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Optical Rotatory Strength of Tris-Bidentate Cobalt(III) Complexes

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The solution and single-crystal d–d circular dichroism spectra of $Co(en)_3^{3+}$, $Co(d\text{-pn})_3^{3+}$, and $Co(tn)_3^{3+}$ and the solution CD spectra of $Co(acac)_3$ have been examined. The single-crystal ^{59}Co nmr spectra of the same materials have also been studied. The results are taken to indicate that there is substantial static distortion of the electronic ground state in these complexes and that the equations of Liehr and of Piper correctly describe the origin of the optical activity in the visible region. A relationship between the geometry of a tris-bidentate complex and its optical activity is proposed.

Introduction

The origin of the significant rotatory strength associated with the "d–d" absorption bands of dissymmetric "almost octahedral" transition metal complexes of the type $M(AA)_3$ (where AA represents a bidentate ligand) has been considered by numerous authors.[1-14] While these rotatory strengths are considerably smaller than those usually associated with fully allowed transitions, they are never the less frequently of the order of magnitude of $(10\text{–}100) \times 10^{-40}$ cgsu, and there has been some difficulty in accounting for the signs and magnitudes of the observed rotations.

In essence, the problem reduces itself to a consideration of the fundamental expression for the rotatory strength associated with a given electronic transition

$$R_{ij} = \mathrm{Im}\langle\psi_i|\mathrm{el}|\psi_j\rangle\cdot\langle\psi_j|\mathrm{m}|\psi_i\rangle \tag{1^{15}}$$

where el and m are the electric and magnetic dipole operators, respectively, ψ_i and ψ_j are the wave functions of the ground and excited states of the system, and Im indicates the imaginary part of the indicated scalar product. Clearly the rotatory strength, R, will have a nonzero value only when both maxtix elements in (1) are nonzero and the two must also transform as the same irreducible representation of the symmetry group of the molecule. The symmetry restriction gives rise to the well-known restriction of optical activity to molecules possessing neither a plane nor a center of symmetry and need not concern us further here.

The behavior of the $\langle\psi_j|\mathrm{m}|\psi_i\rangle$ term has been reasonably well understood since Moffitt's early work.[1] The ligating atoms in an $M(AA)_3$ molecule are nearly octahedrally arranged and the transitions in question are "ligand field" d–d transitions largely localized on the metal atom. Thus a reasonable approximation for $\langle\psi_j|\mathrm{m}|\psi_i\rangle$ would be the value expected for a pure d–d transition in an electrostatic crystal field of octahedral symmetry. The values of $\langle\psi_j|\mathrm{m}|\psi_i\rangle$ estimated by this approximation seem reasonable. This approximation also leads to the selection rule that the only d–d transitions which show significant rotatory strength are those which are allowed for magnetic dipole radiation. This approximation will become poorer as the actual symmetry of the molecule deviates further from O symmetry, but a rather large deviation seems to be necessary before significant breakdown occurs.

The remaining matrix element, the electric dipole term, $\langle\psi_j|\mathrm{el}|\psi_i\rangle$, is the source of most of the difficulty. The octahedral ligand field approximation which seems to work reasonably well for the magnetic dipole term fails completely here giving a value of zero. This is a direct consequence of the d–d nature of the transition which makes it LaPorte forbidden. In essence, all of the theoretical work on this problem has consisted of various attempts to obtain values for this term which are in reasonable agreement with experiment. This can only be done by mixing in some odd (*ungerade*) character into one, or both, of the functions ψ_i and ψ_j. The vibronic mechanism which can produce intensity in the absorption spectrum for such a transition is not helpful here because the magnetic dipole transition takes place between two states having the same vibrational state. Under these conditions the vibronic contributions to the electronic rotational strength will arise only in the second order and are probably small. In addition magnetic dipole transitions can occur between vibronic states, but again these seem to be quite small. Thus generally only the "electronically allowed" part of the oscillator strength is considered to be significant in the rotatory strength expression.

Several possible sources of the required *ungerade* character have been proposed. Moffitt[1] suggested d-p mixing brought about by the *ungerade* portion of the trigonal field. (The ligand field about an $M(AA)_3$ complex of D_3 symmetry can be considered to consist of a large octahedral field plus a small trigonal field.) This process does not lead to any net activity in the first order[2] if the trigonal splitting of the octahedral states is ignored. Recently, however, Richardson[12,13] has shown that a net rotational strength is obtained if the perturbation treatment is carried to the second order. The case where the trigonal splitting is not ignored has been examined by Piper[5] and others.[3,4,8,10,14] The result is that while the net rotatory strengths of the octahedral transitions are zero in the first order, the rotational strengths of the individual components that the octahedral bands are split into by the trigonal field are not zero. For example, the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$ components that result from a trigonal distortion of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in Co(III) complexes have nonzero rotatory strengths, R_a and R_e, respectively, and the first-order theory gives $R_a = -R_e$.

The problem has also been approached from a molecular orbital point of view.[6,9,10,14] From the conventional LCAO point of view this means that ligand orbital character, as well as metal p and f orbital character, can be mixed into the

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transition. Karipides and Piper[6] and Liehr[9] have taken essentially the conventional LCAO-MO approach while the work of Schaffer[10] is cast in terms of the angular overlap model of Jorgensen and Schaffer.[16,17] Karipides and Piper[6] generated the trigonal component by moving the ligating atoms slightly from the octahedral positions while Liehr[9] considered the possibility that the ligand orbitals may not point directly at the metal atoms thus giving a greater distortion of the electronic environment of the metal than would be apparent from the position of the ligating atoms. The very recent work of Strickland and Richardson[14] involves moderately sophisticated molecular orbitals calculated on the basis of both the Piper and Karipides and the Liehr models.

Yet another source of activity has been suggested by McCaffery and Mason.[7] They have proposed the "borrowing" of intensity from the symmetry-allowed change-transfer and ligand-ligand transitions by the mixing of the symmetry-allowed bands into the d-d bands under the influence of the trigonal field.

These various contributions to the rotatory strength are not necessarily mutually exclusive and conceivably several of them might be of considerable importance in the same system or in different systems. However, a careful check of these various theoretical papers shows that there are some differences in the predictions made by the various approaches, and thus in favorable cases at least, some inferences might possibly be drawn about the relative importance of the various effects from experimental observations. In addition it might be possible to make some correlations between some features of the CD spectrum and some structural features of the molecule. A simple correlation between the CD spectrum and the absolute configuration of the complex might be possible. The purpose of this investigation was to obtain some experimental information which might shed some light on this point and see if any reasonable interpretation could be made.

The $^1A_{1g} \rightarrow {}^1T_{1g}$ band region of the solution CD spectra of a number of $Co^{III}(AA)_3$ complexes typically appears to consist of two overlapping bands of opposite sign. There seems to be fairly general agreement that these two bands represent the A_2 and E (of D_3) components of the T_{1g} (of O_h) band, but there still seems to be some question as to the extent of overlapping of the two bands and the actual separation between the bands.[18] If these components can be located with reasonable accuracy and correctly identified, it should be possible to test some of the theoretical developments mentioned above.

We will consider the distortion of the octahedron to D_3 symmetry to consist of an axial (or polar) distortion which will elongate or compress the octahedron along the threefold D_3 axis and a radial (or azimuthal) distortion which consists of a twist about the threefold axis. This corresponds to the description of Stiefel and Brown.[19] We will use their parameters, s/h (side/height) and ϕ, to describe these distortions.[20] The reason for choosing this point of view is that, to the first order, the polar distortion, s/h, gives rise to the A_2-E energy separation but makes no contribution to the rotatory strength while the azimuthal distortion, ϕ, is responsible for the rotatory strength while making no contribution to the A_2-E splitting.

The equations of Piper and Karipides[5,6] and those of Liehr[9] predict that the sign of R for the individual components should change when the direction of the azimuthal distortion changes, *i.e.*, $\phi < 60°$ or $\phi > 60°$, for a given absolute configuration of the complex. The equations of Schaffer[10] and McCaffery and Mason,[7] on the other hand, predict that no such reversal of sign should occur, while the work of Richardson[12,13] makes no prediction at all on this point. Unfortunately, apparently only one simple case where $\phi > 60°$ has been investigated.[21]

The magnitude of the polar distortion can be investigated more or less independently of the optical activity as such, and it has been examined by a number of different techniques in a number of different systems. A number of polarized crystal spectra,[6,22,26] CD studies (both CD[27] and MCD[18]), and esr[28] studies have all been applied to this distortion. For reasons which are not clear, the polarized crystal spectra seem to indicate much smaller splittings than the other methods.

One method which has not been applied to this problem is solid state broad-line nmr. This technique can be used to determine the absolute value of the quadrupole coupling constant of the cobalt ion in the crystal. This coupling constant should be a very direct and sensitive measure of the polar distortion of the complex.

It was felt that an examination of the solution CD, single-crystal CD, and broad line ^{59}Co nmr spectra for several related complexes would help clarify the situation and possibly indicate which of the theoretical approaches is the most useful.

Experimental Section

Materials. The complexes were prepared and resolved by standard methods. $[Co(en)_3]Cl_3 \cdot 3H_2O$ and $[Co(tn)_3]Cl_3$ (tn = 1,3-propanediamine) were prepared by the method of Work.[29] Λ-(+)$_{589}$$[Co(en)_3]I_3 \cdot H_2O$ was prepared and resolved by the procedure of Broomhead, Dwyer, Hogarth.[30] Λ-(+)$_{589}$$[Co(d\text{-pn})_3]Br_3$ was prepared by the procedure of Dwyer, Garvan, and Shulman.[31] Δ-(+)$_{589}$ $[Co(tn)_3]Cl_3$ was prepared by the resolution procedure of Ryschkewitsch and Garrett.[32] $Co(acac)_3$ (acac = 2,4-pentanedionate) was prepared by the method of Bryant and Fernelius.[33] Other salts of the cations were prepared by appropriate metathetical reactions. The specific rotations of all of the active species agreed with reported values within experimental values.

Large single crystals for CD and nmr spectra were grown as described elsewhere.[34]

Spectra. The single-crystal and solution CD spectra were taken

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(20) Unfortunately, only Karipides and Piper[6] and Richardson[12] considered the distortion in this way. All of the other developments considered the distortion with respect to the individual chelate rings and considered distortions in the plane of the chelate ring and normal to this plane. The relationship between the distortion parameters for these two orientations is not a simple one and it has led to some confusion.

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using a JASCO ORD/UV-5 spectrometer. Routine checks of optical rotations were made with a Bendix-Ericsson automatic polarimeter, Type 143A.

The nmr spectra were taken in the same way as and with the same instrument as previously described,[34] the only difference being that the 4.335-MHz ^{14}N fixed-frequency oscillator-receiver unit was replaced with a 15.085-MHz unit suitable for the detection of ^{59}Co. Two complete single-crystal rotation patterns were taken for $\{[Co(en)_3]Cl_3\}_2 \cdot NaCl \cdot 6H_2O$, Δ-$[Co(tn)_3](NO_3)_3$, and $Co(acac)_3$. A partial rotation pattern was taken for Δ-$[Co(tn)_3]Cl_3 \cdot 4H_2O$. Powder patterns were taken for Λ-$\{[Co(en)_3]Cl_3\}_2 \cdot NaCl \cdot 6H_2O$, $[Co(en)_3]Cl_3 \cdot 3H_2O$, and Λ-$[Co(d\text{-}pn)_3]Br_3$.

Results and Discussion

Nmr Results. The magnetic and geometrical parameters were extracted from the nmr data by applying the third-moment equation of Brown and Parker[35] using the general computation procedure previously described.[34] The only change in the procedure was the use of a more efficient nonlinear curve-fitting computer program.[36]

The observed magnetic parameters are given in Table I. The asymmetry parameter, η, is known to be zero from the crystal symmetry for all of the materials containing the $Co(en)_3^{3+}$ ion and for the Λ-$[Co(d\text{-}pn)_3]Br_3$ powder. In all of these cases the cobalt atom is known to lie on a threefold crystallographic axis[37-41] which requires that the principal magnetic axis coincides with the threefold axis and that $\eta = 0$. In the case of $Co(acac)_3$ η is not required to be zero by the crystal symmetry, but it was found to be zero within experimental error. We interpret this to indicate that any distortion of the complex from threefold symmetry by crystal-packing forces must be quite small. One of the rotation patterns for a single crystal of $Co(acac)_3$ is shown in Figure 1. This pattern is given to illustrate the generally excellent fit between the calculated and experimental spectra. This is actually one of the poorer fits. It is presented to show that even the rather complex 14-line spectra caused by the presence of two magnetically nonequivalent sites in this crystal can be fitted quite nicely. The tris(diamine)cobalt(III) crystals all contained only one cobalt site and thus gave seven-line spectra ($^{59}Co, S = {}^7/_2$).

Some difficulty was encountered with the Δ-$[Co(tn)_3]Cl_3 \cdot 4H_2O$ crystal. A large well-formed rhombic prismatic crystal was grown from mixed ethanol-water solution. Unfortunately, the crystal dehydrated and crumbled before a complete rotation pattern could be taken. However, 110° of the complete 180° pattern was obtained. This was enough to indicate clearly that the principal magnetic axis of the cobalt coincided with the prismatic axis of the crystal within experimental error (~±2°). On the other hand, it was felt that the magnetic parameters obtained were not very reliable and so rotation patterns were taken on the more stable $[Co(tn)_3](NO_3)_3$ crystal. The magnetic parameters are given in Table I and were found to be virtually identical with our best values for the Δ-$[Co(tn)_3]Cl_3 \cdot 4H_2O$ crystal. This was true despite the fact that the nitrate crystal has an entirely different crystal habit in which the principal magnetic axis of the cobalt does not lie along any of the crystallographic axes. (It describes an angle of 54° with the crystallographic b axis.) Since in the absence of an asymmetry parameter the principal magnetic axis must lie on the threefold axis of the complex, it is felt that the orientation of the threefold axis of the cation in the Δ-$[Co(tn)_3]Cl_3 \cdot 4H_2O$ crystal is quite well established.

Table I. Observed Magnetic Parameters

Compd	$\lvert e^2qQ/h \rvert$, MHz	η
rac-$\{[Co(en)_3]Cl_3\}_2 \cdot NaCl \cdot 6H_2O$	3.92 ± 0.02	0^a
Λ-$\{[Co(en)_3]Cl_3\}_3 \cdot NaCl \cdot 6H_2O$	4.1 ± 0.2	0^b
rac-$[Co(en)_3]Cl_3 \cdot 3H_2O$	3.3 ± 0.2	0^b
	2.63^c	
$[Co(d\text{-}pn)_3]Br_3$	4.79 ± 0.06	0^b
$[Co(tn)_3]Cl_3 \cdot 4H_2O$	6.19 ± 0.1	0.00 ± 0.01^a
$[Co(tn)_3](NO_3)_3$	6.19 ± 0.02	0.00 ± 0.01^a
rac-$Co(acac)_3$	7.80 ± 0.03	0.00 ± 0.01^a

[a] Single-crystal rotation patterns. [b] Powder spectra. [c] B. A. Scott and R. A. Bernheim, *J. Chem. Phys.*, **44**, 2004 (1966).

We consider the quadrupole coupling constant e^2Qq/h to be a quite good measure of the effective polar distortion of the electronic cloud about the cobalt nucleus. Scott and Bernheim[42,43] have interpreted the quadrupole coupling constant in the $[Co(en)_3]Cl_3 \cdot 3H_2O$ to be due to an electrostatic lattice gradient. They assumed the CoN_6 unit to be exactly octahedral and calculated the electrostatic gradient at the site of the cobalt arrising from the known ionic lattice arrangement of the crystal. In this way, they calculated a quadrupole coupling constant of 3.43 MHz using a Sternheimer antishielding factor of 10. Thus they concluded that the observed coupling constant is essentially a lattice effect. However, it could be argued that a calculation of this type is really not very realistic because it treats all of the ions, including the ion at which the gradient is being calculated, as point charges. Thus the fact that the cobalt ion is almost completely covered with a layer of saturated organic ligands is ignored. It would seem that these ligands should act as reasonably effective electrical insulators.

We find that the electrostatic calculations give much poorer results when applied to some of the other crystals which we have studied. Table II shows the results of the same type of electrostatic calculation for the other crystals for which we have obtained the coupling constant and for which the crystal structures are known accurately enough to make the calculation meaningful. There seems to be no real relationship between the experimental constants and the calculated results.

An attempt was made to improve the fit by delocalizing some of the positive charge from the cobalt out to the crystallographic positions of the attached nitrogens. This did not improve the situation and in fact led to a reduced value for the calculated constant for all three crystals.

Such limited information as we have ($Co(en)_3^{3+}$ in three different crystals and $Co(tn)_3^{3+}$ in two different crystals) would seem to indicate that the coupling constant is largely due simply to the inherent distortion of the ion modified slightly by lattice and packing effects.

If the coupling constant is the result of the distortion of the complex, it might be of interest to estimate the amount of change necessary in the $(t_{2g})^6$ octahedral configuration which would be required to produce the observed coupling constants. An approximate calculation of this type can be

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(43) We are unable to account for the slight discrepancy between our value of 3.3 MHz and Scott and Bernheim's value of 2.63 MHz for the coupling constant in $[Co(en)_3]Cl_3 \cdot 3H_2O$. The difference seems to be outside the limits of probable error even when the differences in calculational procedures are taken into account. However, this numerical difference does not affect either their arguments or ours.

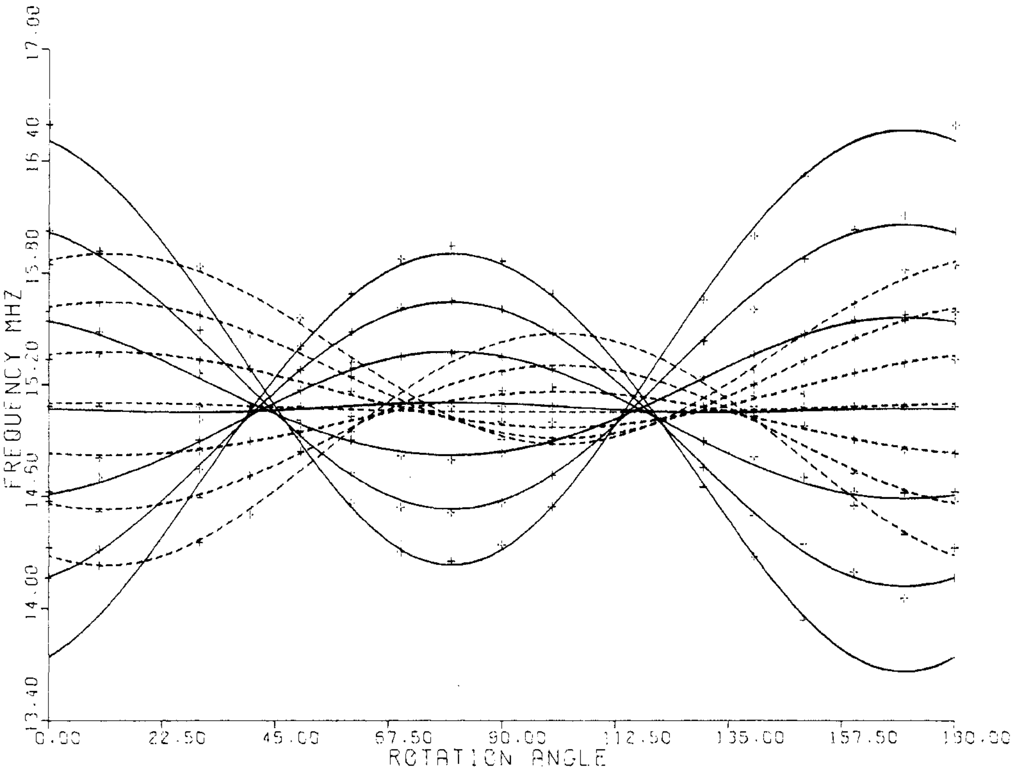

Figure 1. Rotation pattern for a single crystal of Co(acac)$_3$. The rotation axis is in the *ab* plane of the crystal 32.4° from the *a* axis: (+) experimental points; (- - - - - and ——) calculated patterns. The calculated values where obtained by solving the complete 8 × 8 matrix (H. M. Cohen and F. Reif, *Solid State Phys.*, 5, 321 (1957)).

Table II. Calculated Lattice Effects on the Quadrupole Coupling (Sternheimer Antishielding Factor 10)

Crystal	Calcd	Exptl
Co(en)$_3$Cl$_3$·3H$_2$O	3.43[a]	2.63[a] (3.3)
[Co(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O	2.10	3.92
Co(pn)$_3$Br$_3$	1.80	4.79
Co(acac)$_3$	0	7.80

[a] Reference 42.

made.[44] The calculation, which is quite approximate, is the same as that made using nqr data. Coupling constants of the order of magnitude reported here can be generated by moving approximately 0.1 electron from the t_{2g} orbitals to the e_g orbitals. The movement is from the e(D_3) component of t_{2g} if the octahedron is compressed along the threefold axis and from the a_2 component if the octahedron is elongated. Interestingly, shifts of this order of magnitude are predicted by Liehr's equations[9] when the angle of "mismatch" between the ligand unshared pair orbital and the ligand-metal axis is ~15°. This is about the value that Liehr found necessary to generate reasonable values for the rotatory strength. On the other hand, if we simply place point charges at the positions of the ligands reported by the X-ray studies and attempt to calculate the electronic shift, the value obtained seems to be much too small to account for the observed coupling constants. Unfortunately, the X-ray results in all cases are not accurate enough for the results to be very meaningful.

In brief, the most reasonable interpretation of our ^{59}Co nmr results seem to be that there is a substantial static polar deviation from octahedral symmetry in the electronic structure of the Co(AA)$_3$ complexes and that this deviation is more or less characteristic of the individual ion regardless of its environment. Unfortunately, the nmr gives only the absolute value of the coupling constant and so it cannot distinguish between elongation and compression along the threefold axis.

CD Spectra. The solution and single-crystal spectra examined are listed in Table III. Those spectra which had been reported previously were repeated with our own samples on our instrument for the sake of accuracy and internal consistency. The values reported in Table III are the values from our machine. The differences between our results and the previous results were all small and within the limits of error expected for measurements of this type. The two previously unreported single-crystal spectra of [Co(tn)$_3$]Cl$_3$·4H$_2$O and [Co(*d*-pn)$_3$]Br$_3$ were taken with the light beam propagated parallel to the threefold axis of the complexes so that only the E component of the transition would be allowed. As was the case in the nmr study, some difficulty was encountered with dehydration of the Δ-[Co(tn)$_3$]Cl$_3$·4H$_2$O crystals, but it was found that the crystals could be preserved long enough to obtain CD spectra by coating them with mineral oil.

A resolution of the solution spectra into two gaussian components was attempted. The solution spectrum was assumed to consist of two gaussian components corresponding to the a_2 and e components of the transition. In addition the e component was assumed to occur at the same frequency in the solution as in the single-crystal spectrum. With this restriction the spectra were computer fitted to the two best gaussians in the least-squares sense. The results of this curve fitting are shown in Figure 2 and Table IV. The calculated two gaussian spectra were found to agree with the experimental spectra at all points within the limits of error of the measurement.

The removal of the restriction on the position of the e band was found not to make much difference. When the e band was free to move in the fitting procedure, its position changed only slightly in all cases. This was the procedure

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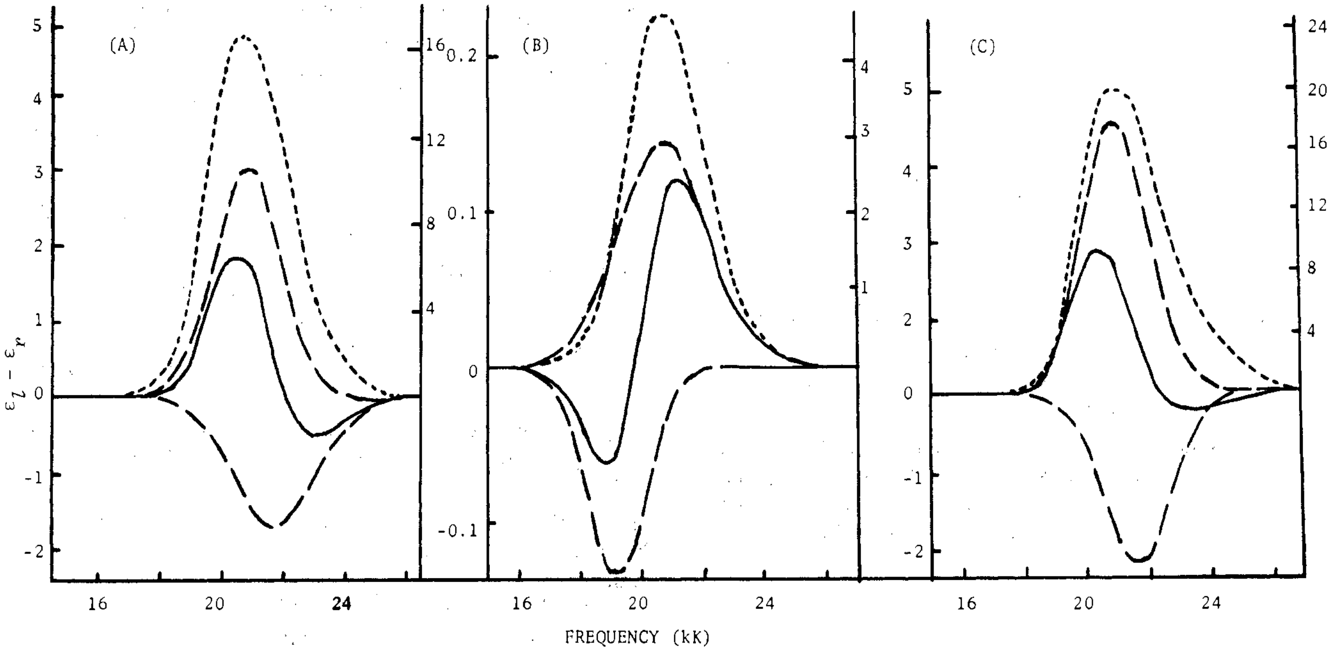

Figure 2. Gaussian resolution of the CD spectra for (A) Λ-Co(*d*-pn)$_3{}^{3+}$, (B) Δ-Co(tn)$_3{}^{3+}$, and (C) Λ-Co(en)$_3{}^{3+}$. In each case the left-hand axis is for the solution spectra and the right-hand axis is for the single-crystal spectra: (———) solution; (- - - - -) single crystal; (– –) calculated resolution.

Table III. Circular Dichroism Spectra in the $^1A_{1g} \rightarrow {}^1T_{1g}$ Region

Species	ν_0, kK	$(\epsilon_l - \epsilon_r)_{max}$	$10^{40}R$, cgsu
Co(en)$_3{}^{3+}$ soln[a]	20.513	1.91	4.86
	23.364	−0.22	−0.38
{[Co(en)$_3$]Cl$_3$}$_2$·NaCl·6H$_2$O[a]	21.053	20.2	76.4
[Co(*d*-pn)$_3$]$^{3+}$ soln[b]	20.367	1.88	4.74
	22.936	−0.49	−1.01
[Co(*d*-pn)$_3$]Br$_3$	20.833	16.7	62.3
[Co(tn)$_3$]$^{3+}$ [c]	18.868	−0.062	−0.11
	21.053	0.124	0.34
[Co(tn)$_3$]Cl$_3$·4H$_2$O	20.682	4.6	15.7

[a] Reference 7. [b] F. Woldbye, *Rec. Chem. Progr.*, **24**, 197 (1963). [c] Reference 21.

used for the Co(acac)$_3$ spectrum reported in Table IV, because no single-crystal crystal CD spectrum has been taken for this compound.

While it is realized that this procedure is strictly empirical and qualitative, the excellent fits and great reproductibility obtained lead us to believe that the results are at least qualitatively meaningful. Certainly there is ample precedent for the resolution of spectra into gaussian curves.

The A$_2$-E separations calculated in this way turn out to be fairly substantial and to be of the same order of magnitude as the splittings found in solution by Russell and Douglas.[18] Our values seem to be somewhat smaller than those of the previous workers. For example, they give a lower limit of 1.25 kK for the splitting in Λ-Co(*d*-pn)$_3{}^{3+}$ while we find a value of 0.86 kK. Certainly our results tend to agree with those of Russell and Douglas that the A$_2$-E split is much greater than the <0.15 kK previously proposed.

A comparison of our calculated A$_2$-E splitting and the ^{59}Co nmr quadrupole coupling constants is given in Figure 3. While the number of points is admittedly not large, there would seem to be a substantial correlation between the two, as we would expect, if they are both results of a substantial electronic deviation from octahedral symmetry in the ground state of the complexes. Figure 3 is *not* meant to imply that there is a direct correlation between the ground-state quadrupole constant and the spectroscopic splitting, which will depend upon both the ground and excited states, but rather that both of these quantities would be expected to correlate with substantial static distortions of the Co(AA)$_3$ moiety.

Table IV. Results of the Computer Resolution of Solution CD into Gaussian Component Bands

Compd	Band	$(\epsilon_l - \epsilon_r)_{max}$	ν_0, kK	$\Delta\nu/2$,[a] kK	$10^{40}R$, cgsu	$\nu_e - \nu_a$, kK
Λ-Co(en)$_3{}^{3+}$	$A_1 \rightarrow E$	+3.53	21.053	2.60	+10.7	−0.586
	$A_1 \rightarrow A_2$	−2.20	21.639	2.50	−6.2	
Λ-Co(*d*-pn)$_3{}^{3+}$	$A_1 \rightarrow E$	+3.08	20.833	2.60	+9.4	−0.863
	$A_1 \rightarrow A_2$	−1.68	21.696	3.03	−5.7	
Δ-Co(tn)$_3{}^{3+}$	$A_1 \rightarrow A_2$	−0.136	19.176	2.22	−0.39	+1.506
	$A_1 \rightarrow E$	+0.207	20.683	3.40	+0.83	
Δ-Co(acac)$_3$	$A_1 \rightarrow A_2$[b]	+2.5	15.910	2.00	+7.67	+1.67
	$A_1 \rightarrow E$[b]	−6.0	17.575	2.33	−19.56	

[a] $\Delta\nu/2$ is the bandwidth at half-height. [b] This assignment is from the polarized spectra: T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).

Conclusions

We feel that the overall weight of our evidence is that there is a substantial deviation from octahedral symmetry in the electronic distribution on the Co(III) ion in the Co(AA)$_3$ complexes. The actual geometrical distortion of the MX$_6$ unit is not known with a high degree of accuracy in many crystals because X-ray studies have rarely concerned themselves directly with this point. However, the general trend of such results as are available clearly indicate that these distortions are quite small and it is difficult to see how they can be reconciled with the relatively large electronic distortions which seem to be present without recourse to something at least resembling the "bent bond" or orbital mismatch concept of Liehr.[9]

The available spectral and structural information for the four complexes considered here is summarized in Table V. The sign of the E-A$_2$ split seems to be fairly clear: A$_2$ > E for compression along the D_3 axis and A$_2$ < E for an elongation.[45] This is in agreement with the previous prediction.

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(45) The reasons for this apparent reversal of the order expected from a simple electrostatic prediction have been discussed.[28]

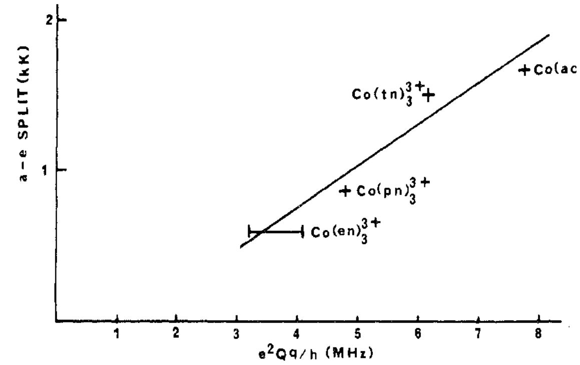
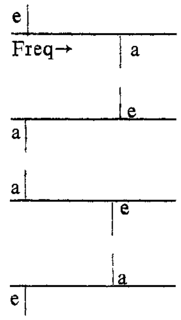


Figure 3. Comparison of the splitting in the CD spectra and the nuclear quadrupole coupling constant.

The two possible A_2-E orders combined with the apparent reversal of sign for $\phi < 60°$ and $\phi > 60°$ leads to four possible theoretical CD spectra for the Λ isomer of $Co(AA)_3$ in this region. These may be represented as shown in Scheme I.

Scheme I



I	$\phi < 60°$	$s/h > 1.22$
II	$\phi < 60°$	$s/h < 1.22$
III	$\phi > 60°$	$s/h < 1.22$
IV	$\phi > 60°$	$s/h > 1.22$

It would seem that $Co(en)_3^{3+}$ and $Co(d\text{-}pn)_3^{3+}$ are examples of case I, $Co(acac)_3$ is an example of case II, and $Co(tn)_3^{3+}$ is an example of case III. The authors have not yet been able to identify a clear-cut example of case IV. This case might be difficult to produce because of the unfavorable ligand-ligand interactions involved.

While our examples are admittedly few in number, all of the information that we have seems to support the scheme proposed above, and we wish to suggest that it might be rather general. The caveat that s/h should actually apply to the electronic distortion at the metal which may not be the same as the geometrical distortion of the MX_6 unit should be kept in mind.

The qualitative behavior predicted by this scheme is essentially that predicted by Piper.[46] The quantitative treatment most in accord with the overall behavior would seem to be that of Liehr,[9] but Liehr's equations are so complex that Piper's[5,6] simpler equations, which lead to essentially the same predictions, will probably be of more use.

The intensity mechanism proposed by McCaffery and Mason[7] does not seem to be important in the complexes studied here. However, it may prove to be important in cases which involve soft or unsaturated ligands. This possibility is under investigation at the present time. The theoretical approach taken by Richardson[13] does not seem to be particularly useful here because of his explicit assumption that the distortions at the metal are small. Interestingly, however, he does correctly predict the small intensity observed for $Co(tn)_3^{3+}$.

Table V. Summary of the Spectral and Geometrical Information

Complex	Band	$10^{40}R$, cgsu	ν_0, kK	$\nu_e - \nu_a$	$\lvert e^2Qq/h \rvert$, MHz	ϕ,[e] deg	s/h[e]
Λ-(+)$Co(en)_3^{3+}$	E	+10.7	21.053		3.91[a]		
				−0.59	4.1[b]	54.8	1.28
	A_2	−6.2	21.639		3.3[c]		
Λ-(+)$Co(d\text{-}pn)_3^{3+}$	E	+9.4	20.833	−0.86	4.79	55	1.23
	A_2	−5.7	21.696				
Λ-(−)$Co(tn)_3^{3+}$	A_2	+0.39	19.176	+1.51	6.19	67	1.22
	E	−0.83	20.683				
Λ-(−)$Co(acac)_3$	A_2	−7.67	15.910	+1.67	7.80	~54[d]	~1.21[d]
	E	+19.56	17.575				

[a] Racemic NaCl double salt. [b] Active NaCl double salt. [c] $Co(en)_3Cl_3 \cdot 3H_2O$. [d] $Fe(acac)_3$; the cobalt values are not reliable. [e] Reference 19.

One unfortunate aspect of the proposed behavior is that if it is indeed correct, then some information about both ϕ and s/h must be known before a relationship between the absolute configuration of $M(AA)_3$ and the signs of the CD spectral components can be made. This would seem to make sector rules rather difficult to apply. However, the situation may not be too bad because the majority of the compounds of interest are probably examples of case I above, but the possibility of exceptions should be kept in mind.

We have not explicitly considered the intensities of the CD bands because we feel, as some previous workers have,[18] that the intensities would be much more sensitive to small changes in conditions than either the signs or positions of the bands would be. One thing that would clearly affect these intensities would be the interaction with the nonligating atoms of the chelate ring.[13]

Our results seem to be in general qualitative agreement with the calculation of Strickland and Richardson.[14] A direct comparison is difficult to make because our results seem to indicate Liehr distortions well outside the range of their calculations.

Acknowledgment. We wish to thank Mr. Nadim Moucharafieh for the use of the optically active $Co(acac)_3$ which he had spent some time resolving.

Registry No. Λ-(+)-$Co(en)_3^{3+}$, 27228-84-8; Λ-(+)-$Co(d\text{-}pn)_3^{3+}$, 25226-32-8; Λ-(−)-$Co(tn)_3^{3+}$, 21657-34-1; Λ-(−)-$Co(acac)_3$, 34248-50-5; Δ-(+)-$Co(tn)_3^{3+}$, 28392-67-8; Δ-(+)-$Co(acac)_3$, 50600-77-6; *rac*-$\{[Co(en)_3]Cl_3\}_2 \cdot NaCl$, 50600-78-7; Λ-$\{[Co(en)_3]Cl_3\}_2 \cdot NaCl$, 50764-57-3; *rac*-$[Co(en)_3]Cl_3$, 13408-73-6; Λ-(+)-$[Co(d\text{-}pn)_3]Br_3$, 28816-84-4; Δ-$[Co(tn)_3]Cl_3$, 50600-79-8; Δ-$[Co(tn)_3](NO_3)_3$, 50600-80-1; *rac*-$Co(acac)_3$, 13681-88-4.

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(46) T. S. Piper, *J. Amer. Chem. Soc.*, **83**, 3908 (1961).