cells was used to obtain visible and near-infrared spectra. The visible spectra of solids were measured in Nujol mulls. The mull was placed on sharkskin filter paper in the sample beam, and a similar piece of filter paper with Nujol was placed in the reference beam.

Chemical Analysis. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. A Coleman model 29A nitrogen analyzer was used to obtain some nitrogen analysis. Chromium analysis was performed by refluxing a weighed amount (~50 mg) of complex in a solution of 50 mL of 6 N NaOH and 3 mL of 30% H_2O_2. After cooling to room temperature, this solution was diluted to a standard volume, and the optical absorbance of the CrO_4^{2-} ion in this solution was measured at 372 nm ($\epsilon = 4815$). An aqueous solution of the complex was introduced into a Na^+ Amberlite IRC-50 cation-exchange column, which absorbed the complex. The column was washed with water to elute free chloride. This was then titrated potentiometrically with a standardized $AgNO_3$ solution by using a pH meter, a silver wire indicator electrode, and a calomel reference electrode.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank G. Brubaker for his helpful assistance in the writing of this paper.

Registry No. *cis*-$[Cr([12]aneN_4)Cl_2]Cl$, 78804-39-4; *cis*-$[Cr([12]aneN_4)(NCS)_2]NCS$, 78804-41-8; *cis*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$, 78804-42-9; *trans*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$, 78854-19-0; *trans*-$[Cr([15]aneN_4)Cl_2]Cl$, 78804-45-2.

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