Conclusion

The cycloaddition reaction between dialkylcyanamides and NSCl units generated from $(NSCl)_3$ in warm carbon tetrachloride represents a much improved synthesis of the six-membered rings $(R_2NCN)(NSCl)_2$ and provides a route to the first example of an eight-membered mixed cyanuric–thiazyl ring, 1,3-$(R_2NCN)_2(NSCl)_2$. Easier access to these bifunctional heterocycles should facilitate investigations of their chemical reactions. This study also draws attention to the need for a better understanding of the species formed from $(NSCl)_3$ in warm solvents. A ^{15}N NMR study of ^{15}N-enriched $(NSCl)_3$ in various solvents at different temperatures should be informative.

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Supplementary Material Available: Listings of anisotropic thermal parameters, bond distances and angles involving H atoms, and structure factors for $(Et_2NCN)(NSCl)_2$ (14 pages). Ordering information is given on any current masthead page.

Contribution from the Central Leather Research Institute,
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Synthesis and Characterization of New Chromium(III) Complexes of Macrocyclic Ligands

Balachandran Unni Nair, T. Ramasami,* and D. Ramaswamy

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Synthesis of new chromium(III) complexes of tetraaza macrocyclic ligands having 13-membered or symmetrical 14-membered intraligand ring sizes is reported here. The complexes of the formulation *trans*-$Cr(macrocycle)(X)(H_2O)^{(3-n)+}$, where macrocycle = Me_6[14]ane, Me_6[14]diene, Me_4[14]tetraene, or Me_2[13]diene, X = OH_2, NCS^-, or $CHCl_2^-$, and n = 0 or 1, have been prepared and characterized by means of elemental analysis, paramolybdate titrations, conductance measurements, and electronic as well as infrared spectra. Considerable steric strain in the cases of macrocycles with imine bonds as in Me_4[14]tetraene and Me_6[14]diene has been inferred from electronic spectral data. Firm experimental evidence for ring opening and breakdown of the macrocyclic ligands investigated under synthetic conditions is also presented. The possible steric advantages of symmetrical 14-membered macrocycles in stabilizing unusual oxidation states of chromium are also highlighted.

Introduction

Whereas many complexes of cobalt(III) with macrocyclic ligands of various structure have been reported,[1-3] the analogous chromium(III) derivatives have been rather few. Until 1982, the only macrocyclic complexes of chromium(III) which had been investigated systematically were those with 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,5,9,12-tetraazacyclopentadecane ([15]ane).[4-6] Although macrocyclic complexes of Cr(III) were relatively few, the preparation and reactivities of many complexes of the metal ion with pseudomacrocyclic ligands had been reported.[7,8] Recently, House et al.[9] reported the synthesis of a dichloro derivative of a Cr(III) macrocycle. While our work was in progress, Swisher et al.[10] reported also an elegant study in which ligand field effects and the importance of intraligand ring size of the macrocyclic ligands in influencing the cis and trans structures of octahedral complexes were considered. Their study[10] indicated that, in the formation of complexes having equatorially coordinated macrocyclic ligands, the Cr(III) ion shows preference to ligands having either unsymmetrical [14]-membered or [15]-membered intraligand ring sizes. At the time of our study, there were only a few examples for *trans*-$Cr(macrocycle)(X)_2^{n+}$, where macrocycle is a symmetrical [14]-membered ligand with the exception of cyclam.

As a part of our efforts[11] to stabilize an unusual oxidation state like Cr(IV) by taking advantage of suspected Franck–Condon barriers for the conversion of octahedral Cr(IV) to tetrahedral Cr(V), we investigated the synthesis of a few Cr(III) macrocyclic complexes. Some of the difficulties in the synthesis of Cr(III) macrocyclic complexes with symmetrical [14]-membered ligands have been often attributed to the relatively smaller intraligand ring size of the macrocycles compared to the size of the Cr(III)[6,10] ion. Since Cr(IV), by virtue of its higher positive charge, is believed to be of smaller size than Cr(III), it may be expected that macrocyclic ligands having smaller intraligand ring size than needed for Cr(III) may minimize the Franck–Condon barriers for the conversion of Cr(III) to Cr(IV). Therefore, we report here the synthesis of a series of complexes of Cr(III) with macrocyclic ligands of structures shown in Figure 1 and with either symmetrical [14]-membered or unsymmetrical [13]-membered intraligand ring sizes.

Experimental Section

Materials. The free lgiands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me_6[14]ane), 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]diene), and 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (Me_4[14]tetraene) were prepared by using known procedures.[12-14] Although the solvents used in this study were generally of reagent grade, most solvents like acetonitrile, methanol, tetrahydrofuran, and di-

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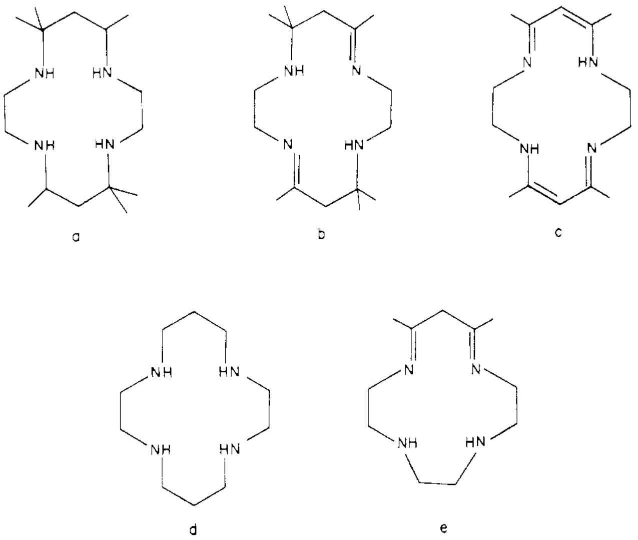

Figure 1. Diagrammatic representation of macrocyclic ligands: (a) $Me_6[14]$ane; (b) $Me_6[14]$diene; (c) $Me_4[14]$tetraene; (d) cyclam; (e) $Me_2[13]$diene.

methylformamide were repurified and dried according to the standard procedures.[15-18] The complexes such as *cis*-diaquo(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate (*cis*-$Cr(cyclam)(H_2O)_2^{3+}$) were prepared by using known procedures.[4,5] The chromium(II) derivatives of the ligands, $Me_6[14]$diene (viz. $Cr(Me_6[14]diene)(py)(PF_6)_2$) and $Me_6[14]$ane (viz. $Cr(Me_6[14]ane)(H_2O)_2^{2+}$) were prepared by known procedures.[19,20] The solutions of Cr(II) were prepared from the stock prepared by the electrolytic reduction of $Cr(H_2O)_6^{3+}$ in aqueous perchloric acid or by the dissolution of chromium(II) chloride (obtained from pure chromium metal dissolved in concentrated hydrochloric acid by standard methods[21,22]). Other reagents used in this study were of reagent grade or better and were used without further purification.

Preparation of Diaquo(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate, $Cr(Me_6[14]ane)(H_2O)_2(ClO_4)_3$ (1). The free ligand, $Me_6[14]$ane (0.1 mol), was dissolved in minimum amount of deaerated dimethylformamide (E. Merck, reagent grade) and treated with $Cr(H_2O)_6(ClO_4)_2$ (0.09 mol) under an atmosphere of nitrogen. The solution gradually turned purple as reported earlier.[19] After 1 h, the mixture was air-oxidized when the corresponding Cr(III) complex was obtained in solution. After reduction of volume to approximately 25 mL, addition of $NaClO_4$ gave the desired product as a reddish purple perchlorate salt. It was washed with ice-cold water followed by alcohol and ethyl ether and air-dried. The crude product was recrystallized from an aqueous ethanol (1:1) mixture. Anal. Calcd for $Cr(Me_6[14]ane)(H_2O)_2(ClO_4)_3 \cdot H_2O$: C, 27.9; H, 5.8; N, 8.2; Cr, 7.57. Found: C, 27.8; H, 5.7; N, 8.7; Cr, 7.35.

Our attempts to synthesize complex **1** by reacting chromium(III) acetate with the free ligand in acetonitrile medium was not successful, even after refluxing for 4 h. Therefore, the synthetic route based on Cr(II) was preferred for this synthesis.

Preparation of Diaquo(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene)chromium(III) Perchlorate, $Cr(Me_4[14]tetraene)(H_2O)_2(ClO_4)_3$ (2). Complex **2** was prepared in solution by using the following procedure. The ligand $Me_4[14]$tetraene (0.105 mol) dissolved in the minimum amount of deaerated methanol (70 mL) was added to $Cr(H_2O)_6(ClO_4)_2$ (0.1 mol) in an atmosphere of nitrogen. The solution turned greenish yellow slowly. After 1 h, the volume of the solution was reduced on a water bath to ca. 20 mL. The desired complex was precipitated by the addition of sodium perchlorate, whereupon, a yellowish brown product was obtained. Further recrystallization from aqueous alcohol mixtures did not yield reproducible results when the electronic spectra and Cr:N ratios were analyzed. Therefore, the complex was purified by means of ion-exchange chromatography. A solution of the crude product (20 mL) was loaded on a Dowex 50W-X 2 column (1.0 cm × 10 cm) and washed with 0.001 M $HClO_4$. The desired complex was eluted from the ion-exchange column with 2.5 M lithium or sodium perchlorate. The chromate analysis and micro-Kjeldahl method for nitrogen gave the value of the Cr:N ratio. By this method, products with a Cr:N ratio of 1:3.93 ± 0.03 as well as reproducible electronic spectra were obtained. The same procedure also afforded small quantities of pure solid samples for infrared spectra.

Attempted Preparation of Diaquo(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)chromium(III) Perchlorate, $Cr(Me_6[14]diene)(H_2O)_2(ClO_4)_3$ (3). Several procedures for the synthesis of **3** starting from both Cr(III) and Cr(II) salts were attempted. The initial methods based on $Cr(H_2O)_6^{2+}$ and free ligand $Me_6[14]$diene in a variety of solvents did not yield isolable products of the macrocyclic complex. When a mixture of $Me_6[14]$diene, $2HClO_4$ (0.05 mol), and chromium(III) acetate hexahydrate (0.05 mol) in acetonitrile (200 mL) was refluxed, an orange product could be precipitated from the reaction mixture by the addition of $NaClO_4$. When the product was recrystallized from an *n*-butanol–acetonitrile (1:1) mixture, needle-shaped shining crystals were obtained. Anal. Calcd for $Cr(Me_6[14]diene)(H_2O)_2)(ClO_4)_3$: C, 28.8; H, 5.4; N, 8.4; Cr, 7.8. Found: C, 20.7; H, 5.2; N, 8.9; Cr, 9.5. The elemental analysis values found may be best fitted to $[Cr(C_{10}H_{23}N_4)(H_2O)_2](ClO_4)_3$ (**4**) for which the calculated values are as follows: C, 20.5; H, 4.8; N, 9.5; Cr, 8.9. Further attempts to synthesize $Cr(Me_6[14]diene)(H_2O)_2(ClO_4)_3$ under various conditions of temperature and acidity yielded only **4**. However, **3** was finally prepared as follows.

An ethanolic slurry of $Cr(Me_6[14]diene)(py)(PF_6)_2$ prepared as described in ref 20 (0.01 mol) was mixed with iron(III) perchlorate (0.01 mol) in aqueous solution at $[H^+] = 10^{-1}$ M. The mixture was rotary evaporated and loaded on a Sephadex SP-C25 column. The desired product was purified from Fe(II) and Fe(III) impurities by elution with 0.2 and 0.3 M $NaClO_4$. The desired product was first eluted with a $NaClO_4$–$HClO_4$ mixture (0.69 M:0.01 M) and the eluate rotary evaporated. The pH of the concentrated solution was adjusted to 2.5. The mixture was cooled in an ice–salt mixture after the addition of 5 mL of acetone. The desired reddish product was precipitated, and it was recrystallized from an aqueous ethanol (1:1) mixture. Anal. Calcd for $Cr(Me_6[14]diene)(H_2O)_2(ClO_4)_3 \cdot H_2O$: C, 27.9; H, 5.5; N, 8.2. Found: C, 27.7; H, 5.8; N, 8.7.

Preparation of *trans*-Diaquo(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate, *trans*-$[Cr(cyclam)(H_2O)_2](ClO_4)_3$ (5). An aqueous solution of *cis*-$Cr(cyclam)(H_2O)_2^{3+}$, which is easily prepared as in ref 4, was adjusted to pH 7.0 with 2,4,6-trimethylpyridine. The resulting complex was refluxed for 3–7 h. The solution was then acidified with $HClO_4$ and the volume of the mixture reduced to 10 mL on a water bath, whereupon a crude product containing pale brown crystals was obtained. The trans isomer was separated from the cis isomer and other impurities by using a chromatographic procedure. A solution of the crude product (20 mL) was loaded on a Sephadex SP-C25 (0.8 cm × 12 cm) column. Elution with 0.5 M $LiClO_4$ gave rise to two bands. The faster moving reddish complex had the electronic spectral data corresponding to that of *trans*-$Cr(cyclam)(H_2O)_2^{3+}$.[4] The chromate and micro-Kjeldahl analyses confirmed the Cr:N ratio of 1:4, which is consistent with the formulation suggested.

Preparation of Aquo(thiocyanato)(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Thiocyanate, $[Cr(Me_6[14]ane)(NCS)(H_2O)](NCS)_2$ (6). Complex **1** (0.02 mol) was dissolved in minimum amount of water (ca. 25 mL), and then potassium thiocyanate (0.06 mol) dissolved in water (20 mL) was added. The white powder of potassium perchlorate precipitated was filtered off and the filtrate evaporated to reduce its volume. The solution, on cooling, gave red-orange crystals of the desired product. The Cr:amine nitrogen: thiocyanato nitrogen ratio was consistent with 1:4:3.

Preparation of (Dichloromethyl)aquo(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate, $[Cr(Me_6[14]ane)(CHCl_2)(H_2O)](ClO_4)_2$ (7). The ligand $Me_6[14]$ane (0.05 mol) dissolved in minimum amount of deaerated dimethylformamide was treated with hexaaquochromium(II) perchlorate (0.048 mol) under an atmosphere of nitrogen. The solution of the Cr(II) complex obtained after 1 h was then mixed with chloroform (0.053 mol), which had been deoxygenated. A reddish violet mixture was obtained. The reaction mixture was loaded on a precooled Dowex 50W-X2 ion-exchange (0.8 cm × 12 cm) column in the H^+ form. The desired complex was eluted by using 1 M $LiClO_4$. The alkylated derivative was eluted as a single band. The characterization of this complex in solution with a Cr:N ratio of 1:3.9 and the mercuric titrations established the formulation as **7**.

Preparation of Diaquo(11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene)chromium(III) Perchlorate, $Cr(Me_2[13]diene)(H_2O)_2(ClO_4)_2$ (8). Acetylacetone (BDH, 0.1 mol) in methanol (200 mL) was refluxed with chromium(III) acetate hexahydrate (0.1 mol) in the presence of a

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few drops of acetic acid. After the mixture was refluxed for 10 min, triethylenetetramine (Riedel, 0.1 mol) was added to this solution and the refluxing continued for another 3 h. The pH of the solution was adjusted to 6. The volume of the solution was reduced to ca. 50 mL by rotary evaporation. The desired product was then salted out by the addition of solid sodium perchlorate. This product was then recrystallized from methanol, whereupon reddish brown crystals were obtained. The complex was characterized by means of the Cr:N ratio, charge/atom, charge/species, and the number of coordinated aquo ligand determinations.

Elemental Analyses. The carbon, hydrogen, and nitrogen contents of the compounds synthesized were analyzed in the Department of Organic Chemistry, University of Madras, School of Chemistry, University of Leeds,[23] England, and Galbraith Laboratory. In some cases, nitrogen content was evaluated by using the micro-Kjeldahl technique after an acid digestion of the compound in solution. Chromium was analyzed as chromate and chlorine by flash combustion methods reported already.[24-26]

Instruments Used. UV–visible spectra were recorded on Pye Unicam SP1800 or Cary 14 double-beam spectrophotometers. The infrared spectra were obtained by using Perkin-Elmer Model 337 or 283 instruments. The ^{1}H NMR of free ligands were recorded on a Varian T-60 spectrometer, and the spectra of the paramagnetic complexes of Cr(III) were investigated by using either a Brucker WH 270 or a Varian XL100 FT NMR instrument.

Physical Measurements. The number of coordinated water ligands in complexes was estimated by using high-frequency titrations, and the electrolytic behavior was assessed by using conductometric measurements. The charge/atom and charge/species estimations for some of the complexes are by the method of Cady and Connick.[27]

Results and Discussion

It is evident from this study that chromium(II) macrocycles (where macrocycles = Me$_6$[14]diene and Me$_4$[14]tetraene) may be prepared and oxidized by means of either O$_2$ or Fe(III) to the corresponding Cr(III) products. The elemental analysis data obtained for the complexes **1**, **2**, **3**, **6**, **7**, and **8** are all consistent with the formulations suggested. Since there have been discussions regarding the mismatch of intraligand ring size of symmetrical [14]-membered macrocycles and a bulky metal ion like Cr(III), the synthetic methods used in this study need further comment. The successful synthesis of chromium(III) macrocycles with even unsaturated macrocycles such as Me$_4$[14]tetraene and Me$_6$[14]diene indicate that the symmetrical [14]-membered macrocycles are capable of complexing with bulky metal ions like Cr(II).[19,20] Although special conditions seem to be needed for the preparation of the Cr(II) derivatives of Me$_6$[14]diene,[20] the complexes with the ligands Me$_4$[14]tetraene and Me$_6$[14]ane[19] seem to lend themselves to easier manipulation. Whereas both folded and planar arrangements of Me$_6$[14]ane ligand in an octahedral complex seem possible,[19] with Me$_4$[14]tetraene, the structure of the tetraaza macrocycle is likely to enforce an equatorial arrangement of the ligand even in the divalent state of the metal ion. With Me$_6$[14]diene, it is interesting to note that the crystal structure of the chromium(I) nitrosyl derivative of the tetraaza ligand is known and the macrocycle in this complex has an equatorial arrangement.[20,28] However, our studies do show that when one starts from Cr(III) acetate and Me$_6$[14]diene, even under anhydrous conditions, the tetraaza macrocycle of the formulation $C_{16}H_{29}N_4$ undergoes ring opening to yield a $C_{10}H_{23}N_4$ type molecule. The steric strain associated with the complexation of symmetrical [14]-membered macrocycles to Cr(III) becomes important. Such steric strains may well influence the number, nature, and position of other ligands coordinated to the metal ion. Our studies of the aquo complexes using paramolybdate titrations and conductance measurements show that complexes **1** and **3** are indeed diaquo systems with a tripositive charge as in Table I.

Table I. Number of Coordinated Water Ligands and Conductance Measurements on Chromium(III) Macrocyclic Complexes, $Cr(L)(H_2O)_x{}^{n+}$ (L = Tetraaza Macrocycle or Pseudomacrocycle)

L	x^a	conductance, mhos cm^2 M^{-1}	electrolytic behavior
Me$_6$[14]ane	1.86 ± 0.1	362	3:1
Me$_4$[14]tetraene	1.9 ± 0.1	394	3:1
Me$_2$[13]diene	1.92 ± 0.1	236	2:1
$C_{10}H_{23}N_4{}^b$	1.9 ± 0.1	404	3:1

^{a} Number of coordinated water ligands per Cr atom, determined by paramolybdate titration. ^{b} Obtained after the direct reaction of Cr(III) with Me$_6$[14]diene.

Complex **8**, on the other hand, shows a dipositive character with two coordinated aquo ligands. Previous instances in which Me$_2$[13]diene undergoes deprotonation to behave as a mono anion are known.[29] The dipositive character of the Cr(III)–Me$_2$[13]diene derivative is further established by the charge/species determination by the method of Cady and Connick,[27] which yielded a value of 1.9 ± 0.1. Similar charge/species studies as well as elemental analyses established the formulations $Cr(Me_6[14]ane)(NCS)(H_2O)^{2+}$ and $Cr(Me_6[14]ane)(CHCl_2)(H_2O)^{2+}$ for complexes **6** and **7**, respectively.

Although no detailed characterization of **5** prepared according to our methods was attempted, the complex *trans*-$Cr(cyclam)(H_2O)_2{}^{3+}$ is a well-characterized species.[4,5] Therefore, on the basis of electronic spectral data, the success of the method of Poon et al.[30] in using 2,4,6-trimethylpyridine for the isomerization of *cis*-$Cr(cyclam)(H_2O)_2{}^{3+}$ to the trans derivative is established. One of the important questions pertaining to other macrocyclic complexes investigated in this study is whether the tetradentate ligands are equatorially arranged to give *trans*-$Cr(macrocycle)(X)_2{}^{n+}$ type structures or folded to yield *cis*-$Cr(macrocycle)(X)_2{}^{n+}$ type compounds.

The assignment of cis and trans structures to Cr(III) complexes is generally based on the splitting of the T_{2g} (O_h) state[31] and the number of bands in the CH$_2$ rocking frequency regions (800–900 cm^{-1}) in the infrared spectra of the compounds.[30,32] In the case of D_{4h} *trans*-$Cr(macrocycle)(X)_2{}^{n+}$ type compounds, $^4T_{2g}$ is expected to split into ^4E_g and $^4B_{2g}$ states.[33] Similarly $^4T_{1g}$ is split into $^4A_{1g}$ and ^4E_g. Therefore for *trans*-$Cr(macrocycle)(X)_2{}^{n+}$ type complexes, four d–d bands arising from $^4A_1 \rightarrow {}^4A_2$, $^4E(^4T_1) \rightarrow {}^4A_2$, $^4B_2 \rightarrow {}^4A_2$, and $^4E(^4T_2) \rightarrow {}^4A_2$ are expected.[33] On the other hand, in lower symmetries, such as C_{2v} for *cis*-$Cr(macrocycle)(X)_2{}^{n+}$ type complexes, ^4T states corresponding to O_h point group symmetries are split further into several components. However, generally the energies of the various d–d transitions in the lower symmetries like C_{2v} do not differ markedly, and cis complexes show only two major d–d bands. In the case of trans compounds three to four bands are observed in the d–d transition regions as seen from Table II. Therefore, on the basis of comparison of the electronic spectral data with those of other known trans complexes including the ones reported by House et al.[9] trans formulations may be assigned also to **1**–**3**. Further support for the assignment is obtained from the analysis of the infrared spectra in the 800–950-cm^{-1} region shown in Figure 2. It is known that cis complexes with C_{2v} point group exhibit four to five bands in the CH$_2$ rocking frequency regions, whereas D_{4h} compounds show

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Table II. Electronic Spectral Data for Chromium(III) Tetraamine (or Ammine) Complexes[a]

complex	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}[b]	ϵ_{max}	ref
cis-$Cr(NH_3)_4(H_2O)_2^{3+}$	366	27			495	36	34
cis-$Cr(en)_2(H_2O)_2^{3+}$	366	44			485	68	35
cis-$Cr(cyclam)(H_2O)_2^{3+}$	370	38			483	26	4
cis-$Cr(trien)(H_2O)_2^{3+}$	372	36			497	72	36
cis-$Cr(en)_2Cl_2^+$	402	69			528	71	34
cis-$Cr(cyclam)Cl_2^+$	404	106			529	111	4
trans-$Cr(NH_3)_4(H_2O)_2^{3+}$	368	30			476	21	33
trans-$Cr(en)_2(H_2O)_2^{3+}$	361	39	442	29	508 sh	23	38
trans-$Cr(cyclam)(H_2O)_2^{3+}$	350	53	405	39	510	24	4
$Cr(Me_6[14]ane)(H_2O)_2^{3+}$	388	49	400 sh	44	525	76	this work
$Cr(Me_6[14]diene)(H_2O)_2^{3+}$	359	78	410	54	528	46	this work
$Cr(Me_4[14]tetraene)(H_2O)_2^{3+}$	350 sh	3510	450 sh	170	545	40	this work
trans-$Cr(cyclam)(NCS)_2^+$	365 sh	117			483	139	this work
$Cr(Me_6[14]ane)(NCS)(H_2O)^{2+}$	292	390	400	241	520	75	this work
trans-$Cr([15]ane)(CH_3)(H_2O)^{2+}$	258	3300	375	22	468	69	6
$Cr(Me_6[14]ane)(CHCl_2)(H_2O)^{2+}$	266	2470	387	106	520	27	this work
trans-$Cr(en)_2Cl_2^+$	396	34	453	23	578	25	37
trans-$Cr(cyclam)Cl_2^+$	365	41	407 sh	35	572	20	4
$Cr(C_{10}H_{23}N_4)(H_2O)_2^{3+}$[c]	350	43	380 sh	34	490	43	this work
$Cr(Me_2[13]diene)(H_2O)_2^{2+}$	355	302			520	57	this work
trans-$Cr(Me_6[14]ane)Cl_2^+$[d,e]	387	47	440 sh	27	574	25	9b

[a] λ_{max} in nm; ϵ_{max} in M^{-1} cm^{-1}. [b] Generally for Cr(III) complexes with *Dq*(eq) > *Dq*(ax) in D_{4h} point group, the lowest energy band is assigned to a $^4E_g \rightarrow {}^4A_{2g}$ transition. [c] The complex was obtained in one of the unsuccessful attempts to prepare *trans*-$Cr(Me_6[14]diene)(H_2O)_2^{3+}$ starting from chromium(III) acetate and $Me_6[14]$diene. [d] The spectrum was measured in DMF. [e] By means of base hydrolysis of the dichloro derivatives *trans*-$[Cr(Me_6[14]ane)Cl_2]^+$ a diaquo complex has been prepared and the spectrum recorded in methanol after this work was completed. The spectral data with λ_{max} at 535 (65 M^{-1} cm^{-1}) and 423 (96 M^{-1} cm^{-1}) published in ref 9b are not in good agreement with our results, and changes in the media and methods of preparation may have well accounted for this difference.

only two to three bands.[30,32] Indeed $Me_6[14]$ane and $Me_6[14]$diene complexes of Cr(III) exhibit only three bands in the CH_2 rocking frequency regions.

The $Me_4[14]$tetraene derivative shows only two bands between 800 and 950 cm^{-1}. Similarly in the case of **4** (obtained from $Me_6[14]$diene decomposition), only three bands were observed in the region of interest. The assignment of trans structures to **1–4**, therefore, seems well supported by the electronic and infrared spectra. In the case of $Cr(Me_2[13]diene)(H_2O)_2^{3+}$, although three bands were observed in the d–d transition region, cis structures cannot be ruled out. Many weak bands were observed in the region of 800–950 cm^{-1} in the infrared spectrum of $Cr(Me_2[13]diene)(H_2O)_2^{3+}$, and the electronic spectrum was complicated by the contributions from the charge-transfer transitions in the far-UV regions. However, the comparison of the electronic spectrum of $Cr(Me_6[14]ane)(CHCl_2)(H_2O)^{2+}$ (**6**) with those of *trans*-$Cr([15]ane)(H_2O)_2^{3+}$ and *trans*-$Cr(Me_6[14]ane)(H_2O)_2^{3+}$ (**1**) favors the assignment of trans structures to **6** also.

There is no firm experimental evidence in this study to assign the geometrical structure for $Cr(Me_6[14]ane)(NCS)(H_2O)^{2+}$ ambiguously. However, it is known that Cr(III) thermal substitutions are stereoretentive.[39] Complex **6** was prepared by ligand substitution in *trans*-$Cr(Me_6[14]ane)(H_2O)_2^{3+}$. Therefore, the trans structure for **6** seems most likely. In the case of **4**, the complex had been obtained in one of the unsuccessful methods used to prepare $Cr(Me_6[14]diene)(H_2O)_2^{3+}$ and the chemical analysis data indicated the possibility of ring opening. The postulate that under synthetic conditions the macrocycle loses its integrity is further supported by ^1H NMR as well as ^{13}C NMR.[40] The methyl and methylene signals are located at 1.8 and 3.2 ppm in the ^1H NMR spectrum with respect to Me_4Si. The ^{13}C NMR spectrum exhibits three signals at 183.92, 40.39, and 26.54 ppm with respect to Me_4Si, which may be assigned to tertiary (C), methylene (CH_2), and methyl (CH_3) carbon atoms, respectively on the basis of resonance decoupling and gated decoupling experiments. The integral ratios observed in the ^1H NMR and ^{13}C NMR spectra are in reasonable agreement with those of structure **4**.

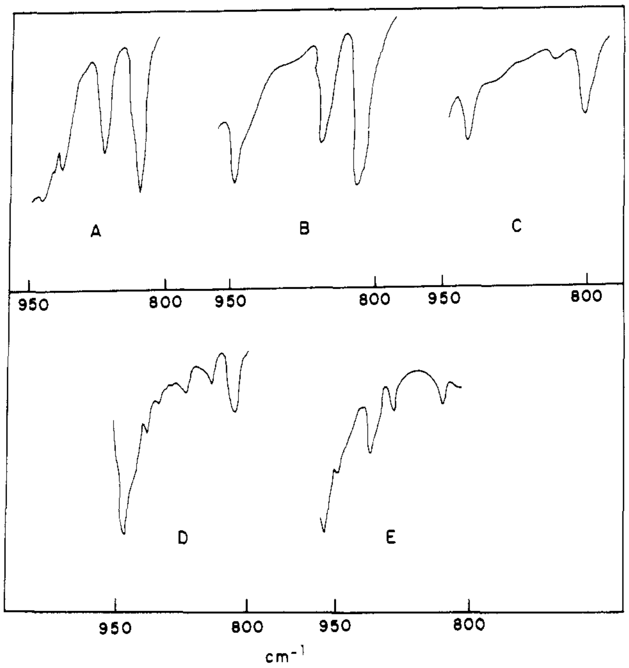

Figure 2. Infrared spectra of $Cr(macrocycle)(H_2O)_2^{3+}$, where macrocycle = (A) $Me_6[14]$ane, (B) $Me_6[14]$diene, (C) $Me_4[14]$tetraene, (D) $Me_2[13]$diene, and (E) $Cr(C_{10}H_{23}N_4)(H_2O)_2^{3+}$ in the CH_2 rocking frequency region of 800–950 cm^{-1}.

The ring strain, if present in the macrocyclic ligand $Me_6[14]$diene when bonded to Cr(III), may be expected to be relieved due to ring opening in **4**. The d–d spectrum lends itself as a powerful tool in analyzing in more detail the contribution of ring strain and other related structural features. It is evident from Table II that the energy of the lowest energy d–d band for the diaquo complexes decreases in the order *cis*-$Cr(cyclam)(H_2O)_2^{3+}$ > $Cr(C_{10}H_{23}N_4)(H_2O)_2^{3+}$ > *trans*-$Cr(cyclam)(H_2O)_2^{3+}$ > $Cr(Me_2[13]diene)(H_2O)_2^{3+}$ > *trans*-$Cr(Me_6[14]ane)(H_2O)_2^{3+}$ > *trans*-$Cr(Me_6[14]diene)(H_2O)_2^{3+}$ > *trans*-$Cr(Me_4[14]tetraene)(H_2O)_2^{3+}$. The observed order needs further comment. The field strength of the macrocycles increases with the number of

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imine nitrogens in the cases of tetraazacyclic ligands when the central metal ion is Co(III). In the case of d^3 systems, the energy of the longest wavelength d–d band is known to give a direct measure of the field strength of the ligands.[33b] The data given in Table II suggest that as the number of imino nitrogens increases, the field strength of macrocycles bonded to Cr(III) decreases. A detailed discussion of the field strength of related macrocycles as a function of intraligand ring size, steric strain, symmetrical nature (or otherwise), etc. was presented by Swisher et al.[10] Following their arguments,[10] it may be suggested that the steric strain associated with symmetrical [14]-membered macrocycles in forming trans complexes contributed to the observed order of field strength for the ligands, Me_6[14]ane > Me_6[14]diene > Me_4[14]tetraene. Since the C═N bond is shorter than the C—N bond, as the number of C═N bonds increases, the intraligand ring size of [14]-membered macrocycles is expected to decrease, thereby increasing the steric strain. At least in the case of Cr(Me_4[14]tetraene)$(H_2O)_2^{3+}$, considerable steric strain may be inferred on the basis of the electronic spectrum.

When the strain due to the mismatch of the intraligand ring size and the size of the metal ion is large, displacement of the central metal ion from the plane of the ring donor atoms (as in Cr(salen)$(H_2O)_2^{+}$) or ring opening of the macrocycles as in the cases of Me_6[14]diene and Me_4[14]tetraene cannot be ruled out. Recently, an X-ray structural study[42,43] of a methoxy-bridged Cr(III) dimer prepared from Cr(II) and Me_4[14]tetraene in methanolic media proved conclusively that Me_4[14]tetraene undergoes breakdown at the time of synthesis.[42] Therefore, in cases where the synthesis of diaquo complexes of the formulation Cr(Me_6[14]diene)$(H_2O)_2^{3+}$ or Cr(Me_4[14]-tetraene)$(H_2O)_2^{3+}$ is possible, substantial steric strain in the trivalent state of the metal ion may be anticipated.

Summarizing the results of this study, it is now possible to synthesize Cr(III) complexes of symmetrical [14]-membered tetraaza macrocycles (with trans structures) in spite of steric strain. The field strength of these macrocycles also seems to be influenced by the cavity sizes. The implication of our results in this study is that there is a possibility of stabilizing the tetravalent state of chromium by way of both destabilizing Cr(III) with respect to Cr(IV) by the choice of macrocyclic ligand and increasing the Franck–Condon barriers for the conversion of octahedral Cr(IV) to tetrahedral Cr(V) through equatorially coordinated macrocyclic ligands.[44,45]

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Contribution from the Department of Chemistry,
Faculty of Science, Hokkaido University, Sapporo 060, Japan

Optical Resolution and Racemization Reaction of Tris(bathophenanthrolinedisulfonato)iron(II): Absence of an Intramolecular Racemization Path in Aqueous Solution

Akihiko Yamagishi

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Tris(bathophenanthrolinedisulfonato)iron(II) (Fe$(BPS)_3^{4-}$) was resolved on a chromatographic column of Λ-tris(1,10-phenanthroline)ruthenium(II)–montmorillonite. The Δ-enantiomer of Fe$(BPS)_3^{4-}$ exhibited higher affinity toward the column than the Λ-enantiomer. The ligand dissociation rate (k_D) and racemization rate (k_R) of Fe$(BPS)_3^{4-}$ were obtained in a mixed solvent of methanol and water. In water, k_R was identical with k_D with the same activation parameters: $\Delta H^* = 130$ kJ mol^{-1}, $\Delta S^* = 90$ J mol^{-1} K^{-1}. The results indicate that the complex racemizes by the dissociation path exclusively.

Introduction

Racemization of tris(1,10-phenanthroline)metal(II) (M$(phen)_3^{2+}$) in water has been a subject of many investigators.[1-3] One interesting aspect on this topic is that M$(phen)_3^{2+}$ follows different paths in racemization, depending on the electronic properties of the central metal ion. For example, the racemization rate (k_R) of Ni$(phen)_3^{2+}$ in water has been compared with the dissociation rate of a ligand (k_D). k_R is identical with k_D over wide ranges of temperature and pressure.[3] The results are interpreted in terms of the mechanism that Ni$(phen)_3^{2+}$ racemizes by dissociating one of its ligands

$$\Delta\text{-M(phen)}_3^{2+} \rightleftharpoons \text{M(phen)}_2^{2+} \rightleftharpoons \Lambda\text{-M(phen)}_3^{2+} \qquad (1)$$

in which a dissociation intermediate, M$(phen)_2^{2+}$, is optically inactive, losing the memory of the configuration of an initial M$(phen)_3^{2+}$.[1]

On the contrary, in the case of Fe$(phen)_3^{2+}$, k_R is about 1 order of magntidue larger than k_D in water.[2] It is concluded that Fe$(phen)_3^{2+}$ racemizes by way of two parallel paths; one is a dissociation path (1) and the other an intramolecular path (2).

$$\Delta\text{-M(phen)}_3^{2+} \rightleftharpoons \text{M(phen)}_3^{2+*} \rightleftharpoons \Lambda\text{-M(phen)}_3^{2+} \qquad (2)$$

In the activated state, the complex, M$(phen)_3^{2+*}$, undergoes an intramolecular configuration change without producing any free ligand.[1] In M$(phen)_3^{2+*}$, the significant lengthening of metal–ligand bonds occurs to satisfy the steric requirement for the change of the coordination positions. The stabilization of such an expanded state due to the contribution of the high-spin state ($(t_{2g})^4(e_g)^2$) is considered to be the main reason that Fe$(phen)_3^{2+}$ racemizes dominantly by wasy of the intramolecular path.[1]

Recently the present author has developed the method of optical resolution by use of an optically active clay–chelate adduct as a resolving agent.[4-6] The method is based on the stereoselective

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