Inorg. Chem. **1980**, *19*, 2812–2816

for the detailed band structures observed in 4f–4f chiroptical spectra. Despite the qualitative nature of the treatment given here, the selection rules and classification schemes given in Tables II–IV should prove useful in identifying those lanthanide transitions most suitable as diagnostic chiroptical probes.

How easily a transition may be studied by absorption/CD measurements is determined by two criteria: (1) the magnitude of the rotatory strength of the transition; and (2) the dissymmetry factor of the transition. In section IIIB, we identified three transition types which are predicted to satisfy these dual criteria. These transition types are 1, 2, and 9, with each satisfying the selection rule $|\Delta J| \leq 1$ (excluding $J = J' = 0$). We designate transitions belonging to any one of these three types as "CD-sensitive" transitions. Another transition type of special interest is type 10. Although the rotatory strengths of transitions belonging to type 10 are predicted to be relatively small in magnitude, the dissymmetry factors associated with these transitions are predicted to be very large. Additionally, type 10 transitions are predicted to be very sensitive to crystal field effects (via V_g and V_u). We shall also designate the type 10 transitions as "CD-sensitive".

All of the transitions listed in Table V are of type 1 and are categorized, therefore, as "CD-sensitive". No CD measurements have been reported for any of these transitions, although they are predicted to have large rotatory strengths and reasonably large dissymmetry factors. Many of these transitions are accessible to study by existing infrared CD spectrophotometers. Some additional examples of transitions predicted to be "CD-sensitive" are given in Table VI (type 9) and in Table VII (types 9, 10).

In our CPL studies of Eu^{3+} complexes in solution,[9–14] the CPL (ΔI) intensities of the $^7F_1 \leftarrow {}^5D_0$ and $^7F_2 \leftarrow {}^5D_0$ transitions are invariably found to be roughly comparable, with the $^7F_1 \leftarrow {}^5D_0$ CPL showing the greater sensitivity to changes in the ligand environment. On the other hand, $g_{\mathrm{lum}}(^7F_1 \leftarrow {}^5D_0)$ is always observed to be about an order-of-magnitude larger (in absolute magnitude) than $g_{\mathrm{lum}}(^7F_2 \leftarrow {}^5D_0)$. Similarly in absorption/CD studies, the $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_2$ transitions exhibit comparable CD intensities ($\Delta\epsilon$) while $g_{\mathrm{abs}}(^7F_0 \rightarrow {}^5D_1)$ is generally found to be about 10 times larger than $g_{\mathrm{abs}}(^7F_0 \rightarrow {}^5D_2)$. It is quite common to observe dissymmetry factors $|g| > 0.3$ for the Eu^{3+} $^7F_0 \rightarrow {}^5D_1$ and $^7F_1 \leftarrow {}^5D_0$ transitions—values which are *extraordinarily* large for *any* optically active system. These results are in complete agreement with our classification of the $^7F_{0(1)} \rightleftarrows {}^5D_{1(0)}$ transitions as (RIII, DI) and our classification of the $^7F_{0(2)} \leftrightarrow {}^5D_{2(0)}$ transitions as (RIII, DIII).

CPL results on Tb^{3+} complexes in solution[9,10,14–17] are also in complete qualitative agreement with predictions based on the classifications of Table VII. The largest dissymmetry factors are observed within the predicted "CD-sensitive" transitions, $^7F_5$, $^7F_4$, and $^7F_3 \leftarrow {}^5D_4$. More quantitatively, the $^7F_5 \leftarrow {}^5D_4$, dissymmetry factors (and CPL intensities) are generally observed to be 3–10 times greater than those observed for the $^7F_4$ and $^7F_3 \leftarrow {}^5D_4$ transitions. These quantitative differences cannot be explained on the basis of the selection rules developed in the present study. However, they *are* explicable in a rather straightforward way when the details of crystal field induced *J*-level mixings are taken into account.[28]

Sen, Bera, and Chowdhury[3] have reported rotatory strengths and dissymmetry factors for the $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, and $^3P_0$ transitions of Pr^{3+} in crystalline $Na_3[Pr(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$. The rotatory strengths are moderately large ($(\sim 1\text{–}3) \times 10^{-42}$ esu² cm²), but the dissymmetry factors are relatively small ($(\sim 1\text{–}25) \times 10^{-3}$ esu² cm²). Each of these transitions belongs to our classes RII and DIII (see Table VI). For Eu^{3+} in the same crystalline host, we have obtained the results[30]

transitions	$^7F_0 \rightarrow {}^5D_1$	$^7F_0 \rightarrow {}^5D_2$
rotatory strength	0.17×10^{-42} esu² cm²	0.12×10^{-42} esu² cm²
dissymmetry factor	0.38	0.061
classifications	RIII, DI	RIII, DIII

These results further support the qualitative correctness of the classification schemes given in Table IV.

The transition types most commonly found to be hypersensitive in absorption are 5, 6, 11, and 12, with the restriction that $|\Delta J| = 2$. We note from Table IV that each of these transition types falls in the dissymmetry factor DIII class and in either the RII or RIII rotatory strength class. From this it may be concluded that the 4f–4f hypersensitive transitions will not, in general, be the most favorable chiroptical probe transitions.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE77-02150) and the Camille and Henry Dreyfus Foundation (through a Teacher-Scholar Award to F.S.R.).

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(30) Morley, J.; Banerjee, A.; Schwartz, R. W.; Richardson, F. S., unpublished results.

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Additivity of d–d Circular Dichroism in Discrimination between the Cis-α and Cis-β Modes of Wrapping of Substituted Triethylenetetramines in Cobalt(III) Complexes

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When solutions of *cis-α* and *cis-β*-(carbonato) and *cis-α*- and *cis-β*-dinitro complexes of (triethylenetetramine)cobalt(III) in 3 M *d*-tartaric acid were heated for a 2-h period, intense CD spectra developed in the visible region. The CD spectra of the β complexes were nearly identical with each other but were dramatically different from those of the α complexes. The same results extended to vicinal effects (calculated from a CD additivity rule) obtained for Λ-α- and Δ-β-(carbonato)- and Λ-α- and Δ-β-dinitrocobalt(III) complexes of the substituted tetraamines (2*S*,9*S*)-2,9-diamino-4,7-diazadecane and (3*S*,10*S*)-3,10-diamino-5,8-diaza-2,11-dimethyldodecane in *d*- and *l*-tartaric acids.

Introduction

The recent work of Schipper has provided a firm theoretical foundation for additivity in circular dichroism of the d–d transitions of chiral complexes.[1] The simplest example of an additivity rule is as follows: consider a complex, AB_1B_2 (composite complex), with two chiral centers, B_1 and B_2, and

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(1) Schipper, P. E. *J. Am. Chem. Soc.* **1978**, *100*, 1433.

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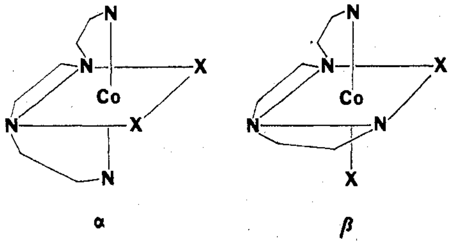

Figure 1. Two cis structures of (triethylenetetramine)cobalt(III) complexes: cis-α and cis-β.

an achiral metal-centered chromophore, A, on which the d–d transitions are localized. If the complexes AB_1, AB_2 (substituent complexes) have the same achiral chromophore as the composite complex and B_1 and B_2 have the same configurational relationship to A in the composite and substituent complexes, then the d–d CD of the composite complex AB_1B_2 is simply the sum of that of the substituent complexes AB_1, AB_2. A common manifestation of this rule has been demonstrated in the near additivity of the configurational and vicinal effects observed for amino acid complexes of tetraaminocobalt(III) moieties.[2,3]

Additivity rules can be used to add to our ability to abstract structural information from CD spectra. For instance, additivity has been used to reveal the chirality of bound, optically active amino acids and to reveal whether they are bound in a β_1 or β_2 fashion.[3] Additivity of induced CD has been used to determine the population of rotational isomers of the chiral D-malate ion in a solution containing Λ-[tris(ethylenediamine)cobalt(III)](3+).[4]

One condition inherent in the above description is that in order for additivity to hold the achiral chromophore must remain constant. This is equivalent to the statement that the vicinal effect of a chiral ligand is dependent upon the nature of and should be sensitive to variations in the achiral chromophore. Figure 1 shows the two cis conformations that a tetraamine may adopt about cobalt(III): α with three noncoplanar chelate rings and β with two coplanar rings. A chiral ligand bridging the cis positions will be exposed to a different achiral chromophore in the α and β complexes. The question to be answered is whether or not this difference in the achiral chromophore is large enough to give a significant difference in vicinal effect between the α and β cases, i.e., whether the observed vicinal effect differences can show utility as a characterization technique. In the present effort we wish to extend the scope of d–d CD additivity, to tetraamine complexes containing achiral but acid labile groups (e.g., XX in Figure 1 is $(NO_2^-)_2$ or CO_3^{2-}), by examination of the vicinal effects created upon displacement of these groups in an optically active acid solvent.

Experimental Section

l-Tartaric acid was purchased from Alrich Chemical Co.

The following compounds were synthesized according to literature procedures:[5] α-dinitro(trien)cobalt(III) chloride monohydrate (**1**)[6] β-dinitro(trien)cobalt(III) perchlorate (**2**),[6] α-(carbonato)(trien)cobalt(III) perchlorate monohydrate (**7**),[6] β-(carbonato)(trien)cobalt(III) chloride sesquihydrate (**8**),[6] $\Lambda(-)_{436}$-α-dinitro(dmt)cobalt(III) chloride hydrate (**3**),[7] $\Delta(+)_{436}$-β-dinitro(dmt)cobalt(III) perchlorate (**4**),[7] $\Lambda(-)_{436}$-β-dinitro(dipt)cobalt(III) perchlorate (**5**).[7] $\Delta(+)_{436}$-β-Dinitro(dipt)cobalt(III) perchlorate (**6**) was prepared according to the synthesis of **4**.[7]

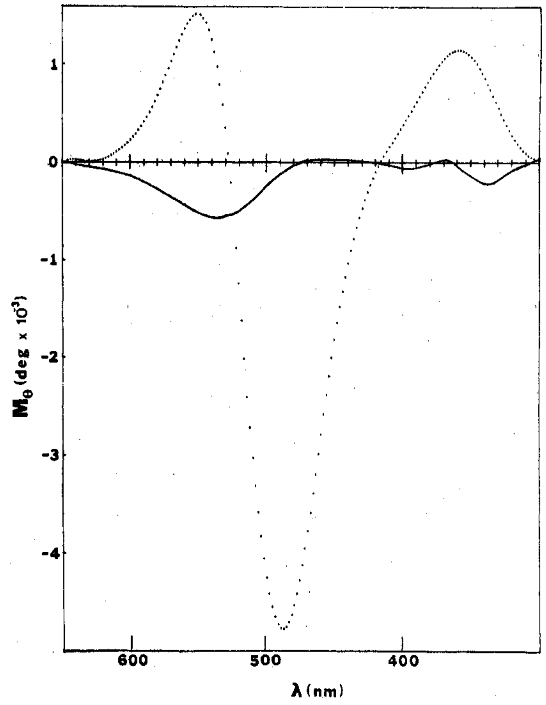

Figure 2. CD spectra of $[(trien)Co(NO_2)_2]^+$ complexes after 2 h at 80 °C in 3.0 M *d*-tartaric acid: (–) cis-α; (···) cis-β.

Compound **9** was prepared from $\Lambda(-)_{436}$-α-dichloro(trien)cobalt(III) chloride[7] under the exact conditions used to prepare compound **7** and as a result of the present study has been shown to be the analogous Λ-α-(carbonato)(dmt)cobalt(III) complex. Compound **10** was prepared as the perchlorate salt under the exact conditions used to synthesize compound **8**; however, its solubility was greater than that of **8** and approximately 40% of the product proved to be colorless NaCl crystals. The results of the present study indicate **10** to be Δ-β-(carbonato)(dmt)cobalt(III) perchlorate (homologous to compound **8**).

CD spectra were obtained on a Cary 61 spectropolarimeter. Solutions of the racemic compounds **1**, **2**, **7**, and **8** were prepared at concentrations of 2–3 mM, by dissolving the weighed crystals in 3.0 M *d*-tartaric acid. Two sets of solutions of the optically active compounds **3**, **4**, **5**, **6**, **9**, and **10** were prepared, at concentrations of 2–3 mM, by dissolving the weighed crystals in both 3.0 M *d*-tartaric acid and 3.0 M *l*-tartaric acid. The sample solutions were heated at 80 °C for 2 h and then cooled in cold water to room temperature, and the CD spectra were obtained. The color of the dinitro complexes (**1**–**6**) changed from yellow to dark pink over the 2-h period while that of the carbonato complexes (**7**–**10**) changed from light pink to dark pink after initial evolution of CO_2.

Time studies were carried out for an α complex (compound **3**) by continuing the heating up to 4.75 days at 85 °C.

Results

When the racemic compound β-$[(trien)Co(NO_2)_2]ClO_4$ (**2**) is dissolved in 3 M *d*-tartaric acid, no significant CD is observed in the visible region. However, when the solution was heated at 80 °C, a CD spectrum with considerable character begins to develop culminating in that of Figure 2 after a 2-h period. This CD does not intensify with further heating but slowly decreases as the solution bleaches, and the compound appears to decompose over a period of several days. Because the cobalt complex is racemic, this observed CD can be thought of as the vicinal effect of *d*-tartaric acid bound in a bidentate fashion to the β-(trien)Co^{III} moiety. When α-[(trien)Co$(NO_2)_2$]Cl (**1**) is treated in the same fashion, a distinctly different CD develops, with intensity at λ_{max} only about one-seventh of that of the corresponding β complex.

Compounds **4** and **6**, containing methyl and isopropyl groups, respectively, at the 2,9 carbons of triethylenetetramine, were synthesized under the same conditions as compound **2**.

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[2] Liu, C. T.; Douglas, B. E. *Inorg. Chem.* **1964**, *3*, 1356.
[3] Job, R. *ACS Symp. Ser.* **1978**, *No. 119* and references therein.
[4] Taura, T.; Yoneda, H. *Chem Lett.* **1977**, 71.
[5] Abbreviations used in this paper: trien = triethylenetetramine; dmt = dimethyltrien = (2*S*,9*S*)-2,9-diamino-4,7-diazadecane; dipt = diisopropyltrien = (3*S*,10*S*)-3,10-diamino-5,8-diaza-2,11-dimethyldodecane.
[6] Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787.
[7] Job, R. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 809.

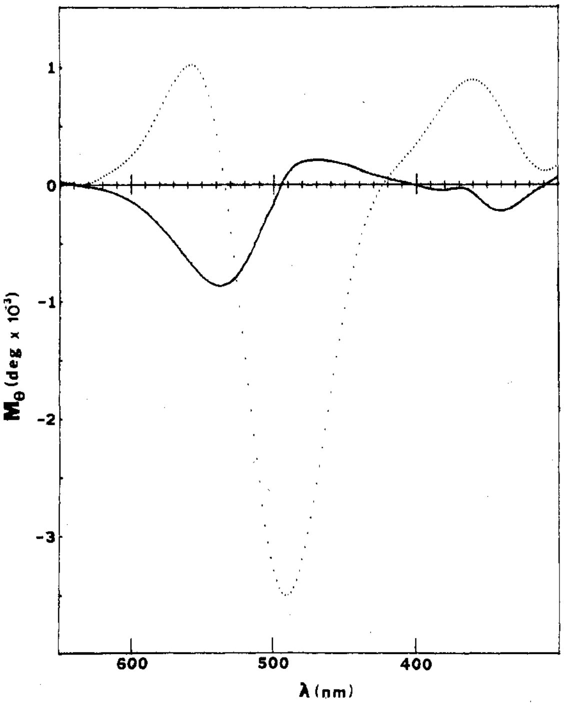

Figure 3. Calculated vicinal effects of $[(dmt)Co(NO_2)_2]^+$ complexes after 2 h at 80 °C in 3.0 M *d*- and *l*-tartaric acids: (—) **3**; (···) **4**.

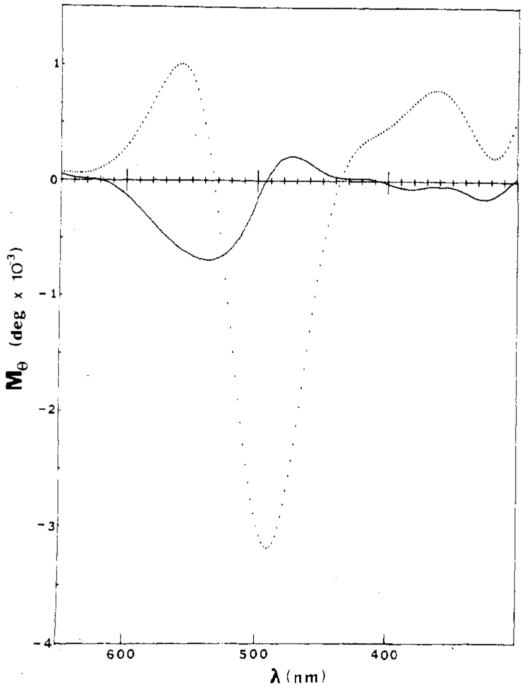

Figure 4. Calculated vicinal effects of $[(dipt)Co(NO_2)_2]^+$ complexes after 2 h at 80 °C in 3.0 M *d*- and *l*-tartaric acids: (—) **5**; (···) **6**.

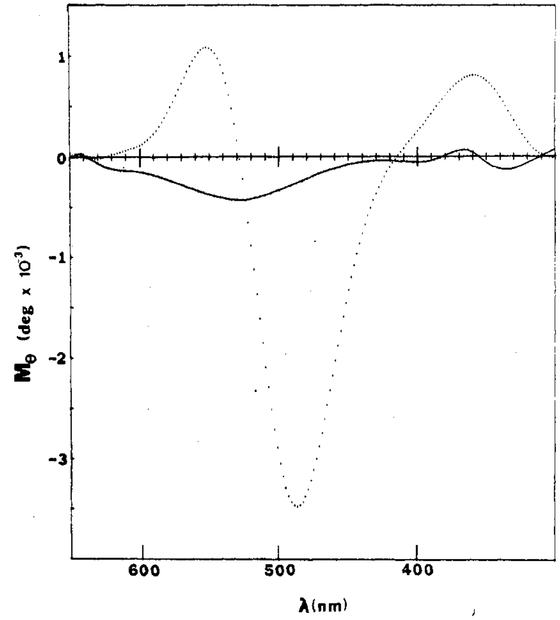

Figure 5. CD spectra of $[(trien)Co(CO_3)]^+$ complexes after 2 h at 80 °C in 3.0 M *d*-tartaric acid: (—) cis-α; (···) cis-β.

On the basis of this similarity of synthetic route, compound **4** had previously been assigned the β configuration.[7] Because of the chirality inherent in the tetraamine skeleton of compounds **4** and **6**, they each exhibit a CD spectrum irrespective of solvent. When each complex was heated in 3 M *d*-tartaric acid, a significant alteration in the CD spectra is observed. In order to determine the vicinal effect for bound tartrate in these optically active complexes, we obtained a CD spectrum under identical conditions, in *l*-tartaric acid. Application of the additivity rule then allows one to abstract the vicinal effect.

Thus AB_1 is considered to be the hypothetical substituent complex composed of the tetraamine ligand about the achiral chromophore. Consider AB_2 to be the substituent complex composed of the bidentate *d*-tartaric acid bound to the achiral chromosphore (and AB_2* the substituent complex composed of bound *l*-tartaric acid). Then eq 1 and 2 define additivity.

$$(\text{CD of } AB_1) + (\text{CD of } AB_2) = (\text{CD in } d\text{-tartrate}) \qquad (1)$$

$$(\text{CD of } AB_1) + (\text{CD of } AB_2^*) = (\text{CD in } l\text{-tartrate}) \qquad (2)$$

Since AB_2 and AB_2* are enantiomeric, their CD spectra will be equal in magnitude but opposite in sign. Subtracting eq 2 from eq 1, to eliminate the CD of AB_1, yields the results of eq 3. The vicinal effects obtained by application of the

$$\text{vicinal effect} = \text{CD of } AB_2 = \tfrac{1}{2}[(\text{CD in } d\text{-tart}) - (\text{CD in } l\text{-tart})] \qquad (3)$$

expression in eq 3 to the CD spectra of compounds **4** and **6** (after 2 h at 80 °C in 3 M *d*- and *l*-tartaric acids) are shown in Figures 3 and 4, respectively.

Complexes **3** and **5**, isomers of **4** and **6**, respectively, were prepared according to the same synthesis described for complex **1**.[6] The α configuration had been assigned to complex **3** on the basis of this similarity in synthetic route.[7] As a consequence of the previously demonstrated stereospecificity of the chiral tetraamine ligands (dmt and dipt),[7,8] the synthetic workup resulted in isolation of compounds **3** and **5** as single enantiomers. Just as for the other optically active complexes, these two compounds were treated with both *d*- and *l*-tartaric acids. The vicinal effect curves calculated by the use of eq 3 are shown in Figures 3 and 4.

The CD curves obtained upon heating the α- and β-(carbonato)(trien) complexes **7** and **8**, in 3 M *d*-tartaric acid, are shown in Figure 5. The (carbonato)(dmt) compound **9** was prepared under the same conditions as for the synthesis of known **7**. The isolated optically active product yielded the vicinal effect shown in Figure 6 after applying eq 3 to the CD's obtained in *d*- and *l*-tartaric acids. An isomeric (carbonato)(dmt) complex **10** was synthesized under the same conditions as known **8** and yielded the vicinal effect of Figure 6 when the CD data were treated as per eq 3.

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(8) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1965**, *4*, 1395.

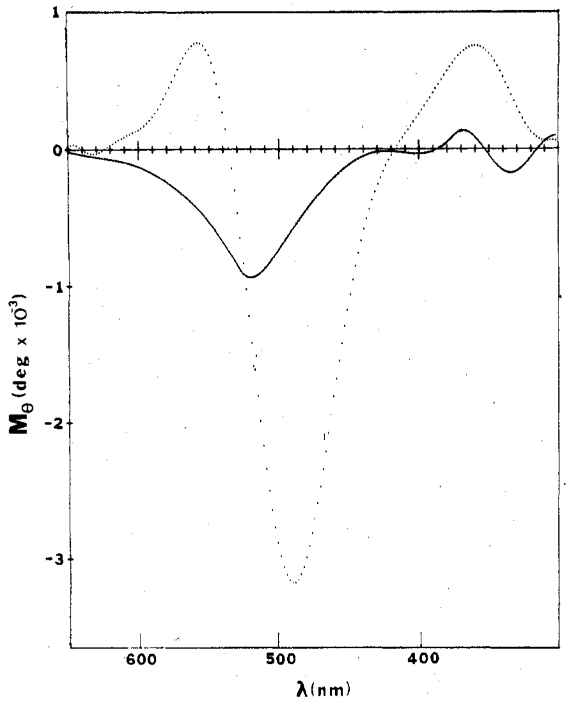


Figure 6. Calculated vicinal effects of [(dmt)Co(CO$_3$)]$^+$ complexes after 2 h at 80 °C in 3.0 M *d*- and *l*-tartaric acids: (—) **9**; (···) **10**.

Table I. Time Dependence of Vicinal Effect for a Solution of Λ-α-[(dmt)Co(NO$_2$)$_2$]$^+$ (3 × 10^{-3} M in 3 M Tartaric Acid at 85 °C) at Selected Wavelengths

	560 nm	500 nm	355 nm
2 h	−650^a	−170^a	−250^a
2.5 days	270	−1800	320
4.75 days	280	−1200	240
b	990	−3300	820

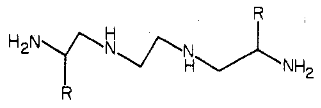
^{a} Values for molar ellipticity calculated in units of deg M^{-1} m^{-1} according to the formula $M = 100\theta/cl$ are routinely abbreviated to deg.^{9} ^{b} Values from vicinal effect for Δ-β-[(dmt)Co(NO$_2$)$_2$]$^+$ after 2 h in 3 M tartaric acid, for comparison.

As opposed to the situation for β complexes (**2**, **4**, **6**, **8**, and **10**), the vicinal effect for the α complexes (**1**, **3**, **5**, **7**, and **9**) altered significantly with time. Solutions of the α-dmt complex **3**, in both 3 M *d*-tartaric and *l*-tartaric acids, were held at 85 °C for 4.75 days. The magnitudes of the vicinal effect calculated at three wavelengths, where there exists a significant difference between the vicinal effects of the α and β complexes, are shown in Table I for three times during this heating. Values obtained for the β-dmt complex **4** after 2 h of heating are also shown in the table for comparison.

Discussion

Buckingham and Jones have shown a difference between several simple anion-substituted α- and β-(trien)Co^{III} complexes (including dinitro and carbonato complexes) in the 990–1090-cm^{-1} region of the IR spectrum.[10] A less clear differentiation was later shown to exist for α and various β-(trien)Co^{III}(amino acid) complexes in the same region of the IR spectrum.[11] However, we have found the IR spectrum of a Δ-β$_1$-(*SR*)-[(dmt)Co(amino acidate)]$^+$ complex, in the 990–1100-cm^{-1} region[12] to more closely resemble that published for an α-[(trien)Co(glycinate)]$^{2+}$ complex[11] than that for the corresponding β-trien complex. A correlation between the NMR spectra of several amino acid adducts of the Λ-*cis*-α- and Δ-*cis*-β-(dmt)Co^{III} moieties has been reported.[13] However the complexes which were assigned the cis-α configuration have since been shown, as the result of an X-ray diffraction study, also to be cis-β complexes.[14] We have reported a symmetrical NMR spectrum for *cis*-β-[(dmt)Co(NO$_2$)$_2$]$^+$ which could lead to its misassignment as an α complex.[7] Because of this demonstrated lack of dependability of IR and NMR spectra as aids in configurational assignment for substituted triethylenetetramine ligands, we sought a technique which might be quite sensitive to the mode of wrapping of the tetraamine ligand (α or β) but yet would be insignificantly affected by bulkiness at the ligand 2,9 positions.

It has been reported that treatment of Λ-α-[(dmt)CoCl$_2$]Cl with amino acids in aqueous solution leads almost exclusively to β-(dmt)Co^{III}(amino acidate) complexes.[3,12] This is presumably because of the rapid rate of the conjugate base promoted α–β isomerization compared to the rate of solvation of the chloride anion.[15] Hydrolysis of carbonato and nitro complexes in acid solution, to evolve CO$_2$ and NO$_2$, respectively, is very rapid because it does not involve Co–O bond cleavage in the rate-determining step.[16] Thus it would seem that the best opportunity to observe differences in complexation behavior between cis-α and cis-β complexes, prior to allowing any appreciable degree of α–β isomerization, would be afforded by working with carbonato and nitro complexes in acid solution. The use of 3 M tartaric acid as a reaction medium not only provides a solvent sufficiently acid to cause evolution of CO$_2$ and NO$_2$ but also provides an optically active ligand which can coordinate to the (tetraamine)cobalt(III) moiety under these mildly acidic conditions. In order to study the effects of added bulk on the reaction products and upon the CD vicinal effects of this product, the optically active substituted triethylenetetramines I were used as ligands.



Ia, trien; R = H
b, dmt; R = -CH$_3$
c, dipt; R = -CH(CH$_3$)$_2$

The vicinal effect curves of the acid treated dinitro complexes **2**, **4**, and **6**, which were all synthesized under conditions previously shown to yield cis-β complexes of the (trien)Co^{III} moiety,[6] are nearly identical in shape, with molar ellipticity minima between −3200 and −4800° located at 488 nm and with maxima located near 360 and 555 nm (Figures 2–6). The large magnitude of this minimum, about 7–10 times that reported for an outer-sphere tartrate complex to the hexaaminocobalt(III) ion,[17] is on the order of the size of the vicinal effect of an inner-sphere amino acid complex.[3] This supports the formulation of these solution species as inner-sphere complexes. The vicinal effect of the acid treated carbonato complexes **8** and **10**, which were prepared under conditions previously shown to yield β complexes of the (trien)Co^{III} moiety,[6] were also nearly identical in shape and intensity to those of the dinitro species **2**, **4**, and **6**. We therefore conclude

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(9) Hooker, T. M.; Schellman, J. A. *Biopolymers* **1970**, *9*, 1319.
(10) Buckingham, D. A.; Jones, D. *Inorg. Chem.* **1965**, *4*, 1387.
(11) Buckingham, D. A.; Dwyer, M.; Gainsford, G. J.; Ho, V. J.; Marzilli, L. G.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *Inorg. Chem.* **1975**, *14*, 1739.
(12) Job, R. *Inorg. Chim. Acta* **1980**, *40*, 59.
(13) Asperger, R. G.; Liu, C. F. *J. Am. Chem. Soc.* **1967**, *89*, 709.
(14) Glusker, J. P.; Carrell, H. L.; Job, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 5741.
(15) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 272.
(16) Reference 15, p 230.
(17) Norden, B. *Acta Chem. Scand.* **1972**, *26*, 111.

that all of the compounds **2**, **4**, **6**, **9**, and **10** are cis-β complexes.

Compounds **1**, **3**, **5**, **7**, and **9** were prepared under conditions previously shown to yield α-dinitro and carbonato complexes, respectively, for the (trien)Co^{III} moiety.[6] The vicinal effects observed for these compounds are quite similar to each other in character, with maxima near 365 and 450 nm and minima near 334, 400, and 530 nm (Figure 2–6). They exhibit distinctly different character from the vicinal effects of the β complexes and vary in maximum intensity from 12 to 30% of that of the isomeric cis-β complexes. We therefore conclude that the compounds **1**, **3**, **5**, **7**, and **9** are all cis-α complexes.

It is evident that the cis-β configuration is more stable than the cis-α in 3 M tartaric acid. Thus a solution of a β-dinitro complex held at 80 °C for several days maintains nearly the same character of the CD spectrum, which only gradually decreases in intensity as the solution fades and the complex undergoes slow decomposition, whereas the vicinal effect of a solution of the α complex **3** begins to increase in magnitude and acquire characteristics of the corresponding β complex (Table I). Calculation using data from Table I and data abstracted from the curves in Figure 3 leads to the estimate that the undecomposed complex, after 4.75 days, is approximately an equal mixture of α and β species. However, this time study reveals that the α–β isomerization is not sufficiently rapid to cause confusion in the results obtained over a 2-h heating period.

Just as it is not to be expected that the Δ and Λ isomers of the racemic (trien)Co^{III} complexes **1**, **2**, **7**, and **8** should react with *d*-tartaric acid at equal rates, so it should not be expected that the optically active Co(III) complexes **3**, **4**, **5**, **6**, **9**, and **10** react equally rapidly with *d*- and *l*-tartaric acids. Because of this, the various disasteromers used to obtain the vicinal effects of Figures 2–6 may be at various degrees of completion in their reaction with tartaric acid at the end of 2 h. Thus these curves may not represent exact vicinal effects. It may also be that the vicinal effect curves are representative of a number of solution species and that determination of a proper vicinal effect must await isolation of a pure complex. However, these reservations do not detract from the efficacy of the method.

Conclusion

Additivity of d–d CD spectra, as manifested through the distinctness of the vicinal effects (which may be ascribed to differences in the achiral chromophore between the cis-α and cis-β complexes), has proven to be a remarkably facile technique for clearly discriminating between α and β complexes of substituted (triethylenetetramine)cobalt(III) with carbonato and nitro ligands.

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Registry No. **1**, 14873-88-2; **2**, 41593-00-4; **3**, 36537-99-2; **4**, 36800-14-3; **5**, 52138-28-0; **6**, 74112-73-5; **7**, 36994-86-2; **8**, 74081-98-4; **9**, 74082-00-1; **10**, 74112-75-7.

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Spin State Dependent Redox Properties of the [Fe^{III}(X-Sal)$_2$trien]$^+$ Spin-Equilibrium System in Solution

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The electroreduction of a series of iron(III) chelates having hexadentate Schiff base ligands, [(X-sal)$_2$trien]$^{2-}$, derived from triethylenetetramine (trien) and various substituted salicylaldehydes (X = H, NO$_2$, OCH$_3$, Br, Cl) has been investigated in nonaqueous media. The electron-transfer properties of the complexes are of special interest since the compounds are known to be $^2T \rightleftharpoons {}^6A$ spin-equilibrium species in both the solid and solution states. In solution, the spin equilibria are dependent on solvent, on the X substituent, and, of course, on temperature. The reduction of the Fe^{III}[(X-sal)$_2$trien]$^+$ complexes involves a reversible, one-electron transfer. Half-wave potentials for the reductions were also found to be dependent on the substituent, nature of the solvent, and temperature. From the temperature dependence (220–300 K) of the half-wave potentials, $(dE/dT)_P$, the electron-transfer entropy change for the reduction processes has been determined and a comparison made between the electron-transfer entropy and the entropy change associated with the spin equilibrium. A mechanism relating the spin equilibrium and the electroreduction is also proposed.

Introduction

In recent years a number of electrochemical studies involving macrocyclic complexes as models for biological heme electron-transfer reactions have been published.[4–6] These electron-transfer reactions have been characterized with respect to solvent media, coordination number, spin state, and position of the iron atom relative to the donor atom plane of the macrocyclic ligands. Although many relationships have been investigated, detailed information as to how changes in spin state affect the Fe(III)/Fe(II) electron-transfer reaction has not been reported.

Several papers have now been published which characterize spin equilibria in solution for various six-coordinate Fe(III)[7–13]

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