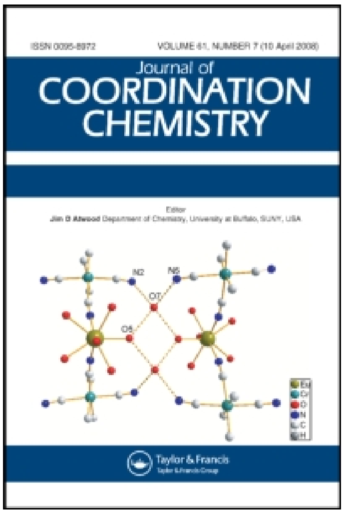

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OPTICAL ACTIVITY AND ELECTRONIC STRUCTURE OF SOME TRANS(DIACIDO)TETRAMINE COBALT(III) COMPLEXES

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Electronic spectra for the *trans*(diacido)tetraminecobalt(III) complexes (anions may be glycinato, acetato R- or S.-alaninato, and the tetramine may be either 4,7-diaza-1,10-decanediamine (3,2,3-tet) or 4,7-diaza-5-methyl-1, 10-decanediamine (5-me-3,2,3-tet)) may be fit to a point charge model with $D_q{}^{xy}$=24.9 kK and $D_q{}^{z} \sim 2$ kK; the pseudo tetragonal ${}^1A_{1g} - {}^1A_{2g}$ and ${}^1A_{1g} - {}^1E_g$ transitions may therefore be assigned with some certainty. In the true lower symmetry of these complexes, the ${}^1E_g$ state is split into two components. Regional rules predict a negative major *CD* component for *trans*(diacido)((–)-5-me-3,2,3-tet)cobalt(III) complexes while two components of opposite, but approximately equal rotatory strength have been observed. In this series of complexes, optical activity may be induced along a "tetragonal" axis, within a "tetragonal" plane, or both. The ${}^1A_{1g} - {}^1A_{2g}$ transition shows no rotatory strength for optically active centers on the z axis. Of the two bands observed in the region of the ${}^1E_g$ electronic transition, the negative band is assigned to the symmetry invariant ${}^1A_1 - {}^1A_2$ transition. These assignments are supported by measurements of rotatory strength as a function of variations in optical activity in the xy plane and along the z axis. The net rotatory strength in the d–d region for this series of complexes in the γλγ configuration is always positive.

INTRODUCTION

The point charge model predicts that the electronic spectrum of octahedral metal complexes with the low spin d^6 configuration will be characterized by two bands which may be assigned to the ${}^1A_{1g} - {}^1T_{2g}$ and ${}^1A_{1g} - {}^1T_{2g}$ transitions, respectively (Figure 1). On descent in symmetry to D_{4h} or C_{4v}, corresponding to a tetragonal distortion, the degeneracy of the octahedral ${}^1T_{1g}$ and ${}^1T_{2g}$ levels is removed. Experimentally, this lowering of symmetry is manifested in a splitting of the low lying d–d absorption band. For the tetragonal complex $[Co(NH_3)_4(oac)_2]^+$ and the pseudo D_{4h} complexes $[Co(en)_2(oac)_2]^+$, $[Co(tetramine)(oac)_2]^+$ and $[Co(tetramine)aaH)_2]^{3+}$, where the tetramine may be either 4,7-diaza-1,10-decanediamine (3,2,3-tet) or 4,7-diaza-5-methyl-1,10-decanediamine (5-me-3,2,3-tet), the ${}^1T_{1g}(O_h)$ excited state is split into a ${}^1E_g$ and a ${}^1A_{2g}$ component, Piper and Wentworth[2] first recognized that the energy of the ${}^1A_{2g}$ state in a complex such as *trans*-$[Co(en)_2Cl_2]^+$ (pseudo D_{4h}) is almost exactly that of the ${}^1T_{1g}$ state of its parent compound, $[Co(en)_3]^{3+}$ (pseudo O_h). Thus, for a series of *trans*-diacido-bis-ethylenediaminecobalt(III) complexes for which the splitting of the lowest lying excited state is resolved in the electronic spectrum, the band at about 21.6 kK may be assigned to the ${}^1A_{1g} - {}^1A_{2g}$ (D_{4h}) transition with reasonable certainty.

In this paper, we shall apply the Piper–Wentworth model to the interpretation of the electronic structure of some *trans*-diacidotetraminecobalt(III) complexes, including the *trans*-bis(amino acid)tetraminecobalt(III) complexes described in a previous communication.[3] In addition we shall present an interpretation of optical activity data for some of these complexes through which we have completed the assignment of electronic states within the ${}^1E_g$ (pseudo D_{4h}) manifold.

Electronic Spectra

Electronic spectra of *trans*-(tetramine)cobalt(III) ions are shown in Figure 2 for representative samples of the various complexes. Electronic absorption parameters for these amino acid complexes of 2,3,2-tet, 3,2,3-tet and (–)-5(R)-methyl-3,2,3-tet are given in Table I.

The spectra of our *trans*-diacidotetraminecobalt(III) complexes may be interpreted in terms of Piper and Wentworth's proposed crystal field model for the D_{4h} complexes, *trans*-$[Co(NH_3)_4X_2]^+$ and *trans*-$[Co(en)_2X_2]^+$ using the empirical parameter $D_t{}'$,

TABLE I
Electronic spectra, splitting parameters and values of D_q' for some trans-diacidotetramine complexes of cobalt(III)

Complex	Band Maxima, $cm^{-1} \times 10^{-2}$ IA	IB	II	$D_t'(cm^{-1})$	$D_q'(cm^{-1})$
$Co(NH_3)_6^{3+}$ (4)	21.05		29.50	---	2490(NH_3)
$Co(NH_3)_4Cl_2^+$ (5)	15.90	21.00	24.94	588	1464(Cl)
$Co(NH_3)_4(NO_2)_2^+$ (2)	22.72			-382	3152(NO_2)
$Co(NH_3)_4(N_3)_2^+$ (2)	17.61		25.00	786	1114(N_3)
$Co(NH_3)_4(O_2C_3H_5)_2^+$ (2)	18.12	21.80	27.36	335	1904(OPr)
$Co(NH_3)_4(OAc)_2^+$ (2)	18.12		27.26	335	1904(OAc)
$Co(en)_3^{3+}$ (5)	21.47		29.50	---	2530(en)
$Co(en)_2F_2^+$ (5)	17.20	22.62	27.60	488	1676(F)
$Co(en)_2Cl_2^+$ (5)	16.12	22.49	25.92	612	1459(Cl)
$Co(en)_2Br_2^+$ (5)	15.21	21.68	Masked	716	1277(Br)
$Co(en)_2(H_2O)_2^{3+}$ (6)	18.2	22.5	29.0	374	1875(H_2O)
$Co(en)_2(NO_2)_2^+$ (7)	23.3		Masked	-418	3262(NO_2)
$Co(en)_2(OAc)_2^+$ (2)	18.52		30.56	337	1901(OAc)

TABLE I (continued)

Complex	Band Maxima, $cm^{-1} \times 10^3$			$D'_t (cm^{-1})$	$D'_q (cm^{-1})$
	IA	IB	II		
$Co(2,3,2\text{-tet})(en)^{3+}$ (8)	21.09		29.16	---	2472(en)
$Co(2,3,2\text{-tet})Cl_2^+$ (8)	16.1		23.4	570	1478(Cl)
$Co(2,3,2\text{-tet})Br_2^+$ (8)	15.05		Masked	690	1197(Br)
$Co(2,3,2\text{-tet})OAc_2^+$ (3)	18.43	22.57	27.72	304	1940(OAc)
$Co(2,3,2\text{-tet})GlyH_2^{+++}$ (3)	18.19	22.89	27.92	331	1915(GlyH)
$Co(2,3,2\text{-tet})(NO_2)_2^+$ (9)	22.5		30.2	-160	2774(NO_2)
$Co(3,2,3\text{-tet})en^{3+}$ (8)	20.92		29.27	---	2494(en)
$Co(3,2,3\text{-tet})Cl_2^+$ (8)	15.67		22.50^s	600	1444(Cl)
$Co(3,2,3\text{-tet})Br_2^+$ (8)	14.83		Masked	696	1267(Br)
$Co(3,2,3\text{-tet})OAc_2^+$ (3)	18.19	21.52	27.18	312	1948(OAc)
$Co(3,2,3\text{-tet})GlyH_2^{+++}$ (3)	17.86	21.73	27.24	350	1881(GlyH)
$Co(3,2,3\text{-tet})(NO_2)_2^+$ (10)	21.9		Masked	-112	2690(NO_2)

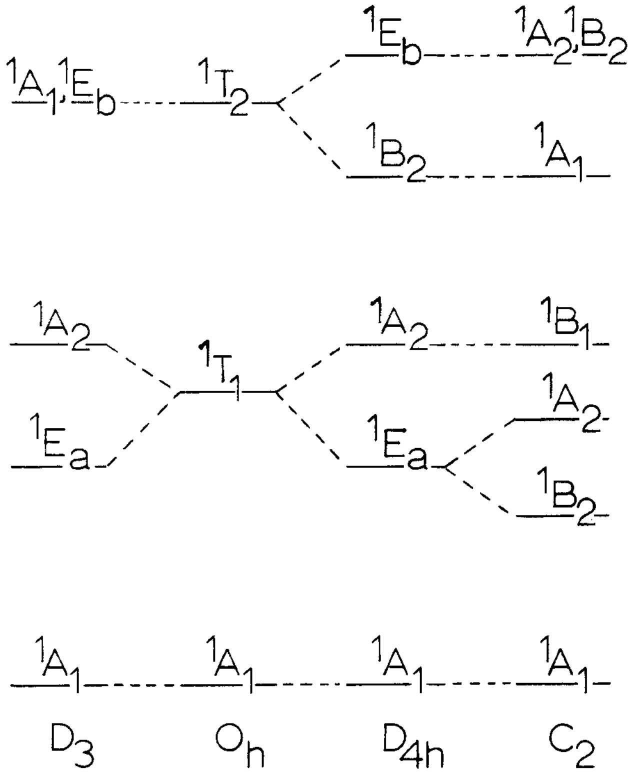

FIGURE 1 Splitting of singlet states of the spin paired d^6 configuration in non-cubic complexes (an arbitrary energy scale has been employed, and g or u subscripts deleted for simplicity).

which can be related to the octahedral field strength, D_q, of the axial groups. D_t', an approximation to D_t,[3] neglects off-diagonal matrix elements. In the tetramine and bis(ethylene-diamine) series, this analysis was based on approximations involving spectral parameters of the parent octahedral complexes, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_2]^{3+}$. For 3,2,3-tet and 2,3,2-tet, we have taken the complexes [Co(2,3,2-tet)en]$^{3+}$ and [Co(3,2,3-tet)en]$^{3+}$ to represent the parent octahedral CoN_6 chromophore (Table II). The equations,

$$E(^1T1) - E(^1A_1) = 10\,D_q - C$$
$$E(^3T_1) - E(^1A_1) = 10\,D_q - 3C,$$

represent the energies of the lowest-lying singlet and triplet states above the ground state and have been used to calculate D_q values for the parent complexes. Bands A and B correspond to the low intensity spin-forbidden $^1A_{1g} - {}^3T_{1g}$ and $^1A_{1g} - {}^3T_{2g}$ transitions, respectively. The electronic mutual replusion parameter C, was determined to be 3825, 3835, 3852, and 3795 cm^{-1} for $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, [Co(2,3,2-tet)en]$^{3+}$ and [Co(3,2,3-tet)en]$^{3+}$, respectively. Wentworth and Piper observed that C is nearly constant (about 3800 cm^{-1}) in several cobalt(III) amine complexes.

The empirical parameter, D_t', can be used to compare the field strength of a ligand, L, in the complexes *trans*-CoA_4L_2. This value is expressed in

TABLE II
Electronic spectra and splitting parameters for parent octahedral complexes of the type CoN_6

Complex	A^a	Band Maxima, cm^{-1} x 10^3			D_q(cm^{-1})^b
		B^a	I	II	
$[Co(NH_3)_6]^{3+}$ (2)	13.37	17.03	21.05	29.50	24.90
$[Co(en)_3]^{3+}$ (2)	13.83	17.33	21.47	29.50	25.30
[Co(2,3,2-tet)(en)]$^{3+}$ (11)	13.33	-----	21.09	29.16	24.72
[Co(3,2,3-tet)(en)]$^{3+}$ (11)	13.48	-----	20.92	29.27	24.94

[a] Spin forbidden $^3T_1 \leftarrow {}^1A_1$ is Band A. The $^3T_2 \leftarrow {}^1A_1$ (Band B) transition is obscured by Band I for the tetramine complexes.

[b] Determined by the method of Wentworth and Piper, *Inorg. Chem.* 4, p. 709 (1965) for the 2,3,2-tet and 3,2,3-tet complexes.

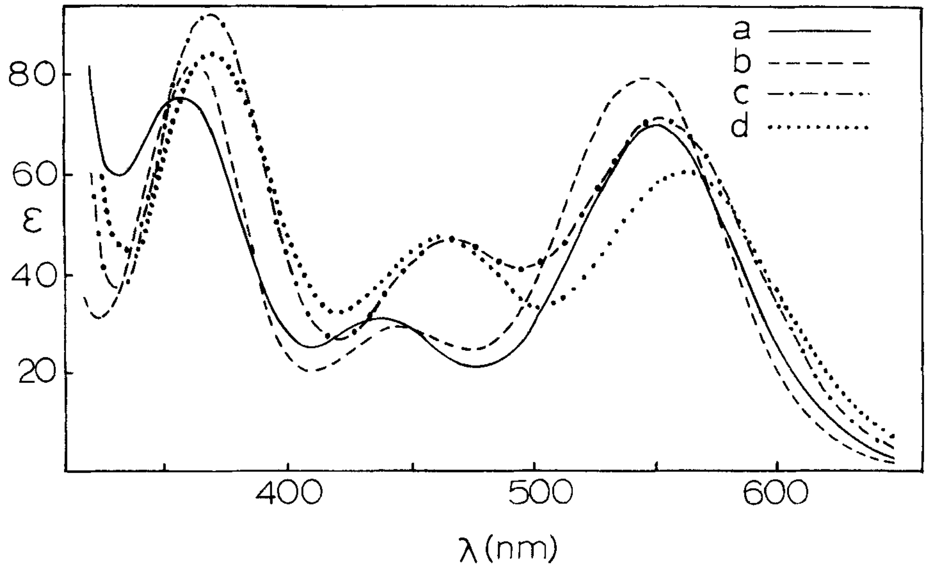

FIGURE 2 Electronic spectra of the complexes: (a) trans-$[Co(2,3,2\text{-tet})(GlyH)_2](ClO_4)_3$; (b) trans-$[Co(2,3,2\text{-tet})(OAc)_2]ClO_4$; (c) trans-$[Co(3,2,3\text{-tet})(OAc)_2]ClO_4$; (d) trans-$[Co(3,2,3\text{-tet})(GlyH)_2](ClO_4)_3$.

terms of D_q for the cobalt(III) complexes,

$$D_t(D_{4h}) = 4/7(Dq^{xy} - D_q{}^z)$$

where $D_q{}^{xy} = D_q(\text{tetramine}); D_q{}^z = D_q(\text{axial ligand})$. Thus, an evaluation of D_t' can be used to determine $D_q'(D_q' \approx D_q{}^z)$ which is the apparent field strength of the axial ligand, if $D_q{}^{xy}$, the inplane field strength, is available from the parent O_h complex. D_t' values are evaluated using the expression

$$D_t' = -4/35[W - (10\,D_q - C)_{xy}]$$

where W = the energy of the Band IA. In the determination of D_t', it is assumed that C is relatively independent of substitution of the octahedral parent, as we have already demonstrated. The excellent correspondence between the point charge model and the observed spectra justifies our assignment of electronic transitions.

Optical Activity

Assignment of absolute configuration to complexes of cobalt(III) is generally accomplished by comparing optical activity data for the complex in question with those of a complex of known absolute configuration. The known absolute configuration of (+)-$[Co(en)_3]^{3+}$[12] is frequently used as a standard, though extrapolation from the D_3 symmetry of the tris(diamine) system to the approximate C_2 symmetry of *cis*-$[Co(N)_4L_2]^{n+}$ complexes is of doubtful validity. Unfortunately, there are few examples of complexes of the appropriate geometry for which both structural and optical activity data are available. Thus, for the only known example of a 3,2,3-tet complex for which both sets of data are available, (+)-*trans*-$[Co(3,2,3\text{-tet})(NO_2)_2]Br$,[10] the electronic and *CD* spectra are shifted to high energy under the influence of the strong NO_2^- ligands, and are not directly comparable with the corresponding spectra of weaker diacido derivatives.

For (+)-$[Co(en)_3]^{3+}$,[13] the lowest energy *CD* band is positive, and is assigned to the $^1A_1 \rightarrow {}^1E_a$ transition (D_3). At slightly higher energy, the $^1A_1 \rightarrow {}^1A_2$ transition appears as a negative *CD* band. The splitting of the energy levels under D_3 symmetry is shown in Figure 1.[14] In complexes approximating to D_{4h} symmetry, the octahedral $^1T_{1g}$ state is split into components of $^1A_{2g}$ and ^1E_g symmetry (Figure 1), giving rise to two transitions in the *CD* spectrum. On further descent in symmetry to C_2, the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition is split into one component with A symmetry and two components with B symmetry (Figure 1). The $^1A_2(C_2)$ state derives from a component of the $^1E_a(D_{4h})$ state, and has a wave function invariant in form throughout the series $[Co(en)_3]^{3+}$, *cis*-$[Co(NH_3)_4L_2]^{n+}$, and *cis*-$[Co(en)_2L_2]^{n+}$,[15,16] whereas the wave functions describing the B states are not symmetry-determined in these complexes. The sign of the $^1A_1 \rightarrow {}^1A_2(C_2)$ transition may be used for correlation of absolute

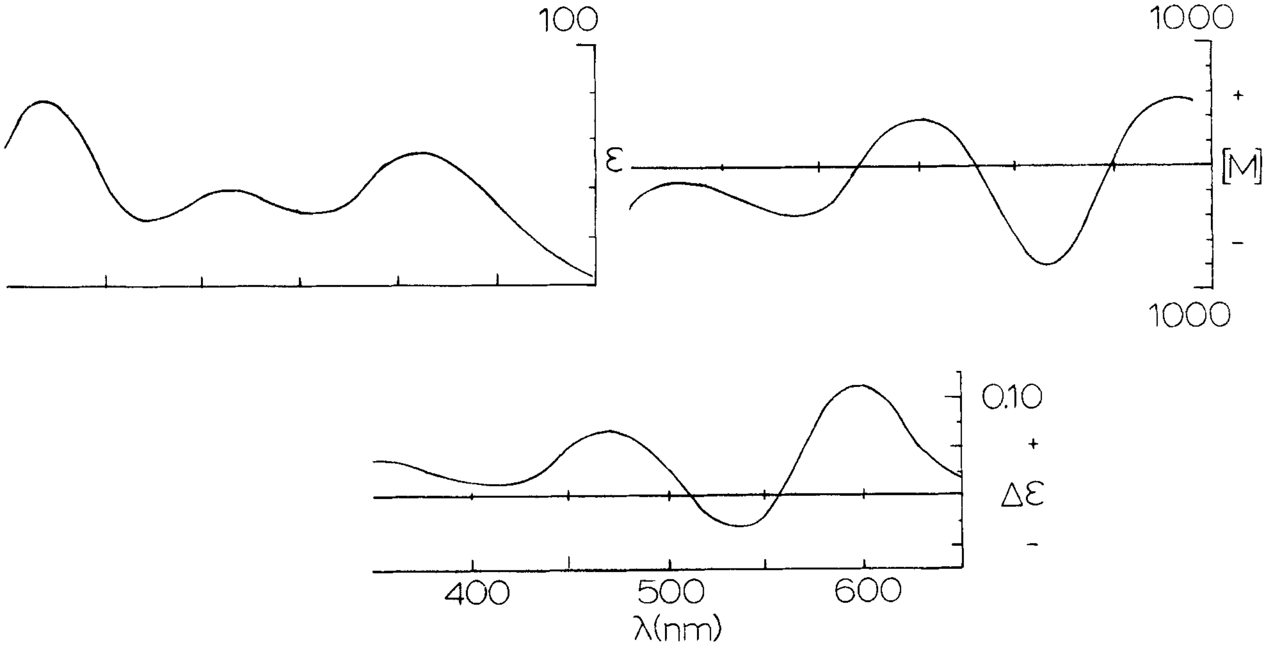

FIGURE 3 Electronic spectrum, ORD curve and circular dichroism spectrum of the complex trans-[Co(( )-5-Methyl-3,2,3-tet)(GlyH)$_2$]$^{3+}$.

configurations for a series of complexes of C_2 symmetry. If the transition with $^1E_a(D_3)$ parentage, $^1A_1 \rightarrow {}^1A_2(C_2)$, is positive, the complex is assigned the Λ absolute configuration. If it is negative, the complex is assigned the Δ absolute configuration. The $^1A_1 \rightarrow {}^1A_2(C_2)$ transition is distinguished as the more intense band. In complexes of C_2 symmetry, this band is usually assigned as the composite transition $^1A_1 \rightarrow {}^1A_2(E_a) + {}^1B_2(E_a)$, that is, accidental degeneracy of the components of the trigonal ^1E_a state. Indeed, *CD* spectra often appear to fit the trigonal or tetragonal model.

We have addressed ourselves to the question of establishing which of the observed transitions arising from the $^1E_g(D_{4h})$ state on descent to C_2 symmetry, for example, is the indicator of absolute configuration. We are particularly interested in those cases for which the "major" *CD* band cannot be unambiguously assigned. For this purpose, we have examined the electronic spectra and optical activity data for a series of complexes in which we can induce optical activity within a pseudo tetragonal plane along a pseudo tetragonal axis, or both, at will. The optical rotatory dispersion curve and the circular dichroism and electronic spectra for the complex *trans*-SS-[Co((−)-5-methyl-3,2,3-tet)(glyH)$_2$]$^{3+}$ are shown in Figure 3. In this and the related *trans*-dichloro complex, the axial ligands approximate to cylindrical symmetry, and the only source of optical activity is found in the tetramine ligand lying in the equatorial plane. The band at *ca.* 473 nm in the electronic and *CD* spectra is assigned to the $^1A_{1g} - {}^1A_{2g}$ transition in pseudo D_{4h} symmetry in accord with the Piper–Wentworth model. The two components of the *CD* spectrum at 536 and 601 nm are both associated with the $^1A_{1g} - {}^1E_g$ transition in the tetragonal model. The splitting of the $^1E_g(D_{4h})$ state arises from the fact that the effective symmetry is lower than D_{4h}, probably not higher than C_2. Since only the $^1A_2$ state arising from the $^1E_g(D_{4h})$ state is symmetry determined, it must correspond to the negative *CD* bands in the 530–550 nm range (Table III), as predicted by the hexadecanal rule.[17] The inverted sign of the *R* alanine complex will be treated later.

Shimura and co-workers[20,21] studied the *CD* spectra of the complexes, [Co(NH$_3$)$_5$(aaH)]$^{3+}$ and *cis*-[Co(NH$_3$)$_4$(aaH)$_2$]$^{3+}$ and *trans*-[Co(en)$_2$(aaH)$_2$]$^{3+}$ of simple amino acids. In the region of the first absorption band corresponding to the magnetic dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, both the [Co(NH$_3$)$_5$aaH]$^{3+}$ and *trans*-[Co(en)$_2$ aaH)$_2$]$^{3+}$ ions show one or two *CD* bands expected for complexes with C_{4v} symmetry (CoN$_5$O) or D_4h

TABLE III
Circular dichroism and electronic spectra data for some complexes of (–)-5-methyl-3,2,3-tet in the $^1A_{1g} \rightarrow {}^1T_{1g}$ region

Complex	λ_{max} (mμ)[a]	λ_{max} (mμ)[b]	$\Delta\varepsilon_{max}$
(-)-*trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})Cl_2]^+$	638	655	+0.37
		580	-0.03
	444	490	+0.11
(-)-*trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})(glyH)_2]^{3+}$	560(IA)	601	+0.11
		536	-0.03
	460(IB)	473	+0.07
(-)-*trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})(OAc)_2]^+$	550(IA)	590	+0.10
		535	-0.07
	466(IB)	470	+0.07
(-)-*trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})(S\text{-alaH})_2]^{3+}$	567(IA)	610	+0.06
		550	-0.12
	462(IB)	470	+0.09
(-)-*trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})(R\text{-alaH})_2]^{3+}$	567(IA)	590	+0.25
	462(IB)	470	+0.07

[a] λ_{max}(*mμ*) refers to absorption maxima in electronic spectra.
[b] λ_{max}(*mμ*) refers to maxima in the CD spectra.

symmetry (*trans*-$[CoN_5O_2]$). The position of the *CD* bands observed in the *trans* complexes coincide with the maxima observed in the electronic spectra for the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E_a$ transitions. The *CD* spectra of the *trans*-$[Co(en)_2(S\text{-alaH})_2]^{3+}$, for example, shows a negative band at low-energy followed by a positive band. Hawkins and Lawson[22] measured the *CD* spectra of pentaamine cobalt(III) complexes of some S- and R-amino acids in the region of the low-energy spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. For S-alanine, the transition with $A_{2g}(D_{4h})$ parentage have opposite signs, and the tetragonal splitting was not large enough to permit an unambiguous assignment. In the case of the bis(ethylenediamine) complexes, *trans*-$[Co(en)_2(aaH)_2]^{3+}$, the tetragonal splittings are large enough (more than twice monocarboxylate complexes) to be observed (*vide infra*).

Optical activity curves, Figure 4, for the complexes, *trans*-$[Co((\pm)\text{-}5\text{-methyl-}3,2,3\text{-tet})(S\text{-alanine})_2]^{3+}$, *trans*-$[Co((\pm)\text{-}5\text{-methyl-}3,2,3\text{-tet})(R\text{-alanine})_2]^{3+}$ and *trans*-$[Co(3,2,3\text{-tet})(S\text{-alanine})_2]^{3+}$, exhibit a single band corresponding in energy to the $^1A_1 \rightarrow {}^1E_a$ transition in pseudo D_{4h} symmetry (cf. electronic spectra), positive in sign for R- and negative for S-alanine complexes. The $^1A_1 \rightarrow {}^1A_2$ transition is forbidden under z polarization in the pseudo D_{4h} model, and accordingly, appears as a broad, weak *CD* band apparently of the same sign as the major component. Further, the rotatory strength of the transition due to the axial ligand decreases less than 5% on addition of sufficient base to neutralize the uncoordinated NH_3^+ group of the amino acid. This result is in accord with the results of a detailed study by Hawkins and Lawson[22] for the complexes, *trans*-$[Co(en)_2(aaH)_2]^{3+}$.

Optical activity data for the complexes, *trans*-$[Co((-)\text{-}5\text{-methyl-}3,2,3\text{-tet})(aaH)_2]^{3+}$, where aaH = acetato, glycine, S-alanine and R-alanine, distinctly show the true lower symmetry of *trans*-$[CoN_4O_2]^{n+}$ chromophores. The *CD* and *ORD* curves (Figure 5) for these complexes show the effect of an axial perturbation on the optical activity derived from the planar tetramine ligand (illustrated by the cor-

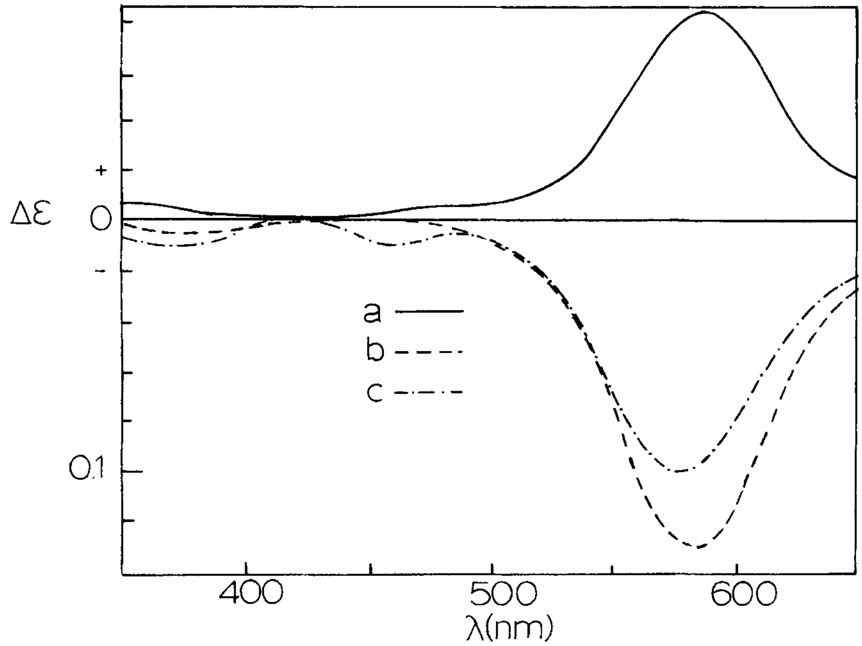

FIGURE 4 Circular dichroism spectra of the complexes: (a) trans-[Co((±)-5-Methyl-3,2,3-tet)(R-AlaH)$_2$]$^{3+}$(Δϵ/2); (b) trans-[Co((±)-5-Methyl-3,2,3-tet)(S-AlaH)$_2$]$^{3+}$(Δϵ/2); (c) trans-[Co(3,2,3-tet)(S-AlaH)$_2$]$^{3+}$.

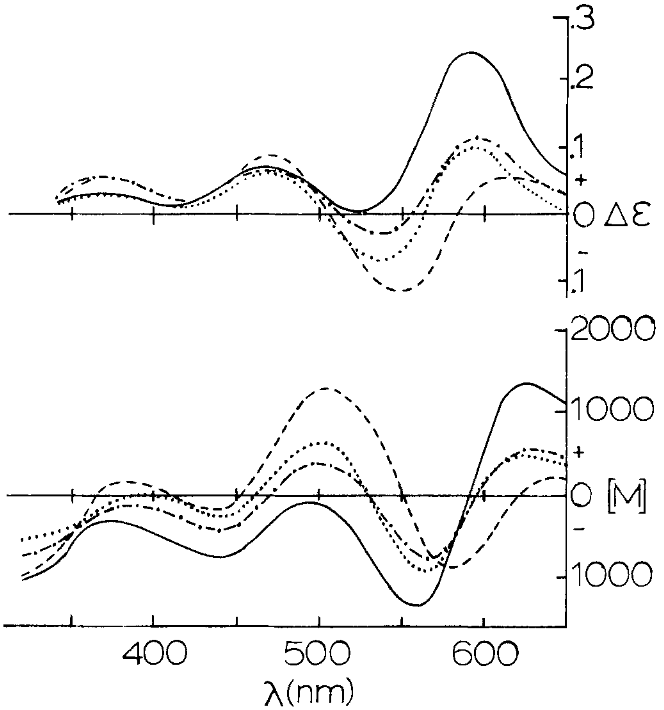

FIGURE 5 Circular Dichroism (Δϵ) and ORD ([M]) data for the complexes
trans-[Co((±)-5-Methyl-3,2,3-tet)(OAc)$_2$]$^{3+}$ ···············
trans-[Co((±)-5-Methyl-3,2,3-tet)(GlyH)$_2$]$^{3+}$ -·-·-·
trans-[Co((±)-5-Methyl-3,2,3-tet)(S-AlaH)$_2$]$^{3+}$ -- -- --
trans-[Co((±)-5-Methyl-3,2,3-tet)(R-AlaH)$_2$]$^{3+}$ ———

responding curves for the *trans*-dichloro complex Figure 6). These results demonstrate the separability of the 'axial' and 'equatorial' contributions to the optical activity of the cobalt(III) chromophore.

The transitions arising from the $^1E_a(D_{4h})$ state are influenced by the axial ligand. The $^1B_2(E_a)$ component is positive in the *CD* spectra, having greatest intensity in the R-alanine complex and weakest in the S-alanine complex. The reverse situation occurs for the negative *CD* band corresponding to the $^1A_2(E_a)$ state, which is largest for the S-alanine and virtually zero for the R-alanine complex.

To evaluate in detail the three transitions arising from the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition, the *CD* curves were resolved into Gaussian components. The experimental curves were fitted using four generated Gaussian curves over the wavelength range 650–350 nm. To evaluate the *CD* bands in the region of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for the bisacetato, bisglycine, and bis(R- and S-) alanine complexes, the area under the curve was normalized to 100%. The relative rotatory strengths are summarized in Table IV, under the assumption of approximate D_{4h} or C_2 symmetry. As shown in the data of Table IV, the highest energy transition in the $^1A_{1g} - {}^1T_{1g}(O_h)$ manifold represents from 27–38% of the total rotatory strength. This is the band

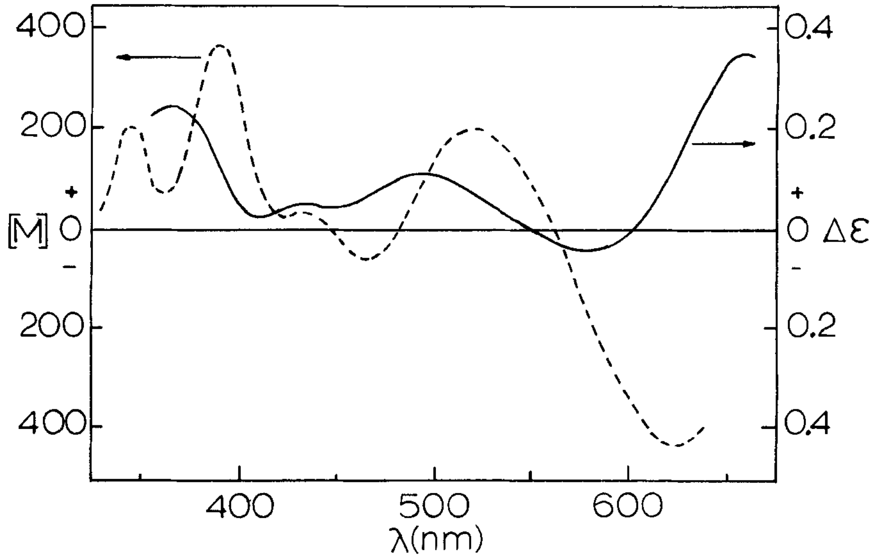

FIGURE 6 Data for the complex trans-SS-[Co((−)-5-Methyl-3,2,3-tet)Cl$_2$]$^+$ in acetonitrile.

TABLE IV
Gaussian curve analysis for the tetragonal complexes *trans*-[Co((−)-5-methyl-3,2,3-tet)(aaH)$_2$]$^{3+}$

aaH	Band #	Transition (C_2)	% Rotatory Strength under $^1A_1$ - $^1T_1$ Band (C_2)	(D_{4h})	Transition (D_{4h})
OAc	1	$^1A_1 - {}^1B_2$	36.3	68.7	$^1A_1 - {}^1E_a$
	2	$^1A_1 - {}^1A_2$	32.4		
	3	$^1A_1 - {}^1B_1$	31.3	31.3	$^1A_1 - {}^1A_2$
Gly	1	$^1A_1 - {}^1B_2$	43.6	61.7	$^1A_1 - {}^1E_a$
	2	$^1A_1 - {}^1A_2$	15.4		
	3	$^1A_1 - {}^1B_1$	38.3	38.2	$^1A_1 - {}^1A_2$
S-Ala	1	$^1A_1 - {}^1B_2$	26.6	71.7	$^1A_1 - {}^1E_a$
	2	$^1A_1 - {}^1A_2$	45.1		
	3	$^1A_1 - {}^1B_1$	28.2	28.2	$^1A_1 - {}^1A_2$
R-Ala	1	$^1A_1 - {}^1B_2$	70.7	72.9	$^1A_1 - {}^1E_a$
	2	$^1A_1 - {}^1A_2$	2.2		
	3	$^1A_1 - {}^1B_1$	27.2	27.1	$^1A_1 - {}^1A_2$

assigned to the $^1A_1 \rightarrow {}^1A_2$ transition in pseudo tetragonal symmetry (*vide supra*) or to the $^1A_1 \rightarrow {}^1B_1$ transition in C_2 symmetry. The remaining bands, together, contribute about 70% of the rotatory strength as the $^1A_1 \rightarrow {}^1E_a(D_{4h})$ or $^1A_1 \rightarrow {}^1A_2 + {}^1A_1 \rightarrow {}^1B_2(C_2)$ transitions. The area under the $^1A_1 \rightarrow {}^1A_2(C_2)$ transition increases with changes in the axial ligand, i.e., R-alanine < glycine < acetato < S-alanine, whereas the $^1A_1 \rightarrow {}^1B_2$ transition increases in the reverse order as a consequence of intensity stealing between these two components. Comparison of the *CD* spectrum of the R-alanine complex with that of the S-alanine complex indicates that the α-carbon methyl substituents appear to lie in opposite hexadecanal sectors. Taking the *trans*-dichloro complex, with an axial ligand of cylindrical symmetry about the metal-ligand axis, as the parent complex and replacing the axial ligand by a nitro or acetato group of non-cylindrical symmetry, the *CD* bands arising from the $^1A_2(C_2)$ and $^1B_2(C_2)$ states decrease in a negative direction, indicating that the axial ligand lies in a negative sector. Addition of an amine group to the α-carbon atom of acetate, to give glycine, produces no substantial change in the *CD* bands. The amine substituent may lie on a nodal plane and thereby cause little change in the *CD* spectra in the $^1E_a(D_{4h})$ region. The α-carbon substituents of alanine, however, produce very large effects. An α-carbon methyl substituent of S-configuration produces a negative change in the spectra, whereas, the R-configuration (D-alanine) produces a positive effect. Thus, the α-carbon substituent of S-alanine lies in a positive sector and the methyl substituent of R-alanine lies in a negative sector.

Infrared Spectra and Structural Interpretation of Spectroscopic Data

Infrared spectra of the complexes *trans*-RS(meso)-[Co(2,3,2-tet)Cl_2]ClO_4, *trans*-RR,SS-[Co(3,2,3-tet)Cl_2]ClO_4 and various *trans*-[Co(tetramine)-$(aaH)_2$]$(ClO_4)_3$ complexes of 2,3,2-tet and 3,2,3-tet were examined in detail in the 3300–3100 cm^{-1} and 1700–1400 cm^{-1} regions, corresponding to amine and carboxyl group absorption regions, respectively. The important bands and our assignments appear in Table V.

Infrared spectra of the dichloro complexes are devoid of analytically useful absorption except for the band at 1592–1603 cm^{-1} corresponding to the NH_2 bending mode.[8] In the *trans*-bis(amino acid)-(tetramine) complexes, however, three sharp bands are seen in this region for the bis(glycine) and bis(sarcosine) complexes and two for the bis(acetato) complexes. We have assigned the bands at about 1655 cm^{-1} to the COO symmetrical stretching mode of the coordinated acids in accord with the postulate that the amino acid residues are bonded to the metal ion through the carboxyl oxygen atom.[3] This band is relatively insensitive to the amino acid, and varies only within the range 1653–1660 cm^{-1} for the complexes listed in Table V. The bands at 1507 cm^{-1} and 1464 cm^{-1} for the glycine and sarcosine complexes, respectively, corresponds to the protonated amine of the bound amino acid. Other oxygen bonded monodentate amino acid complexes such as the $[Co(NH_3)_5(aaH)]^{3+}$ ions prepared by Fujita, Yasui and Shimura[23] exhibit similar infrared absorption for the COO stretching and $-NH_3^+$ deformation modes. We have assigned the bands at *ca.* 1600 cm^{-1} to the NH_2 bending mode of the tetramine ligand, and note that for complexes with 3,2,3-tet, this band is found in the range 1582–1593 cm^{-1}, while for complexes with 2,3,2-tet it lies in the range 1599–1604 cm^{-1}.

The N–H stretching frequencies of cobalt(III) complexes with these and related flexible tetramine ligands have been analyzed in terms of the configuration of the coordinated secondary nitrogen atoms of the tetramine chelate rings.[24] Thus the racemic (RR,SS) forms of these tetramines exhibit only three bands in the 3300–3100 cm^{-1} region, but the *meso* (RS) forms display five sharp bands. We find that all of our 2,3,2-tet derivatives exhibit five bands and the 3,2,3-tet derivatives three, in accord with earlier assignments of the configuration about the coordinated secondary nitrogen atoms of the *trans* dichloro complexes.[24]

We also note a shift in the NH_2 stretching frequencies when comparing our *trans*-bis(amino acid) complexes with the corresponding *trans*-dichloro species. This shift to lower energy of *ca.* 20 cm^{-1} for the 3,2,3-tet series and *ca.* 30 cm^{-1} for the 2,3,2-tet complexes indicates hydrogen bonding involving tetramine NH protons in the amino acid complexes. We have compared the infrared spectrum of *trans*-RR-[Co(3,2,3-tet)$(NO_2)_2$]Br for which a structural study[10] has shown the potential for hydrogen bonding between the axial NO_2^- group and tetramine NH protons, with the spectra of corresponding amino acid and chloro complexes. We find strikingly similar shifts in the infrared spectra (Table V). We therefore interpret these data to indicate that the carboxyl group is oriented by similar hydrogen bonds, and lies in approximately the same plane as the axial nitro group (Figure 7). We further believe

TABLE V
Infrared absorption bands of cobalt(III) complexes

Compound	NH_2	NH_2	NH	NH	NH	COO	NH_2	NH_3^+	NH_2R^+
trans-RS-[Co(2,3,2-tet)Cl$_2$]Cl	3278 s	3185 s	3169 sh	3146 w	3113 w		1603 s		
trans-RS-[Co(2,3,2-tet)Cl$_2$]ClO$_4$	3310 vs	3265 s	3228 s	3129 vs	3110 vs		1602 vs		
trans-RR,SS-[Co-(2,3,2-tet)Cl$_2$]ClO$_4$	3309 vs	3254 vs	3226 vs				1592 vs		
trans-RS-[Co(2,3,2-tet)(OAc)$_2$]ClO$_4$	3283 s	3232 s	3235 s	3124 s	3112 s	1653 vs	1601 vs		
trans-RS-[Co(2,3,2-tet)(glyH)$_2$ClO$_4$	3294 s	3231 s	3238 s	3130 s	3120 s	1660 vs	1599 vs	1507 s	
trans-RS-[Co(2,3,2-tet)(sarH)$_2$]ClO$_4$	3291 s	3245 s	3228 s	3126 s	3120 s	1655 vs	1600 vs		1464 s
trans-RR,SS,-[Co-(3,2,3-tet)Cl$_2$]-ClO$_4$	3301 vs	3240 vs	3214 vs				1587 vs		
trans-RR,SS,-[Co-(3,2,3-tet)(glyH)$_2$]-(ClO$_4$)$_3$	3287 s	3220 s	3190 vs			1652 vs	1593 m	1495 s	
trans-[Co(3,2,3-tet)-(sarH)$_2$](ClO$_4$)$_3$	3291 vs	3220 s	3208 vs			1656 vs	1590 s		1462 s
trans-[Co(3,2,3-tet)(NO$_2$)$_2$]ClO$_4$	3269 s	3226 vs	3185 vs						

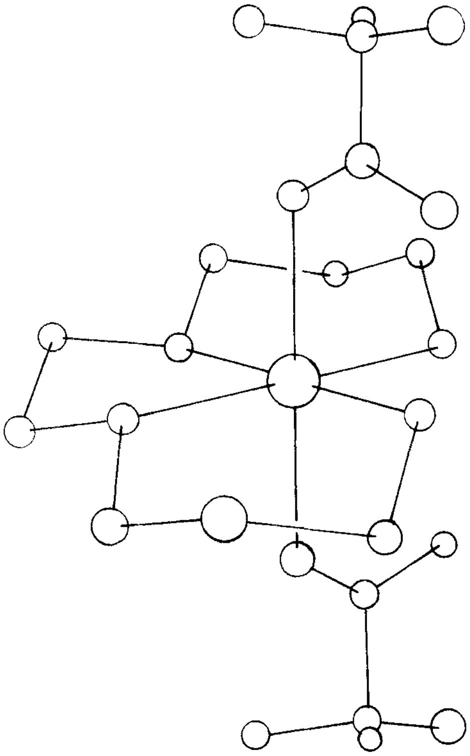

FIGURE 7 Proposed structure of trans-bis(amino acid)(3,2,3-tet)cobalt(III) complexes, showing the orientation of carboxyl groups and amino acid substituents.

that rotation of the carboxyl group is sufficiently hindered (or the orientation is sufficiently securely fixed by this hydrogen bonding mechanism) to determine the hexadecanal sector which is occupied by the amino acid substituent. Thus it is this fixed orientation of the carboxyl group which determines that the methyl substituent of S-alanine lies in a positive sector, and that of R-alanine lies in a negative sector. We note, from a study of space filling molecular models, that the proposed hydrogen bonding scheme involving the uncoordinated carboxyl oxygen also affords an explanation for the remarkable carboxyl specificity of these monodentate amino acid complexes.[3]

EXPERIMENTAL

Syntheses

Complexes employed in this study were prepared as described elsewhere.[1,3]

Spectra

Electronic spectra were obtained with a Beckman Model DB–G Spectrophotometer equipped with a Beckman 1005 ten inch Potentiometric recorder and matched 10.0 mm silica cells; sample concentrations of about 5×10^{-3}M were employed. A Beckman Model DK-2 Spectrophotometer was used in the 1000–600 nm region; sample concentrations of about $10^{-1}M$ were employed. Optical activity data were recorded with a Cary Model 60 Spectropolarimeter equipped with a Cary Model 6002 circular dichroism accessory, and solutions with OD ~ 0.8 at λ_{max} were employed. Infrared spectra were obtained using a Perkin Elmer Model 257 Spectrophotometer and the potassium bromide pellet technique.

Gaussian Analysis

A DuPont 310 Curve Resolver equipped with 310012 individual skew function generator channels and a 310150 curve plotter was employed.

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