TABLE VII

EFFECTIVE Cl^{35} QUADRUPOLE COUPLING CONSTANTS (MHz) IN SOME TETRAHEDRAL AND OCTAHEDRAL MOLECULES (AT 77°K)

$CCl_4{}^a$	81.9				
$SiCl_4{}^a$	40.8	$PCl_4{}^{+\,b}$	64.8	$AlCl_4{}^{-\,c}$	21.2
$GeCl_4{}^a$	51.3	$AsCl_4{}^{+\,b}$	73.9		
$SnCl_4{}^a$	48.2				
$PbCl_4{}^b$	45.4				
		$PCl_6{}^{-\,b}$	60.0		
$SnCl_6{}^{2-\,d}$	31.3	$SbCl_6{}^{-\,b}$	47.6		
$PbCl_6{}^{2-\,d}$	34.6				

[a] From Livingston.[19] [b] This work. [c] From Segel and Barnes.[18] [d] From Nakamura.[3]

We restrict our interpretation of the data presented here to qualitative generalizations. A more complete analysis will be appropriate when data on more extensive sets of isoelectronic molecules are available. Table VII includes only two pairs of isoelectronic species ($GeCl_4$ and $AsCl_4{}^+$, $SnCl_6{}^{2-}$ and $SbCl_6{}^-$) and one set of three ($AlCl_4{}^-$, $SiCl_4$, and $PCl_4{}^+$).

The anomalous behavior of the group IV tetrahalides at $SiCl_4$ and $SiBr_4$ is repeated in our data on $PCl_4{}^+$ and $AsCl_4{}^+$, the former having a chlorine quadrupole coupling constant 0.88 times as large as $AsCl_4{}^+$. (For $SiCl_4$ and $GeCl_4$ the analogous quantity is 0.80, and the ratio of the $SiBr_4$ to $GeBr_4$ Br^{81} quadrupole coupling constants is 0.84).

Schawlow[21] has interpreted this irregularity in the Townes and Dailey[22] framework as possibly arising from double-bond character in the silicon–chlorine bond (presumably of a Si-d—Cl-p π-bond type). In $PCl_4{}^+$ with a larger positive charge on the nucleus of the central atom, one might expect an enhancement of the lowering of the field gradient by that mechanism. Our observation is that the actual effect is to diminish the field gradient lowering compared to that observed for the third-row element. There is a possibility that $AsCl_4{}^+$ constitutes the anomaly rather than $PCl_4{}^+$ in this series, since chlorine compounds of As(V) have been difficult to prepare.

One can however see that a regular increase in eQq (Cl^{35}) accompanies an increase in the charge of the central atom in the tetrahedron.

The data on octahedral chloride ions given here are not extensive enough to draw any strong generalizations. We would rather note that, generally, the intensities of these resonances are weak in comparison to those of the neutral and cationic species studied. This may well reflect an inherent breadth in their resonances due to the presence of many low-frequency vibrational motions which serve to make vibrational effects on the field gradient tensor maximal in these anions.

Further work is presently in progress to detect resonances in other species isoelectronic with those given here in a hope that this direct property of molecular wave functions can become a useful diagnostic tool for bonding studies.

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Some Cobalt(III) Complexes Containing a Tetracoordinate Macrocyclic Schiff Base Amine Ligand: Preparation, Chemistry, and Infrared, Visible, and Ultraviolet Spectra[1]

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Several new complexes of the type $Co^{III}(C_{16}H_{32}N_4)L_2$ have been prepared, where $C_{16}H_{32}N_4$ is a macrocyclic Schiff base amine ligand and L = Cl^-, Br^-, OH^-, NCS^-, $N_3{}^-$, CN^-, $NO_2{}^-$, or OH_2. Two very closely related geometrical isomers of $[Co(C_{16}H_{32}N_4)Cl_2]ClO_4$ have been prepared and characterized. Analysis of infrared spectra, chemical properties, and especially of the visible spectra of the $Co^{III}(C_{16}H_{32}N_4)L_2$ complexes implies that the ligands L are *trans* to one another. Analysis of visible spectra of the $Co^{III}(C_{16}H_{32}N_4)L_2$ complexes indicates that the macrocyclic Schiff base amine ligand, $C_{16}H_{32}N_4$, has an appreciably higher crystal field strength (Dq) than one finds for related primary and secondary amine ligands.

Of the known coordination complexes of Co(III) only a relatively few involve a macrocyclic ligand. The known macrocyclic complexes of Co(III) include vitamin B_{12},[3] the porphyrin and the phthalocyanine[4] complexes, and four cyclic tetradentate secondary amine complexes.[5-8] The chemistry of the B_{12} series of compounds exhibits many unusual features,[3,9] at least

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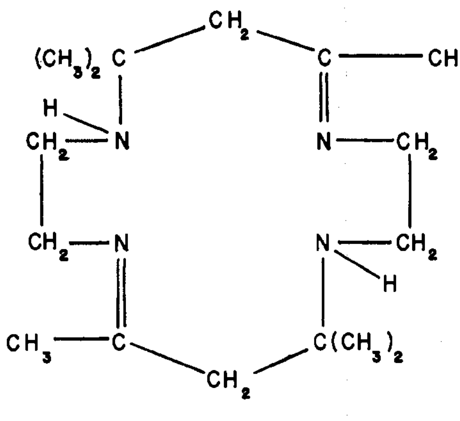

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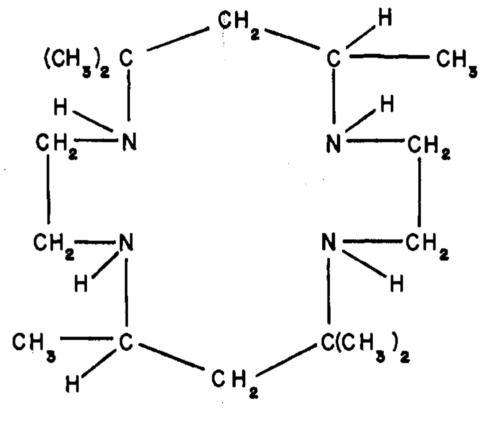

tet*a* or tet*b*

one of which, the formation of Co–alkyl bonds, has also been found to occur in porphyrin,[10] dimethylglyoxime,[11] and cyanide[12] complexes of Co(III). It has been suggested that the total crystal field stabilization energy of the complex is the most important factor in the stabilization of metal–alkyl bonds.[13] Thus, any simple macrocyclic ligand in which back donation of electron density may increase the crystal field stabilization energy of the complex is a potential analog of vitamin B_{12}. One of the simplest such ligands is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, A, which Curtis and co-workers have coordinated to Ni(II) and Cu(II).[14–18]

Curtis and co-workers have found that the macrocyclic Schiff base amine complexes of Ni(II) and Cu(II) are characterized by a relative inertness to displacement of the macrocyclic ligand, A, even by CN^-,[19,20] or concentrated mineral acids.[14,15,17] Since the macrocyclic ligand, A, is an aliphatic Schiff base, the inertness of the coordinated[14,15,17] or the protonated[21] ligand to acid hydrolysis is very striking.[22]

The Co(II) complexes of the macrocyclic Schiff base ligand, A, are of interest since (1) few macrocyclic complexes of Co(III) are known, (2) the ligand is much simpler than the porphyrins or phthalocyanine, (3) coordination of the metal to the ligand is entirely through nitrogen atoms, but (4) the ligand is a Schiff base amine rather than an aliphatic secondary amine. In this paper we report the preparation of several coordination complexes of the type $Co^{III}AL_2$. Our preparation of these complexes depends on the recent discovery that the dihydrogen perchlorate salt of the free ligand (*i.e.*, $A\cdot 2HClO_4$) may be prepared easily and in large yield.[21,23]

The complexes reported here are certain to become very important in studies of the stereochemistry of Co(III) and the mechanisms of reactions of Co(III) as well as serving as B_{12} analogs. Certain of our observations concerning the chemistry of these complexes are included in this report.

Experimental Section

Infrared spectra were determined from Nujol and hexachlorobutadiene mulls of the dry solids, using Perkin-Elmer Model 137 and 237 spectrometers. Visible and ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrometer.

Titrations were performed using an Instrumentation Laboratories Model 145 pH meter with a glass–Ag|AgCl combination electrode. The meter was calibrated against standard buffer solutions of pH 6.86 and pH 4.01.

Elemental analyses were performed by Spang and/or Schwarzkopf Microanalytical Laboratories.

Preparations.—The preparations of the macrocyclic Schiff base dihydrogen perchlorate ($A\cdot 2HClO_4$) and its reaction with $Na_3[Co(CO_3)_3]\cdot 3H_2O$ to form $[CoACO_3]ClO_4$ have been described elsewhere.[21] $[CoA(OH_2)_2](ClO_4)_3$ has been prepared by treating $[CoACO_3]ClO_4$ with concentrated $HClO_4$. The perchlorate salt of the diaquo complex is very difficult to crystallize although we have obtained solid material by adding cold (0°) concentrated $HClO_4$ to solid $[CoACO_3]ClO_4$ and filtering rapidly. $CoA(OH)_2^+$ has been obtained as the conjugate base of the diaquo complex or directly from the basic hydrolysis of $CoACl_2^+$.

The preparation and isolation of the *a* and *b* isomers of the macrocyclic tetramine are in the literature.[16,17] The preparation and characterization of several complexes of the types $Co^{III}(tet\textit{a})L_2$ and $Co^{III}(tet\textit{b})L_2$ have been reported very recently.[7,8] Generally we have found it most convenient to prepare the $Co^{III}(tet\textit{a})L_2$ complexes from the $[Co(tet\textit{a})(OH_2)_2](ClO_4)_3$ complex described below.

Chloride salts of Co(III) complexes have been prepared by means of the metathetical reaction between an excess of solid KCl and the corresponding complex Co(III) perchlorate in methanol. Chlorides of $Co^{III}AL_2$ complexes seem to be very soluble in water and methanol.

Dichloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, $[Co(C_{16}H_{32}N_4)Cl_2]ClO_4$.—We have prepared this complex several different ways. Two of these preparations lead to products which have the same elemental composition yet exhibit markedly different infra-

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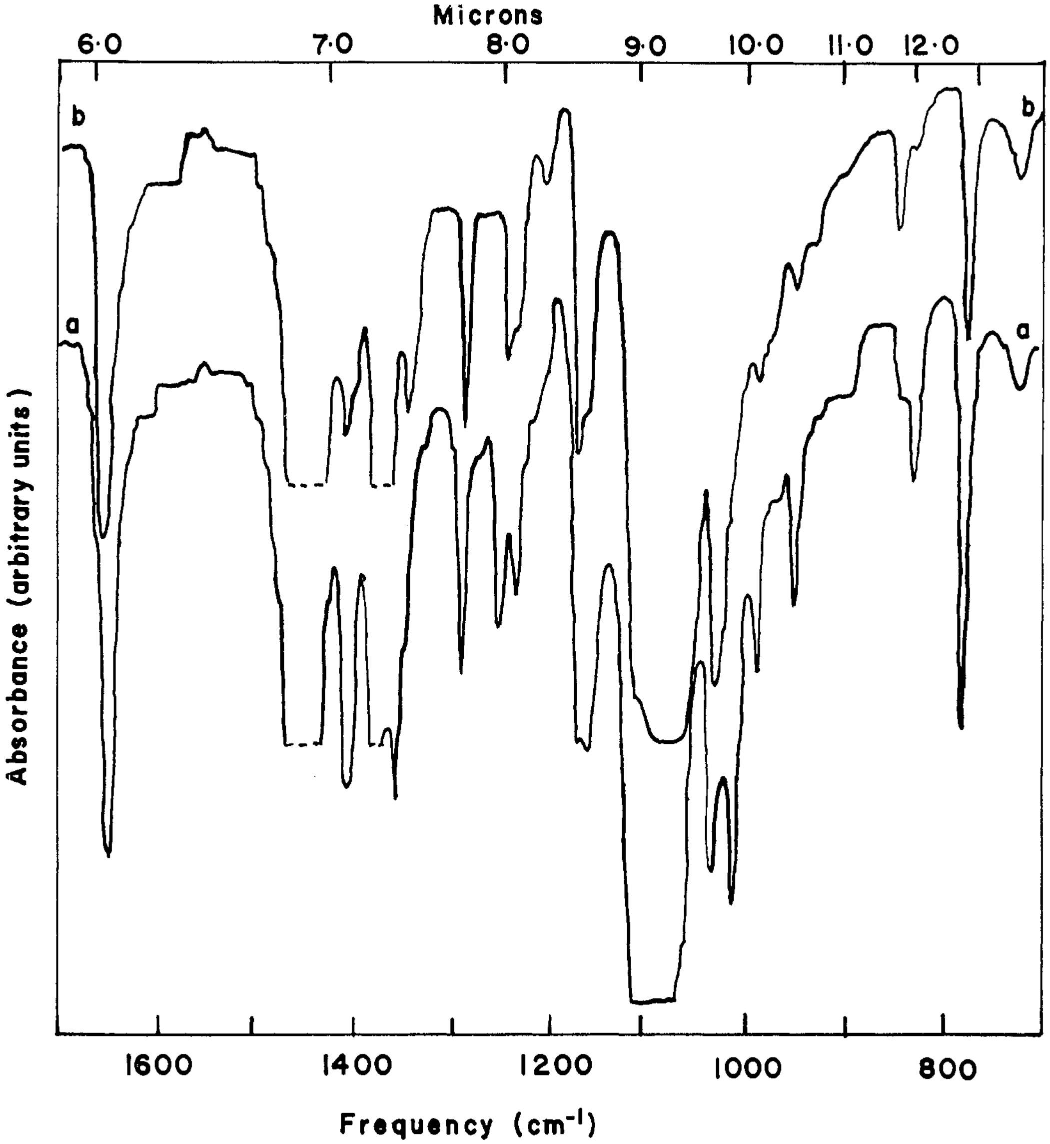

Figure 1.—Infrared spectra of (a) [Co(A*a*)Cl$_2$]ClO$_4$ and (b) [Co(A*b*)Cl$_2$ClO$_4$. Spectra were determined in Nujol muls and spectral regions obscured by Nujol absorptions are indicated with a broken line (- - - -).

red spectra (see Figures 1 and 2 and the discussion below). From the preparative mixtures we have isolated crystal fractions that appear to be pure samples of two different isomers.

Preparation of Isomer *a*.—A mixture of CoCO$_3$ and a slight excess of the crude Schiff base dihydrogen perchlorate (A·2HClO$_4$) in aqueous methanol was heated on a steam bath for about 4 min. The initial wine red color deepened as the solution was heated. The red solution was filtered, and air was passed through the solution for about 12 hr or until crystalline [CoACO$_3$]ClO$_4$ separated. Concentrated HCl was added to the resulting solid until it turned green. This mixture was slowly evaporated on the steam bath until green crystals started to form. On cooling, most of the dichloro compound (I) crystallized. After the crystals were separated from the preparative mixture, they were recrystallized from hot water acidified with HCl or from hot methanol. It is possible to grow the crystals very slowly from aqueous HCl, and we have obtained square plates (of isomer *a*) up to 0.5 cm on an edge by this means.[24] Recrystallization from aqueous solutions always results in a loss of some complex due to aquation or to acid hydrolysis of the imine groups of the macrocyclic ligand. This preparation appears to give about 90% of isomer *a*, [Co(A*a*)Cl$_2$]ClO$_4$, before recrystallization. The yield, based on A·2HClO$_4$, is about 50%.

Preparation of Isomer *b*.—A hot methanolic solution (100 ml) of 7 g of cobaltous acetate was added to 48 g of A·2HClO$_4$. The mixture was heated for about 30 min on a steam bath, then cooled, diluted to about 200 ml with methanol, and filtered. A stream of O$_2$ was passed through the filtrate for about 24 hr and methanol was permitted to evaporate from the solution until a dark red glassy residue remained. Concentrated HCl was added to the residue and the mixture was filtered as soon as the last traces of the red acetate residue had disappeared. The green crystalline product was washed with methanol. On recrystallization of the product from methanol, we observed that two distinctly different kinds of crystals grew from the same solution: a few (about 15–20% by weight) dark green square plates (which were identical with the predominant product of the preceding preparation) and a large quantity of very fine green crystals. Isomer *a* appears to be significantly less soluble in methanol than this second isomer. The isomeric products are readily separated by fractional recrystallization from methanol. If the *b* isomer, [Co(A*b*)Cl$_2$]ClO$_4$, is recrystallized slowly from a

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[24] We have found that when aqueous HCl (~2 *M*) solutions of [Co(ACl$_2$]ClO$_4$ are allowed to stand for long periods of time (~1 week) at room temperature a very dark green crystalline substance, II, is formed. The infrared spectra of II exhibit a strong NH$_2$ deformation band indicating that the coordinated Schiff base ligand has partially hydrolyzed. Both the *a* and *b* isomers exhibit this behavior.

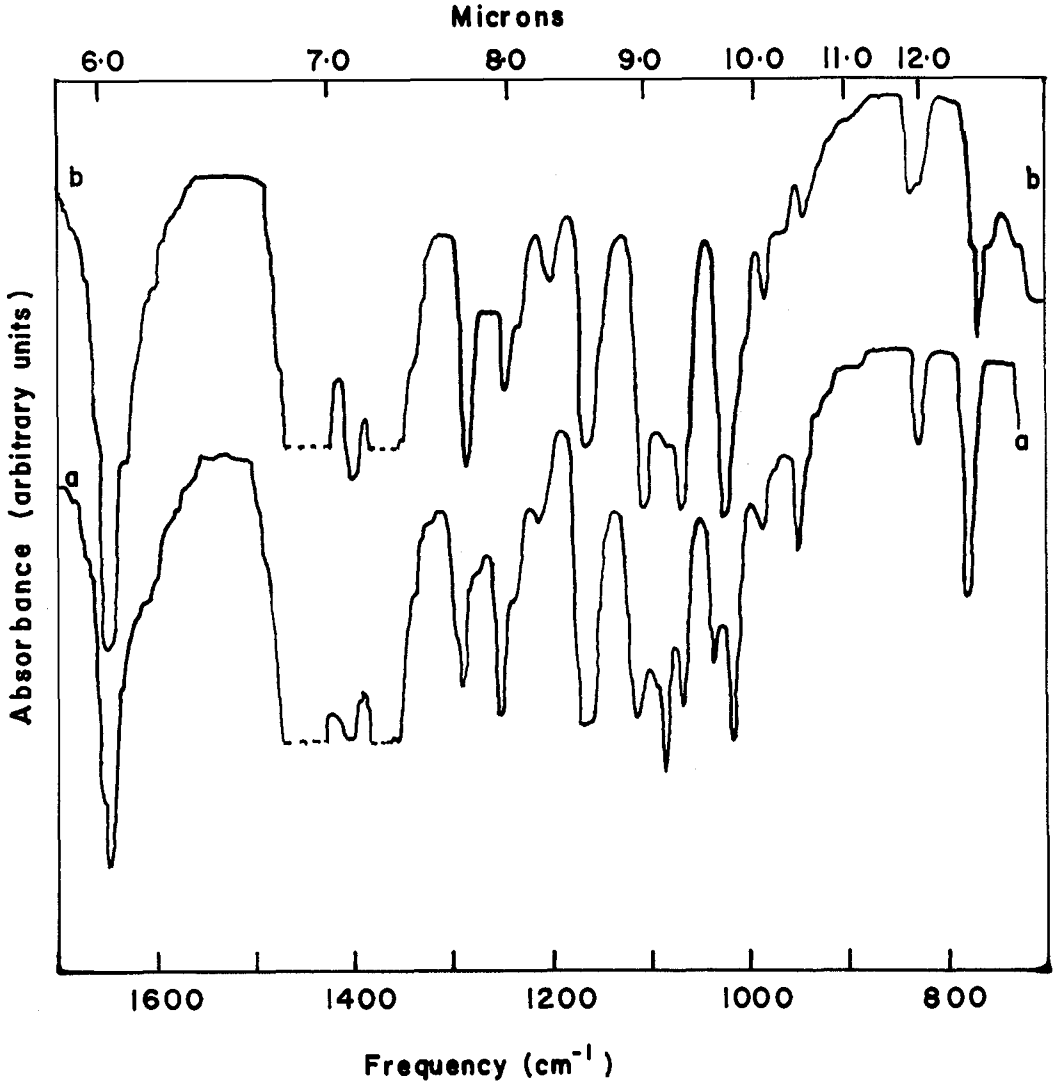

Figure 2.—Infrared spectra of (a) [Co(A*a*)Cl_2]Cl and (b) [Co(A*b*)Cl_2]Cl. Spectra were determined in Nujol mulls and spectral regions obscured by Nujol absorptions are indicated with a broken line (– – – –).

methanol–water mixture, large crystals can be obtained. Large crystals of [Co(A*a*)Cl_2]ClO_4 differ somewhat from large crystals of [Co(A*b*)Cl_2]ClO_4 since the former tend to crystallize as thin square green plates while the latter tend to crystallize as thin (somewhat paler) green rhombohedral flakes. The total yield of [CoACl_2]ClO_4 based on A·2HClO_4 was about 80%. *Anal.* Calcd for $C_{16}H_{32}ClN_4O_4Co$: C, 37.7; H, 6.3; N, 11.0; Cl, 20.9. Found for isomer *a*: C, 37.9; H, 6.6; N, 11.2; Cl, 20.8. Found for isomer *b*: C, 38.1; H, 6.5; N, 10.9; Cl, 21.1.

Aquochloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, [CoAH_2OCl](ClO_4)$_2$. —An excess of [Co(A*a*)Cl_2]ClO_4 was added to 100 ml of hot (about 50°) water. The mixture was filtered quickly and the filtrate was mixed with 5 ml of concentrated HClO_4. The resulting solution was allowed to stand for about 1 week, during which time the dark green needle-shaped crystals grew slowly. *Anal.* Calcd for $C_{16}H_{34}Cl_3N_4O_9Co$: C, 32.5; H, 5.8; N, 9.5; Cl, 17.9. Found: C, 33.2; H, 6.3; N, 9.0; Cl, 17.6.

The substitution of other ligands for Cl^- in CoACl_2^+ is readily accomplished and is described below. The complexes described below have all been prepared from the *a* isomer, [Co(A*a*)Cl_2]ClO_4, described above and hereafter referred to as I.

Dicyano(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, [CoA(CN)$_2$]ClO_4.—Sodium cyanide (0.6 g) was added to a solution of 2.5 g of I in 50 ml of hot (60°) aqueous methanol. The green color of the solution turned orange-yellow, and on standing yellow crystals separated. The crystals were filtered, washed twice with ice-cold water, and recrystallized from a minimum of hot water. *Anal.* Calcd for $C_{18}H_{32}ClN_6O_4Co$: C, 44.0; H, 6.5; N, 17.2. Found: C, 43.8; H, 6.6; N, 17.2.

Diazido(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, [Co($C_{16}H_{32}N_4$)(N_3)$_2$]ClO_4.—The procedure was similar to that followed for the dicyano complex, described above, except that NaN_3, rather than NaCN, was added to the methanolic solution of I. The solution turned violet, and as it cooled slowly violet needle crystals separated. The products were filtered, washed twice with ice-cold water, and dried under vacuum. *Anal.* Calcd for $C_{16}H_{32}ClN_{10}O_4Co$: C, 36.8; H, 6.2. Found: C, 36.8; H, 6.3.

Dinitro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, [Co($C_{16}H_{32}N_4$)(NO_2)$_2$]ClO_4.—The procedure followed was similar to that described for the preceding complexes, adding NaNO_2 to a hot methanolic solution of I. The green solution soon turned yellow, and orange-yellow needle-shaped crystals formed as the solution cooled. The product was recrystallized from hot water, washed with ice-cold water, and dried under vacuum. *Anal.* Calcd for $C_{16}H_{32}ClN_6O_8Co$: C, 35.2; H, 6.2. Found: C, 35.5; H, 6.2.

Dibromo(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, [Co($C_{16}H_{32}N_4$)Br_2]ClO_4.—Analogous to the above, NaBr was added to a hot methanolic solution of I This mixture was heated for about 30 min on a steam bath. The yellow-green needle-shaped crystals of

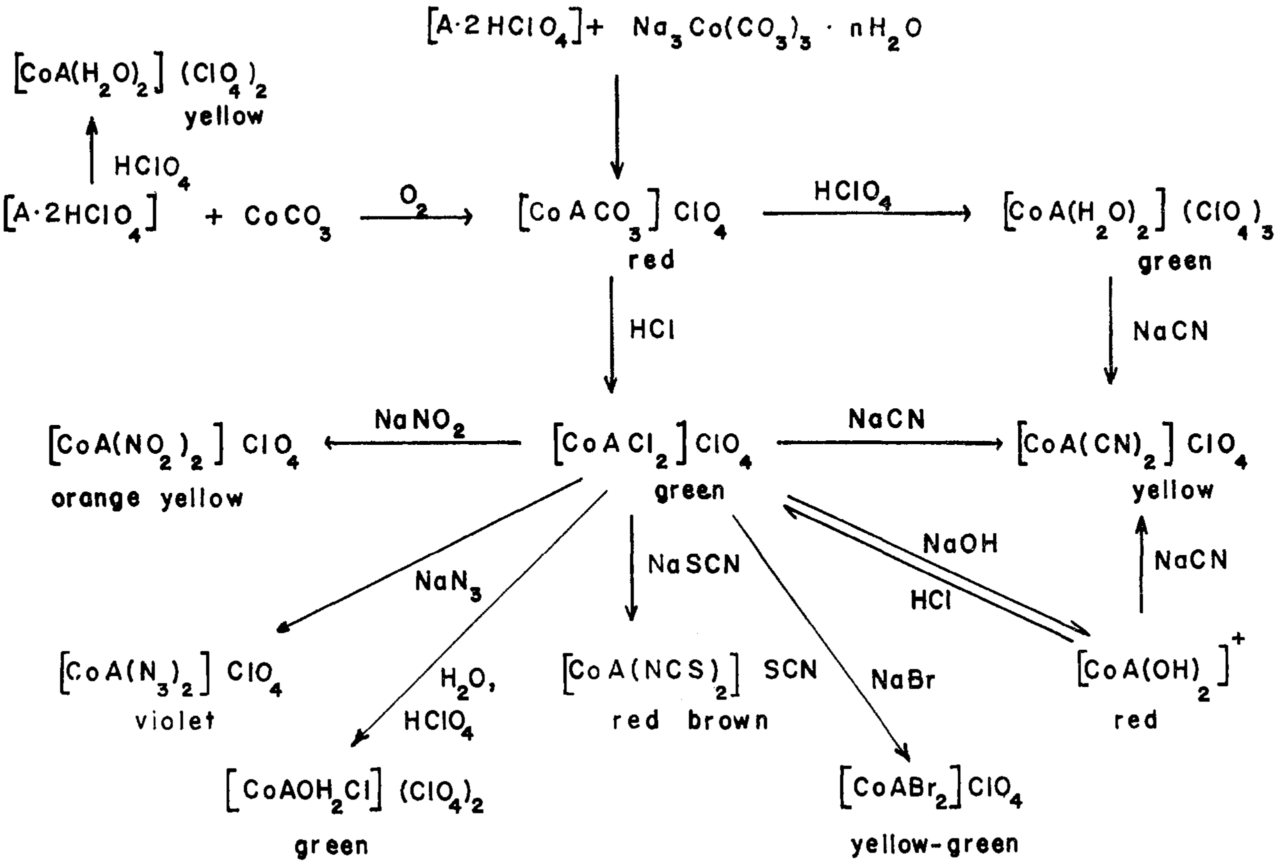

Figure 3.—Preparative reactions of the $Co^{III}AL_2$ complexes.

the product were recrystallized from methanol. *Anal.* Calcd for $C_{16}H_{32}Br_2ClN_4O_4Co$: C, 32.1; H, 5.4; N, 9.4; Cl, 5.9; Br, 26.8. Found: C, 32.4; H, 5.5; N, 9.4; Cl, 6.1; Br, 27.0.

Diisothiocyanato(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) Thiocyanate Perchlorate, $[Co(C_{16}H_{32}N_4)(NCS)_2]_2(ClO_4)(SCN)$.—The procedure described for preparation of the preceding complexes was repeated using NaSCN. Reddish brown needle-shaped crystals formed from the dark red solution as it cooled. The product was recrystallized from hot water. The infrared spectrum of the compound showed the perchlorate and ionic thiocyanate as well as coordinated thiocyanate. When the product was recrystallized from hot aqueous NaSCN, crystals of the more soluble thiocyanate salt, $[Co(C_{16}H_{32}N_4)(NCS)_2]SCN$, were formed. The infrared spectrum of this latter compound exhibited no perchlorate absorption. *Anal.* Calcd for $C_{37}H_{64}ClN_{13}O_4S_5Co_2$: C, 41.7; H, 6.1; N, 17.2; S, 15.1. Found: C, 41.9; H, 6.2; N, 17.3; S, 15.2.

Diaquo(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane isomer *a*)cobalt(III) Perchlorate, $[Co(C_{16}H_{36}N_4)(H_2O)_2](ClO_4)_3$.—The free amine, hexamethyl-1,4,8,11-tetraazacyclotetradecane, was prepared by the method of Curtis.[7,14,16] The isomeric NiA^{2+} and NiB^{2+} perchlorates were prepared and separated as described by Curtis, *et al.*[14,15,18] The predominant product, (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene)nickel(II) perchlorate ($NiA(ClO_4)_2$), was reduced with $NaBH_4$, and after decomposition of the excess BH_4^-, Ni(tet*b*)$(C_2O_4)_{1/2}ClO_4$ was precipitated with excess $Na_2C_2O_4$. When this oxalate complex and the free oxalate were removed, the free amine was obtained from the solution by reaction with excess NaCN.

Equimolar ethanolic solutions of the free amine and $Co(ClO_4)_2 \cdot 6H_2O$ were mixed and the precipitate filtered off. This precipitate was boiled in water, together with a small amount of "Charcoal Activated Norit." During the boiling, air or oxygen was passed through the mixture. After 15 min the mixture was filtered while hot, and the filtrate was made about 30% in $HClO_4$. After 1 hr fine green crystals of [Co(tet*a*)$(H_2O)_2](ClO_4)_3$ appeared. The yield was about 60%. The product was recrystallized from dilute $HClO_4$. *Anal.* Calcd for $C_{16}H_{40}Cl_3N_4O_{14}Co$: C, 28.3; H, 5.8; N, 8.3. Found: C, 28.6; H, 5.4; N, 8.1.

Results and Discussion

(A) General.—In this study we have prepared and characterized several Co(III) complexes of the macrocyclic Schiff base ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Figure 3 summarizes the preparations of the $Co^{III}AL_2$ complexes. The various complexes represented in Figure 3 are solids isolated from the preparative mixture (an exception is the case of $CoA(OH)_2^+$). The aquo, hydroxy, and acetato complexes proved to be exceptionally soluble and generally formed oils or amorphous solids rather than crystalline products. Since we have been unable to induce *cis–trans* isomerization in the $Co^{III}AL_2$ complexes and since the Schiff base macrocycle generally has been found to give nearly square-planar coordination geometry,[14,15,18] it seems reasonable to assume that most of the $Co^{III}AL_2$ complexes have the ligands L arranged *trans* to one another. The spectral properties of the complexes, which are discussed in detail below, are consistent with a *trans* arrangement of the ligands L.

Since Co(III) generally requires a coordination number of 6, the $Co^{III}AL_2$ complexes prepared in this study form an interesting contrast to the tetracoordinate complexes of Ni(II) and Cu(II)[14–18] and of Co(II) and Zn(II)[21] reported previously. In the case of the

Ni(II) complexes three geometrical isomers of Ni-$(C_{16}H_{32}N_4)^{2+}$ have been reported.[18] One of these isomers, NiB^{2+} (in which the imine groups are *cis* to one another), cannot be prepared from the Schiff base dihydrogen perchlorate, $A{\cdot}2HClO_4$, because the protonated ligand is prepared as the A isomer (in which the imine groups are *trans* to one another).[21,23] Two isomers have been reported[18] for NiA^{2+} (designated $Ni(A\alpha)^{2+}$ and $Ni(A\beta)^{2+}$ by Curtis, *et al.*[18]). These isomers have been shown to correspond to the two possible geometrical arrangements (*i.e.*, the *meso* and *dl* geometries) of the protons on the two secondary amine nitrogen atoms of the ligand A.[25] It has been of some interest to us to demonstrate the existence of an analogous isomerism in the six-coordinate Co(III) complexes. It seems very remarkable that in the case of the Co(III) complexes different choices of the ligands, L, in the preparative routes lead to nearly pure *a* or pure *b* isomers. Whether a particular preparative route yields the *a* or the *b* isomer (or a mixture of the two) apparently depends on the interaction of the macrocyclic ligand A with the ligands L during the reactions forming the Co(III) complex. In this connection it is relevant to note that the preparation of $[CoACl_2]ClO_4$ can be accomplished with less basic salts than $CoCO_3$ and $Co(O_2CCH_3)_2$. Thus oxidation of a methanolic solution of $CoCl_2$ and $A{\cdot}2HClO_4$ gives $[CoACl_2]ClO_4$ (in about 25% yield); the $[CoACl_2]ClO_4$ product in this case seems to contain both the *a* and *b* isomers with perhaps a slight preponderance of the *b* isomer.

It is tempting to postulate that the role played by the CO_3^{2-} in the preparation of $[Co(Aa)Cl_2]ClO_4$ is to force the macrocycle to fold, thus favoring a particular geometry for the secondary nitrogen protons, while the acetate ligands may stabilize the opposite geometry by means of hydrogen bonding to the secondary amine hydrogen atoms. Since we do not at present know if one or the other isomer is thermodynamically more stable, we can only conclude that at least one of the two preparations which we have employed gives a nonequilibrium distribution of $Co(Aa)Cl_2^+$ and $Co(Ab)Cl_2^+$ isomers. This isomerization might be expected to occur with greater difficulty in the case of the hexacoordinate Co(III) complexes than in the case of the tetracoordinate Ni(II) or Cu(II) complexes. However, it must be noted that base-catalyzed $a \rightarrow b$ isomerization in the case of the Co(III) complexes (analogous to the base-catalyzed $\alpha \rightarrow \beta$ isomerization of the Ni(II)[25] and Cu(II)[26] complexes) is complicated by base-catalyzed substitution of the ligands L and by the apparent decomposition of the macrocyclic ligand A when $Co^{III}AL_2$ complexes are treated with very strong bases. In the cases of $CoA(SCN)_2^+$ and $CoA(CN)_2^+$ (both prepared from $Co(Aa)Cl_2^+$) we have identified only a single isomer, despite the fact that the former complex can be obtained in several crystal forms (and different salts) while the latter is necessarily prepared in basic solution. It appears that the particular isomeric geometry (*a* or *b*) of the ligand A is retained in at least some substitution reactions of the type $Co^{III}AL_2 + 2X \rightarrow Co^{III}AX_2 + 2L$.

A point of interest in the preparative reactions concerns the apparent ease of substitution into the first coordination sphere of Co(III). It has recently been pointed out[27] that the substitution lability of $Co(diamine)_2Cl_2^+$ complexes can be correlated with the number of axial methyl groups in the Bailar–Corey conformational analysis.[28] In this context the $Co^{III}AL_2$ complexes provide an interesting comparison to the Co^{III}(teta or tetb)L_2 complexes because both macrocyclic ligands have the same number of axial methyl groups; but the geometry required by the imine groups of the macrocyclic Schiff base, A, may result in less steric interaction in $Co^{III}AL_2$ complexes than occurs in the case of the $Co^{III}(teta)L_2$ complexes. The $Co^{III}AL_2$ complexes seem somewhat less labile than the $Co^{III}(teta)L_2$ complexes, although substitution in either case occurs much more readily than in the case of the $Co^{III}(en)_2L_2$ complexes. For example, we have encountered difficulty in repressing the aquation of $Co(Aa)Cl_2^+$ in weakly acidic aqueous solution as might be expected for a relatively labile complex, while the coordinated water of $Co(teta)(OH_2)_2^{3+}$ has been shown to be relatively labile.[29]

We have begun to investigate the reaction chemistry of some of these macrocyclic systems and wish to report at this time an observation which is at least consistent with a *trans* geometry for the $Co^{III}AL_2$ complexes. We find that the $Co^{III}AL_2$ complexes are readily reduced by Zn or BH_4^-. The solutions of the reduced complexes are generally observed to have visible absorption spectra similar to those of aqueous solutions of $[CoA(OH_2)_2](ClO_4)_2$.[21] However, there is one striking exception to this: when $CoA(CN)_2^+$ is reduced with BH_4^- the insoluble *trans*-$[Co(teta)(CN)_2]ClO_4{\cdot}H_2O$ precipitates from the reaction mixture. The *trans*-$[Co(teta)(CN)_2]ClO_4{\cdot}H_2O$ thus obtained is identical with the complex reported by Whimp and Curtis[7] and also prepared by us from $[Co(teta)(OH_2)_2](ClO_4)_3$. The color changes which occur in this reaction indicate that there are some intermediate stages, and we are investigating the system further.

(B) Infrared Absorption Spectra.—The main infrared absorption frequencies and the band assignments are shown in Table I. Apart from the bands due to the anionic ligands, the spectra of all the Co(III) complexes containing the macrocyclic Schiff base ligand are very similar. All show a strong sharp band in the region of 3200 cm^{-1}, assigned to the N–H stretch. This value is not significantly different from those found for the analogous Cu(II), Ni(II), and Co(II) complexes.[21] On the other hand, the ν_{N-H} frequencies of the $Co^{III}AL_2$ complexes are generally about 40 cm^{-1} lower than the ν_{N-H} frequencies of the corresponding

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(25) L. G. Warner, N. J. Rose, and D. H. Busch, Abstracts of Papers Presented to the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Paper No. O 142.

(26) J. M. Palmer, private communication.

(27) M. D. Alexander, *Inorg. Chem.*, **5**, 2084 (1966).

(28) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(29) J. A. Kernohan and J. F. Endicott, work in progress.

TABLE I

PROMINENT INFRARED ABSORPTION FREQUENCIES (CM^{-1} × 10^{-3}) OF THE Co^{III}AL$_2$ COMPLEXES[a]

Compound	O–H	N–H	Ligand bands		C=N	ClO$_4^-$
$[CoA(CO)_3]ClO_4$	. . .	3.25 s, sp	1.66 vs, b $\nu_1{}^b$	Nonbonded	Obscured	
			1.63 vs, sp	CO str	by CO str	1.09 vs, b
			1.22 $\nu_5{}^b$	$\delta_{C-O} + \nu_{CO}$		
			0.820 m, sp $\nu_8{}^b$			
			0.750 ms $\nu_3{}^b$			
$[CoACl_2]ClO_4$	. . .	3.20 s, sp			1.65 s, sp	1.10 vs, b
$[CoABr_2]ClO_4$	. . .	3.22 m, sp			1.65 s, sp	1.09 s, b
$[CoA(OH_2)Cl](ClO_4)_2$	3.6 m, b	3.33 m, sp	1.65 w, b	O–H	1.66 s	1.09 s, b
$[CoA(H_2O)_2](ClO_4)_3$	3.57 s, b	3.20 m, sp	1.62 w, b	O–H	1.65 s, sp	1.10 vs, b
$[CoA(NO_2)_2]ClO_4$	. . .	3.13 m, sp	1.40 s	$\nu_{asy}(NO_2)$		
			1.38 m			
			1.32 s, sp	$\nu_{sy}(NO_2)$	1.65 s, sp	1.09 vs, b
			0.83	$\delta(NO_2)$		
			0.82			
$[CoA(CN)_2]ClO_4$	. . .	3.15 m, sp	2.12 m, sp	$\nu_{C=N}$	1.66 s, sp	1.10 vs, b
$[CoA(N_3)_2]ClO_4$	. . .	3.20 s, sp	2.06 vs, sh	ν_{N-N}	1.65 s, sp	1.10 vs, b
			2.03 vs, sp			1.08 s
$[CoA(NCS)_2]_2(ClO_4)(SCN)$	. . .	3.18 w, sh	2.12 vs	Coordinated		1.12
				C=N	1.66 s, sp	1.10 vs, b
		3.10 m, sp	2.06 vs	Ionic C=N		1.08
			2.04 vs			
$[CoA(NCS)_2]SCN$	3.50 w, b	3.10 m, b	2.13 vs	Coordinated		
				C=N	1.66 s, sp	Absent
			2.05 vs			
			2.04	Ionic C=N		
$[Co(teta)(OH_2)_2](ClO_4)_3$	3.55 s, b	3.23 s, sp	1.62 m, b	O–H		1.10 s, b
	1.62 w, sh	3.19 w, sh				
$[Co(teta)(CN)_2]ClO_4 \cdot H_2O$	3.62 m, b	3.22 s, sp	2.14 s, sp		2.14 s, sp	1.10 s, b
	1.62 m, sp	3.19 m, sp				
		3.17 m, sp				

[a] A = $C_{16}H_{32}N_4$; s, strong; w, weak; m, medium; sh, shoulder; sp, sharp; b, broad. [b] Ligand frequencies of the carbonate ligand are assigned using the notation of Nakamoto.[30] ν_2 is obscured by ClO_4^- in $[CoACO_3]ClO_4$.

Co^{III}(teta)L$_2$ complexes (see Table I). Differences of more than 40 cm^{-1} are often observed in ν_{N-H} frequencies between different salts of the same complex amine.[30] Although we have observed less than 10 cm^{-1} variation in the ν_{N-H} for $[CoACl_2]ClO_4$ and $[CoACl_2]Cl$, the differences in ν_{N-H} for the various Co^{III}AL$_2$ complexes in Table I as well as the 40 cm^{-1} difference between ν_{N-H} for Co^{III}AL$_2$ and Co^{III}(teta)L$_2$ complexes may result from different local environments of the N–H groups in these several complexes.

The infrared spectra of $[CoACO_3]ClO_4$ and $[CoACO_3]Cl$ (Figure 4 and Table I) indicate that the CO_3^{2-} group functions as a bidentate ligand.[16,29] We have assigned to the CO_3^{2-} ligand vibrations those relatively intense broad bands which occur in the spectrum of $[CoACO_3]Cl$ but not in the spectrum of [Co(Aa)Cl$_2$]Cl. Both of the CO stretching absorptions, ν_1 and ν_2, appear at higher frequencies in the spectrum of $[CoACO_3]Cl$ than in the spectrum of $[Co(en)_2CO_3]Cl$, whereas the ligand deformation and combination frequencies are very similar in the two compounds. There is some ambiguity in the assignments of the CO stretch, ν_2, and the deformation frequency, ν_5, since the macrocyclic ligand also absorbs strongly in these regions. The deformation band is particularly difficult to assign since the spectrum of $[CoACO_3]ClO_4$ (Figure 4) exhibits two strong broad bands in this region (at 1220 and 1280 cm^{-1}, respectively) which appear to have combined into one band (at 1260 cm^{-1}) in $[CoACO_3]Cl$. The ligand absorptions which appear at 1230, 1255, and 1290 cm^{-1} for [Co(Aa)Cl$_2$]ClO$_4$ either have been shifted sufficiently in $[CoACO_3]ClO_4$ that they are obscured by the new bands at 1220 and 1280 cm^{-1}, or those particular ligand bands do not occur in the latter complex. The skeletal vibrations of the macrocyclic ligand (in the 750–1400 cm^{-1} region) are quite important as they should reflect any important changes in the geometry of the macrocycle. If one compares the spectrum of $[CoACO_3]X$ (for X = Cl or ClO$_4$, Figure 4) with the spectrum of the [Co(Aa)Cl$_2$]X complex derived from it (Figures 1 and 2), there are striking differences even when the probable CO_3^{2-} absorptions are eliminated from consideration. The bands which occur at 780, 990, 1115, 1250, and 1405 cm^{-1} in the [Co(Aa)Cl$_2$]X spectra do not appear (or are too weak to be observed) in the corresponding $[CoACO_3]X$ spectra. Many bands which appear to be similar in both spectra are slightly shifted; *e.g.*, absorptions which occur at 830, 950, 1015, 1035, 1160, 1170, and 1360 cm^{-1} in [Co(Aa)Cl$_2$]ClO$_4$ appear at 845, 960, 1015, 1030, 1155, 1170, and 1345 cm^{-1} in $[CoACO_3]ClO_4$. These several differences and similarities between the spectra of $[CoACO_3]X$ and [Co(Aa)Cl$_2$]X in the 750–1400 cm^{-1} region are at least consistent with our suggestion that the macrocycle is folded in the case of $[CoACO_3]X$, whereas the nitrogen

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(30) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

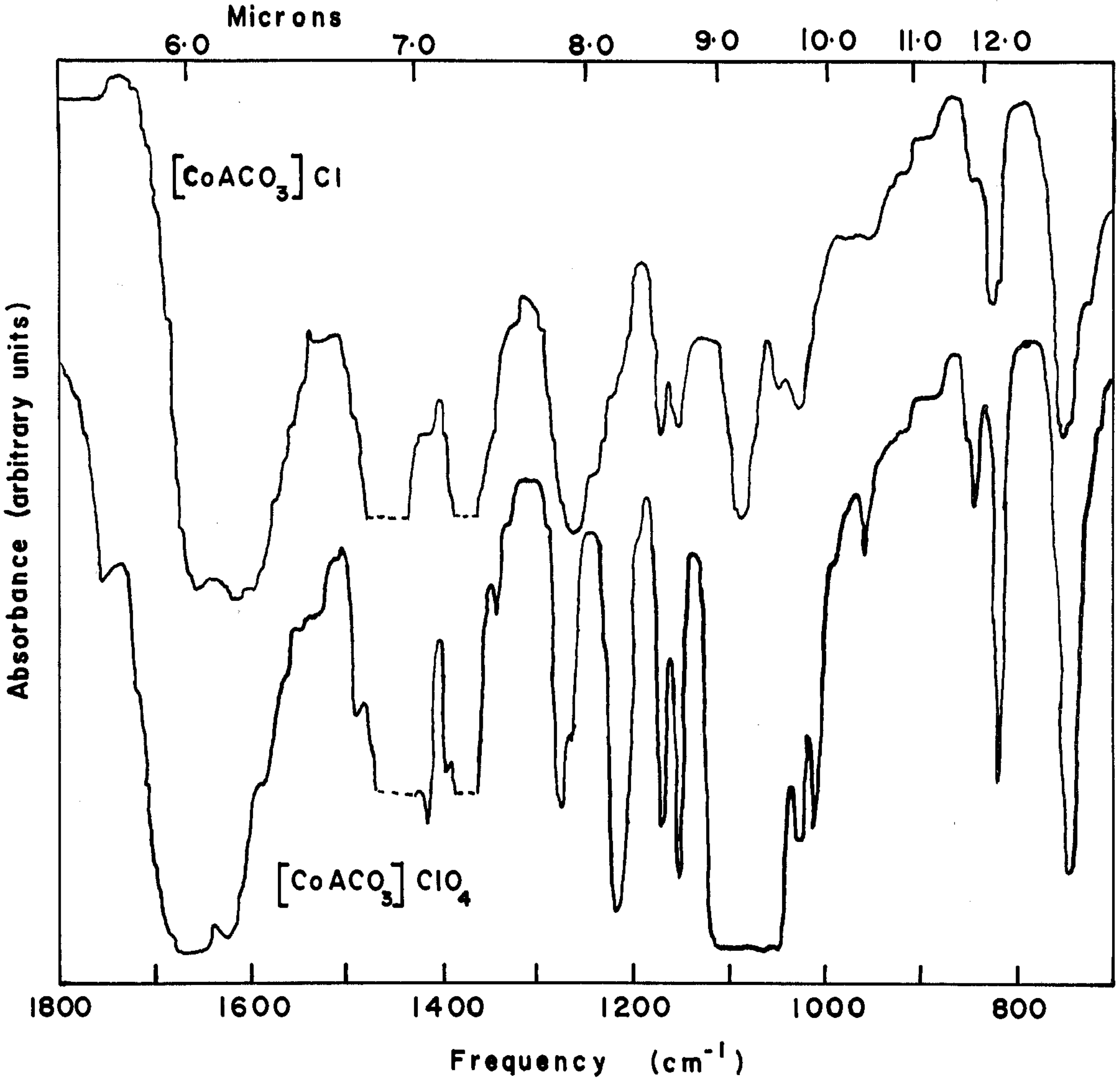

Figure 4.—Infrared spectra of [CoACO$_3$]ClO$_4$ and [CoACO$_3$]Cl. Spectra were determined in Nujol mulls and spectral regions obscured by Nujol absorptions are indicated with a broken line (– – – –).

atoms of the ligand lie in the same plane for the other Co^{III}AL$_2$ complexes. Thus some (but not necessarily all) of the skeletal vibrations of the folded ligand must be different from the skeletal vibrations of the "flat" ligand, while at least some of the C–H deformation frequencies should be very little changed when the ligand is folded. It is to be noted that Curtis has previously prepared a Ni^{II}A complex in which the macrocyclic ligand was folded.[31]

It is quite interesting that the high-energy CO stretching frequency, ν_1, for [CoACO$_3$]ClO$_4$, [Co(en)$_2$CO$_3$]ClO$_4$, and [Co(tet*b*)CO$_3$]ClO$_4$ occurs at 1665, 1643, and 1597 cm^{-1}, respectively. This trend may parallel a variation in the strength of the Co^{III}CO$_3$ bond,[29,32] but this is by no means certain since the broadness of the bands and the superposition of other absorptions ($\nu_{C=N}$ in the case of [CoACO$_3$]ClO$_4$) make it difficult to assign comparable vibrations accurately.

The infrared spectra of [Co(A*a*)Cl$_2$X] and [Co(A*b*)Cl$_2$]X (for X = Cl or ClO$_4$) are very similar. There are several ligand absorption bands which are relatively more intense in [Co(A*a*)Cl$_2$]X than in [Co(A*b*)Cl$_2$]X, most notably in the 900–1100 cm^{-1} region. The infrared spectra of the [CuAα](ClO$_4$)$_2$ and [CuAβ](ClO$_4$)$_2$ complexes also differ greatly in the 900–1100 cm^{-1} region.[21,26,33]

The evidence for the isothiocyanato structure of CoA(NCS)$_2^+$ is obtained from the observed C–N frequencies.[34,35] The more sensitive C–S[29,35] frequency is not very useful in this case because of the many ligand absorptions which occur in the 700–900 cm^{-1} region. Bonding to nitrogen is to be expected in the case of Co(III).[36]

(C) **Visible and Ultraviolet Absorption Spectra.**—The wavenumbers and extinction coefficients of the visible and ultraviolet absorption maxima of the

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(31) N. F. Curtis, *J. Chem. Soc.*, 4109 (1963).

(32) B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *ibid.*, 3137 (1958).

(33) N. F. Curtis, private communication.

(34) M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 6412 (1959).

(35) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(36) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

TABLE II

VISIBLE–ULTRAVIOLET ABSORPTION SPECTRAL DATA IN AQUEOUS SOLUTION
(Room temperature, molar extinction coefficients in parentheses)

	Band maxima (units of 10^3 cm^{-1})				
	Metal Atom			Charge transfer	
Compound[a]	IA	IB	II		
$CoACl_2^+$ [b]	16.7 (30)	23.8 sh[c]	32.3 sh		45.4 (1.6×10^4)
$CoACl_2^+$ [b,d]	17.3 (27)	24.2 sh	39.0 sh		44.0 (1.9×10^4)
$CoABr_2^+$ [e]	16.0 (45)	27.4 sh	36.3 sh	~39.6	
$CoA(OH_2)_2^{3+}$ [f]	17.2 (27)	23.2 sh	Masked	Not determined	
$CoA(OH)_2^+$ [g]	19.2 (40)	26.6 (52)	Masked	Not determined	
$CoA(N_3)_2^+$	18.2 (450)		Masked	29.2 (1.6×10^4)	46.4 (4.0×10^4)
$CoA(NCS)_2^+$	19.5 (320)		29.4 (3.1×10^3)[h]		46.5 (5.2×10^4)
$CoA(NO_2)_2^+$	22.7 (135)		29.2 (1.9×10^3)[h]	40.6 (1.5×10^4)	47.2 (1.9×10^4)
$CoA(CN)_2^+$	24.4 (90)				47.7 (4.2×10^4)
$CoACO_3^+$	20.0 (121)		28.6 (135)	41.2 (1.6×10^4)	~52 (~10^4)
Co(tet*a*)$(OH_2)_2^{3+}$ [f]	17.7 (36.4)	22.3 sh	38.9 (4.0×10^3)[h]		<50(>10^4)
Co(tet*a*)$(OH)_2^+$ [g]	18.7 (47.5)	25.1 (71.8)	40 sh[h]		<50(>10^4)
Co(tet*b*)$(OH_2)_2^{3+}$ [f]	17.1 (~35)	21.3 sh	39.7 (~4×10^3)[h]		<50(<10^4)

[a] A = $C_{16}H_{32}N_4$; all complexes are derived from the *a* isomer of $[CoACl_2]ClO_4$, except as indicated. [b] Determined in 0.1 *M* HCl. sh, shoulder. [d] The *b* isomer of $[CoACl_2]ClO_4$. [e] Determined in 0.1 *M* HBr. [f] Determined in 1.0 *M* $HClO_4$. [g] Determined at pH [c]11. [h] Assignment as a metal transition is uncertain.

$Co^{III}AL_2$ complexes which we have prepared are presented in Table II. Since the spectra of several of these complexes exhibit the three low-intensity absorption bands in the visible and near-ultraviolet spectral regions which are characteristic of *trans*-$Co^{III}Am_4L_2$ (where Am represents any amine nitrogen atom) complexes,[5,37-39] we have assigned these three transitions to the metal atom, labeling the bands IA, IB, and II according to the convention of Linhard and Weigel.[37] It is to be noted that the absorption spectra of the two $CoACl_2^+$ complexes are very similar to the spectrum of *trans*-$Co(en)_2Cl_2^+$ [37-39] in that these spectra all exhibit three low-intensity bands in the visible and near-ultraviolet regions. The spectra of the $CoACl_2^+$ complexes differ somewhat from the spectrum of *trans*-$Co(en)_2Cl_2^+$ in the following ways: (1) the difference in energy between the IA and IB bands is greater in the former complexes (~7 × 10^3 cm^{-1} compared to 6.4 × 10^3 cm^{-1}), (2) the near-ultraviolet transitions are more intense in the case of $CoACl_2^+$ complexes so that the IB and II bands cannot be completely resolved, and (3) the IA band of $CoACl_2^+$ is asymmetric (Figure 5). It has been noted[18] that there is an allowed transition characteristic of the C=N group which occurs at about 40 × 10^3 cm^{-1}. This C=N transition appears to be masked in the $Co^{III}AL_2$ complexes by the more intense ligand-to-metal charge-transfer transitions in the same spectral region.[40]

The fact that the low-energy metal absorption band, assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition,[39,41,42] splits into two components ($^1A_{1g} \rightarrow {}^1E_g{}^a$ and $^1A_{1g} \rightarrow {}^1A_{2g}$, respectively)[39,42] for $CoACl_2^+$, $CoABr_2^+$, and $CoA(OH_2)_2^{3+}$ while only one band (of relatively high intensity) can be resolved in this spectral region for $CoA(NCS)_2^+$, $CoA(NO_2)_2^+$, $CoA(CN)_2^+$, and $CoA(N_3)_2^+$ is typical of the spectra of the corresponding *trans*-$Co^{III}Am_4L_2$ complexes.[5,37-39,42,43] Spectral data for $CoACO_3^+$ have been reported previously[21] but are included in Table II for purposes of ready comparison. The visible spectrum of $CoACO_3^+$ is similar to the spectrum of $Co(en)_2CO_3^+$.[44]

A simple crystal field model for analyzing the spectra of *trans*-$Co^{III}Am_4L_2$ complexes has recently been proposed by Wentworth and Piper.[42] According to this model the splitting of the $^1T_{1g}$ state in a tetragonally distorted octahedral field (*i.e.*, a descent in symmetry from O_h to D_{4h}) is given by the single splitting parameter *Dt*. This parameter, *Dt*, may be approximated by *Dt'*, where $Dt' = {}^4/_{35}[W - (10Dq - C)_{xy}]$ and *W* is the energy of the $^1A_{1g} \rightarrow {}^1E_g{}^a$ transition. In the treatment of Wentworth and Piper, $(10Dq - C)_{xy}$ is taken from the energy of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the octahedral complex, $Co^{III}Am_6$. In the case of the $Co^{III}AL_2$ complexes which we have prepared, the macrocyclic ligand may be regarded as presenting an average field in the *x,y* plane; but there is no corresponding octahedral complex from which we can obtain an appropriate value of $(10Dq - C)_{xy}$. Wentworth and Piper observed that the electronic repulsion term, *C*, had a value of about 3800 cm^{-1} independent of the ligands L or Am, and they also noted that for a complex of the type *trans*-$Co^{III}Am_4L_2$ $Dt = {}^4/_7(Dq^{xy} - Dq^{z+})$, where Dq^{xy} and Dq^{z+} are the values of *Dq* for the respective octahedral complexes, $Co^{III}Am_6$ and $Co^{III}L_6$. Thus it is possible to calculate an appropriate average value of Dq^{xy} for a cyclic ligand provided the IA and IB bands are clearly resolved. The crystal field splitting parameters Dq'^{xy} and *Dt'* for several cyclic amine ligands are

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(37) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **264**, 321 (1951); *ibid.*, **267**, 113, 121 (1951).

(38) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(39) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

(40) Note that spectra of both Co(tet*a*)$(OH_2)_2^{3+}$ and Co(tet*b*)$_2^{3+}$ exhibit absorption maxima, assigned tentatively to band II of the metal, in this region, despite the fact that neither the tet*a* nor tet*b* ligand contains a C=N group. Some of the intensity of the maximum at ~40 × 10^3 cm^{-1} for these two complexes results from the fact that this band is superimposed on the side of a very intense charge-transfer band.

(41) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(42) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(43) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(44) G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

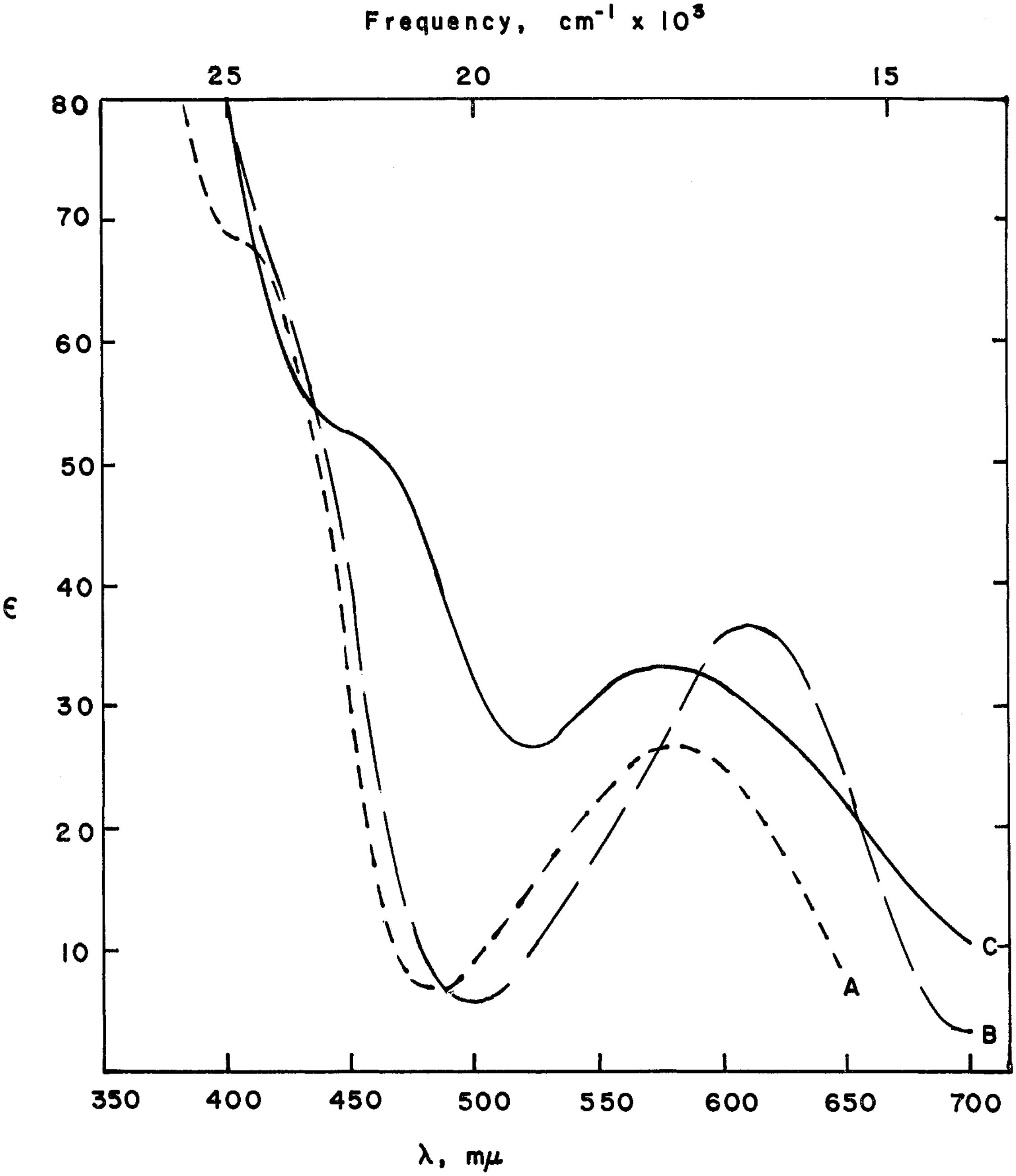

Figure 5.—Visible absorption spectra of (A) $CoA(OH_2)_2^{3+}$, (B) $Co(Aa)Cl_2^+$, and (C) $Co(teta)(OH_2)_2^{3+}$ determined in aqueous solution.

compared in Table III to the Dq'^{xy} and Dt' values for *trans*-$Co(en)_2Cl_2^+$ and *trans*-$Co(NH_3)_4Cl_2^+$ as determined by Wentworth and Piper.[42] It is significant that the approximate crystal field strengths (as reflected in Dq' values in Table III) place all the amine ligands together in a group, whereas the Dq' value for the macrocyclic Schiff base ligand, A, is higher.[45] The several amine ligands considered in Table III may be arranged in decreasing order of crystal field strength: A > en ~ teta ~ tet*b* ~ cyclam ~ NH_3. Since the Dq' values in Table III represent an average of the crystal field strengths of the two different kinds of nitrogen atoms of the macrocyclic ligand A, it seems reasonable to conclude that the secondary amine nitrogen atoms interact less strongly with the Co(III) center than do the imine nitrogens. Thus, the imine nitrogens of the macrocyclic Schiff base ligand must have a crystal field strength intermediate between NH_3 and NO_2^-.

There are a few additional points concerning interpretation of the visible spectra of the $Co^{III}AL_2$ complexes which deserve comment. We have not found a consistent means for estimating Dt for the $Co^{III}AL_2$ complexes in which the IA and IB bands are not resolved. Neither of the two simple approximations[46]

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[45] Note that if it is assumed there is only a negligible shift in the energy of the $^1A_{2g}$ state (with respect to the original $^1T_{1g}$ state of the "corresponding octahedral complex")[43] then the energy of the $^1A_{1g} \longrightarrow {}^1A_{2g}$ transition should be approximately equal to $(10Dq - C)^{xy}$ and Dq'^{xy} for the ligand A would be ~2900 cm^{-1}.

[46] These are (1) that the energy of the observed band maximum can be taken to be a simple average of the energy of the $^1T_{1g}$ band of the parent compound (*i.e.*, $Co^{III}Am_6$) and the energy of the $^1E_g{}^a$ state above the ground state, or (2) that the energy of the $^1A_{1g} \longrightarrow {}^1E_g{}^a$ transition may be simply equated with the energy of the maximum of the unresolved band.[43]

TABLE III

APPROXIMATE CRYSTAL FIELD SPLITTING PARAMETERS FOR SEVERAL *trans*-Co^{III}(CYCLIC AMINE)L_2 COMPLEXES

Ligand	Complex	Dq'^{xy}, cm^{-1}	Dt', cm^{-1} [a]
A (*a* isomer)	$Co(Aa)Cl_2^+$ [b]	2640	674
	$CoABr_2^+$ [b]	2680	802
A (*b* isomer)	$Co(Ab)Cl_2^+$ [b]	2760	743
cyclam	$Co(cyclam)Cl_2^+$ [c]	2480	594
tet*a*	$Co(teta)Cl_2^+$ [d]	2440	560
	$Co(teta)Br_2^+$ [d]	2520	708
tet*b*	$Co(tetb)Cl_2^+$ [d]	2400	536
	$Co(tetb)Br_2^+$ [d]	2520	708
en	$Co(en)_2Cl_2^+$	2530[e]	612[e]
NH_3	$Co(NH_3)_4Cl_2^+$	2490[e]	588[e]

[a] Calculated using the crystal field model of Wentworth and Piper[42] assuming that $Dq^{z+} = 1459$ cm^{-1} for Cl^-, $Dq^{z+} = 1277$ cm^{-1} for Br^-, and that $C = 3800$ cm^{-1}. [b] Using as the energy of the ${}^1A_{1g} \rightarrow E_g{}^a$ transition the wavenumber of band IA in Table II. [c] Using data reported in ref 5. For the three complexes *trans*-$Co(cyclam)(NO_2)_2^+$, *trans*-$Co(cyclam)(NCS)_2^+$, and *trans*-$Co(cyclam)(N_3)_2^+$, the IA and IB bands are not resolved (the low-energy absorption occurring at 21.7, 19.2, and 17.4 cm^{-1}, respectively);[5] using the first approximation suggested by Wentworth and Piper[42] we estimate Dq'^{xy} for these complexes as 2690, 2140, and 2410, respectively (av $Dq'^{xy} = (2410 \pm 170)$ cm^{-1}). [d] We have determined that in acetone solution the IA bands of $Co(teta)Cl_2^+$ and $Co(teta)Br_2^+$ occur at 15.7 and 15.2 cm^{-1}, respectively; the IA bands of $Co(tetb)Cl_2^+$ and $Co(tetb)Br_2^+$ occur at 15.5 and 15.2 cm^{-1}, respectively. [e] Value obtained by Wentworth and Piper.[42]

considered by Wentworth and Piper[42] works well with those $Co^{III}AL_2$ complexes in which the IA and IB bands are unresolved, despite the fact that the first approximation appears to work very well for simple amine complexes.[42,47] The failure of this simple approximation for the $Co^{III}AL_2$ complexes may be a result of the lower symmetry (D_{2h} rather than D_{4h}) in these cases since this may result in a partial removal of the degeneracy of the ${}^1E_g{}^a$ state. It has been noted above that even for those complexes whose absorption spectra exhibit resolved IA and IB absorption bands, the IA bands are often asymmetric (Figure 5). Thus the IA bands of these complexes may be more complex than would be the case if they corresponded to a pure ${}^1A_{1g} \rightarrow {}^1E_g{}^a$ transition.

A surprising feature of the spectra of the $Co^{III}AL_2$ complexes is that water appears to have about the same crystal field strength as chloride.[48] It is also to be noted that the IA and IB bands of $CoA(OH)_2^+$ and $Co(teta)(OH)_2^+$ appear to be resolved, whereas the spectrum of *trans*-$Co(en)_2(OH)_2^+$ exhibits only I (unresolved) and II bands.[40] If one assumes the Dq^{xy} values calculated in Table III for the A and tet*a* ligands, then Dq'^{z+} for OH^- in $CoA(OH)_2^+$ is 1940 cm^{-1} and Dq'^{z+} for OH^- in $Co(teta)(OH)_2^+$ is 2000 cm^{-1}. This is an exceptionally large crystal field strength for OH^-,[49] and is to be contrasted to the apparently low crystal field strength of OH_2 in $CoA(OH_2)_2^{3+}$. This reversal of the usual order of OH^- and OH_2 in the spectrochemical series[39] is most unexpected, and we are examining the chemistry of these systems in order to gain further insight into the reasons for this behavior.

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(47) This approximation also works well for the $Co^{III}(cyclam)L_2$ complexes. See note *c* in Table III.

(48) Note the similar energies of the IA bands of the chloro and aquo complexes (Table II and Figure 5). Assuming $Dq^{xy} = 2660$ cm^{-1}, as found in Table III, we find $Dq^{z+} = 1540$ cm^{-1} for H_2O in $CoA(OH_2)_2^{3+}$. This is to be compared to $Dq^{z+} = 1875$ for H_2O in *trans*-$Co(en)_2(OH_2)_2^{3+}$.[42]

(49) Using Wentworth and Piper's first approximation[46] we estimate Dq'^{z+} for OH^- in $Co(en)_2(OH)_2^+$ to be 1650 cm^{-1} and in $Co(NH_3)_5OH^{2+}$ to be 1500 cm^{-1}.