Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Spectra and Structure of Tris-Bidentate Cobalt(III) Complexes Containing Planar Ligands

N. C. MOUCHARAFIEH, P. G. ELLER, J. A. BERTRAND, and D. J. ROYER*

Received July 6, 1977

The d–d circular dichroism spectra and linear dichroism spectra of tris(biguanide)cobalt(III), $Co(C_2H_7N_4)_3^{3+}$, tris(biguanidato)cobalt(III), $Co(C_2H_6N_4)_3$, and tris(2,4-pentanedionato)cobalt(III), $Co(C_5H_7O_2)_3$, have been examined. The CD spectra were studied both in the solid state and in various solutions, and substantial relative intensity differences were observed which cannot be explained by conformational changes or vicinal hydrogen bonding. It is concluded that the A_2–E energy order in the CD spectrum can be predicted from the LD spectrum only if the energy separation is rather large. The crystal structure of *rac*-$Co(C_2H_6N_4)_3\cdot 2H_2O$ is also reported. The complex crystallizes in space group $P2_1/c$ ($a = 9.321$ (1) Å, $b = 10.121$ (1) Å, $c = 16.814$ (2) Å, $\beta = 103.43$ (1)°, $Z = 4$). The structure was refined to a conventional R value of 0.041. The geometry of the complex is compared to that of $Co(Hbgd)_3^{3+}$. The overall results indicate that the Piper model cannot be used to describe the optical activity of these complexes. The general problem of CD spectra–structure correlations in tris-bidentate cobalt(III) and chromium(III) complexes is discussed.

Introduction

The optical activity of transition-metal complexes in the region of the d–d ligand field bands of their spectra has been a subject of theoretical and experimental interest for some time.[1–4] A rather extensive body of theoretical work involving a variety of theoretical models has appeared. In general, this work has concentrated on the chiroptical properties of the simple trigonal (D_3) cobalt(III) and chromium(III) complexes of "nearly octahedral" geometry.

One of the problems in this area has been the relatively small amount of relevant experimental structural and spectroscopic data which has been available. In recent years, much more information about the geometries and absolute configurations of these complexes has become available from many sources, especially from the work of Saito and co-workers. However, there is still very little useful spectroscopic information available. The many solution circular dichroism spectra available in the literature have proved to be of limited usefulness for structure–spectra correlations and for testing the theoretical models, and very few solid-state spectra have been reported.

Tris-bidentate cobalt(III) and chromium(III) complexes usually give two circular dichroism bands of opposite sign in the region of the lowest energy ligand field absorption band. The symmetry of the transition responsible for this absorption band is T_{1g} in O_h, and the two CD bands correspond to the A_2 and E components of the originally T_{1g} transition generated when the symmetry of the complex is reduced from O_h to D_3. The simpler theoretical models relate the magnitude of this A_2–E splitting to an axial distortion of the octahedron along the threefold axis of the complex. This distortion is frequently described in terms of a single trigonal distortion parameter K.[5,6]

The signs and magnitudes of the rotatory strengths of the individual bands (and the net rotation of the entire T_{1g} term) are usually considered to be the result of a conformational effect due to any chiral puckering of the chelate rings and a configurational effect due to the screw dissymmetry of the chelate rings.[1] The simpler models ignore the conformational effect entirely and reduce the configurational effect to a consideration of the displacement of the ligating atoms from the octahedral positions. The various models then make some predictions about the relationship between these octahedral distortions and the signs and magnitudes of the CD bands, and a tentative general rule relating the signs and relative energies of the A_2 and E bands to such octahedral distortions has been proposed by Judkins and Royer.[7]

Unfortunately, the A_2–E separation is usually relatively small and extensive mutual cancelation of the two bands occurs in ordinary solution spectra. Therefore, accurate values for the positions and rotatory strengths of the two components normally cannot be obtained from such spectra. Indeed, there is no direct unambiguous method of assigning the two transitions in such a spectrum. (There are several more or less empirical ways of making this assignment,[8,9] but their accuracy and general applicability are open to question.[7,10,11]) An additional problem is that most of the work that has been done has involved complexes which contain saturated bidentate ligands which give rise to more or less flexible nonplanar chelate rings so that it is not clear how applicable solid-state structural information is to the complexes in solution. In at least some cases, it is clear that conformational changes do occur upon dissolution.[12,13]

It is becoming increasingly apparent that structure–spectra relationships are meaningful for these complexes only when solid-state spectra are considered. These may be single-crystal spectra or microcrystalline (alkali halide disk) spectra.

The disk spectra do not solve the band overlap problem, but they do ensure that the observed CD spectrum has not been affected by possible conformational changes induced by dissolution or other medium effects. A number of such spectra have been reported,[6,10] and they frequently differ significantly from the solution spectra. Both the relative intensities of the two bands and the energies of the apparent band maxima frequently change markedly. In some cases, it is not clear whether the actual band energies really change or if the apparent change is simply due to the change in relative intensities of the strongly overlapping bands.

Single-crystal CD spectra appear to be the only method currently available which, in principle, can produce accurate values for the band positions and rotatory strengths as well as the only completely unambiguous method of identifying the two bands. However, as is well-known, single-crystal CD spectra are beset with difficulties from linear dichroism and birefringence which severely limit the scope of the technique. Such spectra can be simply interpreted only when they are taken parallel to the optic axis of a uniaxial crystal. This limitation and the experimental difficulty of taking such spectra have severely limited the technique and only a very small number of such spectra have been reported.[14]

It has been suggested[15] that the A_2 and E bands could be identified using plane-polarized single-crystal spectra. This possibility arises because if the electronic selection rules in D_3 apply, the A_2 and E bands should be plane polarized parallel and perpendicular to the threefold axis of the complex, respectively. This possibility does not appear to have received much consideration, and there seem to be only three cases in the literature where the linear dichroism (LD) and CD spectra have been taken on the same crystal so that a direct comparison of the band positions in the two types of spectra can

0020-1669/78/1317-1220$01.00/0

be made. An examination of these three cases shows that the results are somewhat equivocal: $Cr(Ox)_3^{3-}$ shows the same energy order, $A_2 < E$, in the LD[16] and CD[15] spectra, $Co(en)_3^{3+}$ gives $E < A_2$ in the CD spectrum,[15] while $A_2 < E$ in the LD spectrum at room temperature[17] and $A_2 = E$ at 4 K,[18] and comparison cannot be made with $Co(Ox)_3^{3-}$ because the A_2 cannot be located in the CD spectrum.[15] Despite this questionable record, the LD spectrum has been used to assign the CD transitions in $Co(acac)_3$.[19]

One class of complexes which seem to warrant further study are those containing essentially rigid planar chelate rings. The bipyridine and *o*-phenanthroline complexes seem to be reasonably well described by the exciton model[8] but this model does not seem to be useful with complexes containing smaller ligands such as the biguanide complexes.[20] While many solution CD spectra have been reported for such complexes, relatively little solid-state spectral or structural work has been reported. At the time that the work reported here was undertaken, the only complexes of essentially D_3 symmetry with planar rings for which x-ray structural parameters (including absolute configurations) and solid-state CD[15] and LD[16] spectra were available were $Co(Ox)_3^{3-}$ and $Cr(Ox)_3^{3-}$. Thus it was decided to study the solid-state properties of several additional cobalt(III) complexes containing relatively simple planar rigid ligands. The complexes chosen were tris(biguanide)cobalt(III), $Co(Hbgd)_3^{3+}$, tris(biguanidato)cobalt(III), $Co(bgd)_3$, and tris(acetylacetonato)cobalt(III), $Co(acac)_3$. These were chosen to give a range of distortions from octahedral geometry and different charge types.

It was felt that such a study should be helpful in several ways: first, to see whether the relationships previously proposed between the CD spectrum and the distortions from octahedral geometry hold for this class of compounds; second, to further explore the possibility of assigning the transitions in the CD spectrum from the LD spectrum; and third, by examining the solution and crystalline CD spectra in these cases where no conformational contributions should appear, to possibly shed some light on the question of whether these effects are important in other cases.

While this work was in progress, the crystal structure of Δ-$Co(Hbgd)_3Cl_3 \cdot H_2O$[20] and a more accurate structure for *rac*-$Co(acac)_3$[21] were reported. We report here the crystal structure of *rac*-$Co(bgd)_3 \cdot 2H_2O$ and spectral results on Λ-$Co(Hbgd)_3Br_3 \cdot H_2O$, $Co(bgd)_3 \cdot 2H_2O$, and $Co(acac)_3$.

Experimental Section

Preparations and Optical Resolutions. Biguanide sulfate was prepared by the procedure of Karipides and Fernelius.[22]

Tris(biguanidato)cobalt(III) dihydrate, $Co(bgd)_3 \cdot 2H_2O$, and Λ-$(-)_{589}$-tris(biguanide)cobalt(III) bromide, Λ-$[Co(Hbgd)_3]Br_3 \cdot H_2O$, were prepared by the procedures described by Ray and Dutt.[23,24] The molecular rotation of Λ-$[Co(Hbgd)_3]Br_3 \cdot H_2O$ was found to be −2243° (589 nm).

Optically active $Co(bgd)_3$ was prepared by the following procedure. A weighed sample of Λ-$[Co(Hbgd)_3]Br_3 \cdot H_2O$ was dissolved in a minimum amount of dimethyl sulfoxide, a fourfold excess of calcium oxide was added, and the mixture was stirred for 15 min. The solid was then removed by filtration, and the dark red solution was slowly added to twice its volume of 1-butanol. The suspension was then cooled to ice temperature for several hours and the liquid decanted off. The finely divided dark red precipitate was thoroughly washed with anhydrous ether and stored in an evacuated desiccator until used. Some racemization of the material probably occurred during the deprotonation, but once prepared, the material could be kept for long periods of time, as either the solid or Me_2SO solutions, without further racemization. The deprotonation of the complex was confirmed by proton NMR (in Me_2SO-d_6: $Co(Hbgd)_3^{3+}$, three peaks, τ 3.31, 4.76, 6.4; $Co(bgd)_3$, two peaks, τ 6.43, 6.60).

Tris(2,4-pentanedionato)cobalt(III), $Co(acac)_3$, was prepared by the method of Bryant and Fernelius[25] and resolved by the procedure of Fay et al.[19]

Crystallographic Data Collection for *rac*-$Co(bgd)_3 \cdot 2H_2O$. Space group photographs taken with crystals mounted with the long dimension along the spindle axis, and along the x-ray beam, indicated that the space group was $P2_1/c$ (No. 14).[26] A crystal was then placed on a Picker automated four-circle diffractometer, and 16 reflections were accurately centered using Zr-filtered Mo Kα radiation. The unit-cell parameters are $a = 9.323$ (1) Å, $b = 10.121$ (1) Å, $c = 16.814$ (2) Å, $\beta = 103.43$ (1)°, and $V = 1543.2$ (3) Å^3. The calculated density, 1.701 g cm^{-3}, for $Z = 4$ agrees well with the measured density, 1.702 (2) g cm^{-3}.

The intensities were measured with a scintillation counter mounted 26.5 cm from the crystal and a source–crystal distance of 21.0 cm by the θ–2θ technique to a 2θ limit of 50° using a takeoff angle of 2.8° and at a scan rate of 1° min^{-1}. A symmetric scan of 2° was taken about the calculated position and stationary background counts of 20 s were taken at the beginning (B_1) and at the end (B_2) of the scan. Copper attenuators, calibrated as described previously,[27] were used in the collection of the data. A total of 2761 reflections were collected. Corrected intensities (I) were obtained by subtracting 3 times the actual measured background from the total integrated peak count (CT), i.e.

$$I = \mathrm{CT} - 3(B_1 + B_2)$$

The factor of 3 in the calculation arises from the peak scan being 3 times as long as the total background time. The corrected intensities were assigned standard deviations according to the formula[28]

$$\sigma(I) = [\mathrm{CT} + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where t_c is the scan time, t_b is the counting time for each background (either B_1 or B_2), and p is an "ignorance factor" included to avoid overweighting very strong reflections. A total of 2139 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.33 with p set at 0.02. Three axial reflections (700), (0$\bar{4}$0), and (060) were checked at intervals of 150 reflections. An isotropic linear decrease of 15% in the intensities of the standards was observed and appropriate corrections were applied. The intensities were corrected for Lorentz and polarization effects. The crystal measured 0.2 mm × 0.3 mm × 0.5 mm and was bounded by the (010), (100), (100), (001), (021), and (02$\bar{1}$) faces. Absorption corrections were applied by the Gaussian quadrature method; transmission coefficients ranged from 0.801 to 0.649.

Solution and Refinement of the Structure. Computations were carried out on a Univac 1108 computer. Programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy XFLS and ORFFE least-squares and function and error programs, the Johnson ORTEP thermal ellipsoid plotting program, the ABSORB absorption correction from Stewart's X-Ray 72 system, and various locally written programs. Cromer and Waber's scattering factors were used for all nonhydrogen atoms[29] and Stewart's scattering factors were employed for hydrogen.[30] The cobalt scattering factor was corrected for anomalous scattering using Cromer's dispersion factors.[31]

Coordinates for the four symmetry-related cobalt atoms were obtained from a three-dimensional Patterson function. An electron density calculation, phased on the cobalt coordinates, revealed the remaining nonhydrogen atoms. Full-matrix least-squares refinement of a scale factor, coordinates, and anisotropic temperature factors of all nonhydrogen atoms was carried out using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$) and minimizing $w(|F_o| - |F_c|)^2$; the refinement converged to a weighted residual, $R_2 = \{\sum_i w_i(|F_o| - |F_c|)^2/\sum_i w_i(|F_o|)^2\}^{1/2}$, of 0.071 and a conventional residual, $R_1 = \sum_i(|F_o| - |F_c|)/\sum_i|F_o|$, of 0.065.

A difference electron density map revealed reasonable positions for all of the hydrogen atoms. The hydrogens were entered into the refinement with fixed isotropic temperature factors of 4.0 and their positions refined. The refinement converged to $R_1 = 0.054$ and $R_2 = 0.060$.

At this point, a careful check of the original data indicated that a machine malfunction had resulted in the double scanning of 21 reflections. These reflections were removed from the data set and refinement with the remaining 2118 reflections converged to $R_1 = 0.041$ and $R_2 = 0.035$. A final difference Fourier synthesis contained no peaks greater than 0.48 Å^3. Final atomic coordinates and thermal

Table I. Final Positional Parameters for Racemic $Co(C_2N_5H_6)_3 \cdot 2H_2O$

Atom	x	y	z
Co	0.14743 (5)	0.06929 (4)	−0.17986 (3)
N(1a)	0.3271 (3)	0.1324 (3)	−0.2024 (2)
N(2a)	0.4989 (3)	0.1750 (3)	−0.2791 (2)
C(1a)	0.3838 (3)	0.1022 (3)	−0.2635 (2)
N(3a)	0.3357 (3)	0.0046 (3)	−0.3191 (2)
C(2a)	0.2378 (3)	−0.0864 (3)	−0.3039 (2)
N(4a)	0.2203 (4)	−0.1927 (3)	−0.3553 (2)
N(5a)	0.1683 (3)	−0.0823 (3)	−0.2452 (2)
N(1b)	0.0318 (3)	0.1535 (3)	−0.2769 (2)
N(2b)	−0.1371 (4)	0.1396 (3)	−0.4032 (2)
C(1b)	−0.0905 (4)	0.1051 (3)	−0.3215 (2)
N(3b)	−0.1837 (3)	0.0198 (3)	−0.2977 (2)
C(2b)	−0.1565 (4)	−0.0188 (3)	−0.2173 (2)
N(4b)	−0.2672 (3)	0.0888 (3)	−0.1978 (2)
N(5b)	−0.0361 (3)	0.0044 (3)	−0.1623 (2)
N(1c)	0.1396 (3)	0.2223 (3)	−0.1129 (2)
N(2c)	0.1541 (4)	0.3480 (3)	0.0047 (2)
C(1c)	0.1787 (4)	0.2318 (3)	−0.0329 (2)
N(3c)	0.2412 (4)	0.1373 (3)	0.0202 (2)
C(2c)	0.2812 (4)	0.0195 (3)	−0.0085 (2)
N(4c)	0.3568 (5)	−0.0631 (3)	0.0516 (2)
N(5c)	0.2530 (3)	−0.0190 (3)	−0.0837 (2)
O(1)	0.4484 (3)	0.3931 (2)	−0.1117 (2)
O(2)	0.4612 (3)	−0.2896 (3)	−0.0408 (2)
H(1a)	0.369 (5)	0.194 (4)	−0.175 (3)
H(2a1)	0.545 (5)	0.152 (4)	−0.312 (3)
H(2a2)	0.549 (5)	0.208 (4)	−0.237 (3)
H(4a1)	0.246 (5)	−0.181 (4)	−0.401 (3)
H(4a2)	0.153 (5)	−0.246 (4)	−0.356 (3)
H(5a)	0.114 (5)	−0.161 (4)	−0.246 (3)
H(1b)	0.075 (5)	0.207 (4)	−0.303 (3)
H(2c1)	0.198 (5)	0.363 (4)	0.948 (3)
H(2c2)	0.131 (5)	0.416 (4)	−0.025 (3)
H(4c1)	0.395 (5)	−0.026 (4)	0.101 (3)
H(4c2)	0.396 (5)	−0.126 (4)	0.034 (3)
H(5c)	0.293 (5)	−0.091 (4)	−0.019 (3)
H(1(O-1))	0.373 (5)	0.445 (4)	−0.132 (3)
H(2(O-1))	0.508 (5)	0.430 (4)	−0.128 (3)
H(1(O-2))	0.491 (5)	−0.344 (4)	−0.002 (3)
H(2(O-2))	0.519 (5)	−0.260 (4)	−0.053 (3)

Table II. Final Anisotropic Thermal Parameters (Å^2) for Racemic $Co(C_2N_5H_6)_3 \cdot 2H_2O^a$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1.41 (2)	1.39 (2)	1.28 (2)	0.00 (1)	0.24 (1)	0.00 (1)
N(1a)	1.6 (1)	2.0 (1)	1.9 (1)	−0.4 (1)	0.2 (1)	−0.3 (1)
N(2a)	2.0 (1)	2.5 (1)	3.1 (1)	−0.6 (1)	1.1 (1)	−0.5 (1)
C(1a)	1.3 (1)	1.7 (1)	1.9 (1)	0.5 (1)	0.4 (1)	0.5 (1)
N(3a)	2.1 (1)	2.5 (1)	2.1 (1)	0.3 (1)	0.8 (1)	−0.4 (1)
C(2a)	1.5 (1)	1.7 (1)	1.9 (1)	0.1 (1)	0.1 (1)	−0.4 (1)
N(4a)	3.4 (2)	3.2 (1)	3.5 (2)	−1.2 (1)	1.8 (1)	−1.7 (1)
N(5a)	1.8 (1)	1.5 (1)	2.0 (1)	0.0 (1)	0.5 (1)	0.0 (1)
N(1b)	1.8 (1)	1.8 (1)	1.7 (1)	−0.2 (1)	0.4 (1)	0.2 (1)
N(2b)	2.4 (1)	4.0 (2)	1.5 (1)	−0.8 (1)	−0.1 (1)	0.7 (1)
C(1b)	1.8 (1)	1.4 (1)	1.7 (1)	0.3 (1)	0.7 (1)	0.1 (1)
N(3b)	1.9 (1)	1.3 (1)	1.5 (1)	−0.4 (1)	0.3 (1)	−0.1 (1)
C(2b)	2.0 (1)	1.5 (1)	1.8 (1)	−0.1 (1)	0.8 (1)	−0.5 (1)
N(4b)	2.8 (1)	3.4 (1)	1.8 (1)	−1.4 (1)	0.6 (1)	−0.1 (1)
N(5b)	2.0 (1)	2.5 (1)	1.5 (1)	−0.2 (1)	0.5 (1)	0.3 (1)
N(1c)	1.9 (1)	1.7 (1)	1.8 (1)	0.3 (1)	0.2 (1)	−0.1 (1)
N(2c)	4.0 (2)	2.5 (1)	2.0 (1)	0.7 (1)	0.1 (1)	−0.5 (1)
C(1c)	1.7 (1)	2.0 (1)	1.8 (1)	−0.1 (1)	0.5 (1)	−0.1 (1)
N(3c)	4.1 (2)	2.3 (1)	1.6 (1)	0.3 (1)	0.5 (1)	−0.1 (1)
C(2c)	2.0 (1)	2.5 (1)	1.8 (1)	−0.3 (1)	0.5 (1)	0.3 (1)
N(4c)	5.9 (2)	3.2 (1)	1.7 (1)	1.7 (1)	0.4 (1)	0.6 (1)
N(5c)	2.2 (1)	2.0 (1)	1.7 (1)	0.4 (1)	0.2 (1)	0.0 (1)
O(1)	2.7 (1)	2.9 (1)	3.2 (1)	−0.1 (1)	0.7 (1)	0.6 (1)
O(2)	2.9 (1)	4.0 (1)	3.5 (1)	0.3 (1)	0.1 (1)	0.3 (1)

[a] The expression for the anisotropic temperature factor of an atom is $\exp[-0.25(a^{*2}h^2B_{11} + b^{*2}k^2B_{22} + c^{*2}l^2B_{33} + 2a^*b^*hkB_{12} + 2a^*c^*hlB_{13} + 2b^*c^*klB_{23})]$. The hydrogens were all assigned isotropic temperature factors B of 4.0 Å^2.

parameters are given in Tables I and II. A table of observed and calculated structure amplitudes is available as supplementary material.

Single-Crystal Spectra. The single crystals as grown were all too thick for spectroscopic use. Therefore, they were set in polystyrene resin and ground to a suitable thickness, ~0.05 mm. When the spectrum was to be taken through one of the naturally occurring crystal faces, the crystal was cast in resin with the desired face pressed against an optical glass disk 18 mm in diameter. The free surface of the resin plus crystal was then ground to the desired thickness using carborundum paper and polished with 4/0 grade polishing paper and a dry paper towel. When the spectrum was to be taken in a direction where a naturally occurring face was not available, the crystals were first mounted in polystyrene and sawed and polished in the appropriate direction before proceeding as described above. Crystal slices prepared in this way were easy to prepare and handle and gave satisfactory spectra. However, the presence of polystyrene in the light path limited the spectra to wavelengths greater than 300 nm. In those cases where the crystal slice used was not parallel to a well-identified naturally occurring face, the actual orientation of the slice with respect to the crystallographic axes was determined by means of x-ray precession photographs.

The plane-polarized spectra were taken using a Cary Model 14 spectrophotometer with matched corotated Nicol prisms in the sample and reference beams. The CD spectra were taken using a JASCO ORD/UV-5 with the crystal mounted in a simple rotatable cylindrical mount.

KCl Disk Spectra. Approximately 650 mg of dry KCl and from 1 to 3 mg of complex were ground together in an agate mortar and dried by heating under vacuum for 24 h. Clear disks 1 mm thick and 18 mm in diameter were then formed by pressing in a specially constructed press, made of 304 grade stainless steel, for 4 h. These disks remained transparent for at least 3 h when exposed to ambient conditions, after which time they slowly became opaque.

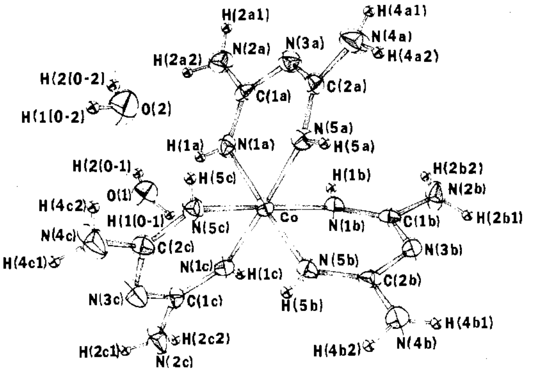

Figure 1. Molecular structure and atom labeling of *rac*-Co(bgd)$_3$·2H$_2$O.

Results

Crystallographic Results. (−)$_{589}$-$Co(C_2N_5H_7)_3Br_3 \cdot H_2O$. This material is isostructural[32] with the (+)$_{589}$-$Co(C_2N_5H_7)_3Cl_3 \cdot H_2O$ reported by Snow.[20] The packing in the two crystals is very similar, and there are no significant differences in the bond distances and bond angles in the cation (averaged bond distances all differ by less than 0.02 Å and all averaged bond angles differ by less than 2°). We report this here primarily because our spectroscopic studies were carried out on the bromide salt.

***rac*-$Co(C_2N_5H_6)_3 \cdot 2H_2O$.** The structure consists of individual neutral molecules linked together by hydrogen bonding, both in a direct way and through one of the waters of hydration. While the hydrogen bonding is extensive, there are no notably short contacts, the shortest base–base distance being slightly greater than 2.8 Å. Figure 1 illustrates the labeling scheme and the molecular structure.

The structure of the neutral complex is generally very similar to that of the $Co(Hbgd)_3^{3+}$ ion. In both cases the coordination geometry about the cobalt is only slightly distorted from an idealized octahedron, and the chelate rings show similar significant deviations from planarity. In both cases, the individual chelate rings are probably best described as having

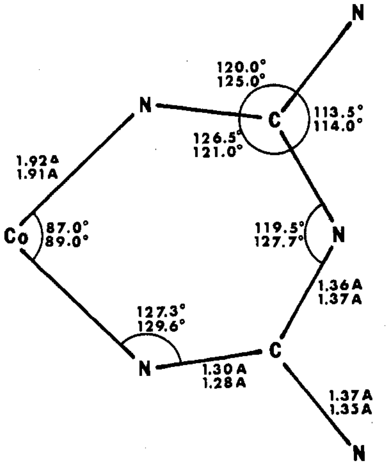

Figure 2. Comparison of the average chelate bond angles and distances of Co(bgd)$_3$ and Co(Hbgd)$_3{}^{3+}$. The upper number is for Co(bgd)$_3$ and the lower number is for Co(Hbgd)$_3{}^{3+}$. The Co(Hbgd)$_3{}^{3+}$ values are the average of Snow's values for Co(Hbgd)$_3$Cl$_3$·H$_2$O[30] and our values for Co(Hbgd)$_3$Br$_3$·H$_2$O.[32]

Table III. Deviations (Å) of Ligand Planes[a] from the Least-Squares-Plane through N(1), C(1), C(2), N(5)

	Ring A	Ring B	Ring C
N(1)	−0.010	+0.030	−0.007
C(1)	+0.012	−0.037	+0.008
C(2)	−0.019	+0.032	−0.008
N(5)	+0.019	−0.021	+0.008
Co	−0.460	−0.563	+0.143
N(3)	−0.114	−0.075	+0.063

[a] Equations for the planes: ring A, $+0.58105X - 0.55607Y + 0.59428Z + 0.47098 = 0$; ring B, $-0.54760X + 0.78509Y + 0.28943Z + 0.87550 = 0$; ring C, $-0.93308X - 0.35170Y + 0.07531Z + 2.54872 = 0$.

very shallow boat conformations with the cobalt and the N(3) nitrogen deviating in the same direction from the plane defined by the N(1), C(1), C(2), and N(5) atoms. These shallow boats are then oriented such that two point toward one end of the pseudothreefold axis of the complex while the third points toward the other end of this axis. Thus, even the idealized geometry of the complex is reduced to C_1 when the ring conformations are included.

The average bond distances and angles for the nonhydrogen atoms in Co(bgd)$_3$ and Co(Hbgd)$_3{}^{3+}$ are compared in Figure 2, and the best least-squares planes through N(1), C(1), C(2), and N(5) for Co(bgd)$_3$ are listed in Table III.

The most significant difference between the two structures is that upon deprotonation of the N(3) nitrogen, the C(1)–N(3)–C(2) angle decreases approximately 8°. This would be expected on the basis of simple VSEPR arguments. The other slight changes upon deprotonation—the increase in the N(1)–C(1)–N(3) angle, the decrease in ligand bite, the decrease in the N(1)–Co–N(5) angle, and the greater deviation of the ring from planarity—could all be considered to be results of decreasing the C(1)–N(3)–C(2) angle.

The C–N bond distances all indicate the presence of multiple bonding, indicating the expected extensive delocalized π bonding. Also, as would be expected, the π bonding is greatest in the N(1)–C(1) (and N(5)–C(2)) positions. The strong π bonding in these positions could be considered to be responsible for constraining the deviation of the chelate rings from planarity to the boat conformation.

The coordination geometry about the metal in symmetrical tris-bidentate complexes has commonly been described in terms of an idealized D_3 symmetry, and then various geometrical parameters have been used to describe this geometry and its relation to an undistorted octahedron.[33-35] Some of the parameters are illustrated in Figure 3. The calculation of these parameters in the cases where a crystallographic threefold axis is not present has been discussed.[34] We have adopted method (1) of Dymock and Palenik.[34]

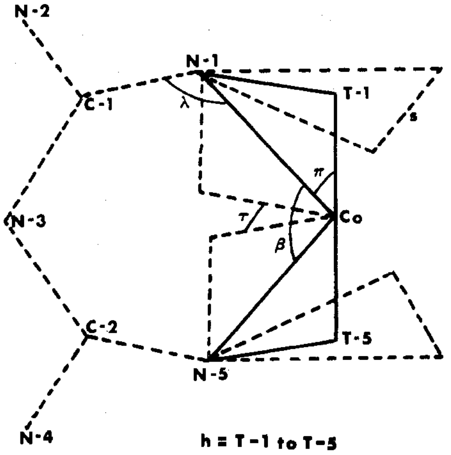

Figure 3.

The significance of all of the parameters listed in Table V should be obvious from Figure 3.

Spectroscopic Calculations and Results. Solution Spectra. The visible solution circular dichroism spectra of Λ-Co(Hbgd)$_3{}^{3+}$, Λ-Co(bgd)$_3$, and Δ-Co(acac)$_3$ in various solvents are given in Figure 4, and the visible region absorption and CD spectra are summarized in Table IV. The Λ-Co(Hbgd)$_3{}^{3+}$ and Δ-Co(acac)$_3$ data agree reasonably well with comparable results reported by other investigators.[19,36] The very similar results observed for Co(Hbgd)$_3{}^{3+}$ and Co(bgd)$_3$ suggest the possibility that the neutral species might be protonated in solution, but the solid-state spectra reported below, where very similar small red shifts are observed, would seem to discount this possibility.

An interesting feature of the Co(Hbgd)$_3{}^{3+}$ and Co(bgd)$_3$ CD spectra are the changes in the relative intensity of the two peaks in the $^1A_1 \rightarrow {}^1T_1$ (octahedral) region of the spectrum with changes in solvent.

Powder CD Spectra. The visible region CD spectra of powdered Λ-[Co(Hbgd)$_3$]Br$_3$·H$_2$O, Λ-Co(bgd)$_3$·2H$_2$O, and Δ-Co(acac)$_3$ in pressed KCl disks are shown in Figure 4. A comparison of these spectra with the corresponding solution spectra shows that the frequencies of the positive and negative components in the $^1A_1 \rightarrow {}^1T_1$ (octahedral) region have changed very little. The only change has been a small red shift of all of the bands. However, there have been marked changes in the relative intensities of the two bands in a given spectrum. In both the Λ-[Co(Hbgd)$_3$]Br$_3$·H$_2$O and Λ-Co(bgd)$_3$·2H$_2$O spectra, the intensity of the low-energy negative peak is much reduced relative to the high-energy positive peak, but a similar effect is not seen in the Δ-Co(acac)$_3$ spectrum.

Plane-Polarized Crystal Spectra. Because of the low symmetry of the crystals considered here, it is not possible to obtain plane-polarized single-crystal spectra parallel and perpendicular to the molecular threefold axis directly. Therefore, an elaboration of the procedure used by Piper[37] was used. Piper resolved the spectrum into two components perpendicular and parallel to the molecular threefold axis; we chose, instead, to resolve the spectrum into three mutually perpendicular components: one parallel to the molecular threefold axis (the A$_2$ component) and two mutually perpendicular components perpendicular to the threefold axis (the E$_\alpha$ and E$_\beta$ components). It was thought that, even if the electronic selection rules hold well enough to give reasonably good A$_2$ and E components, the intensity and position of the

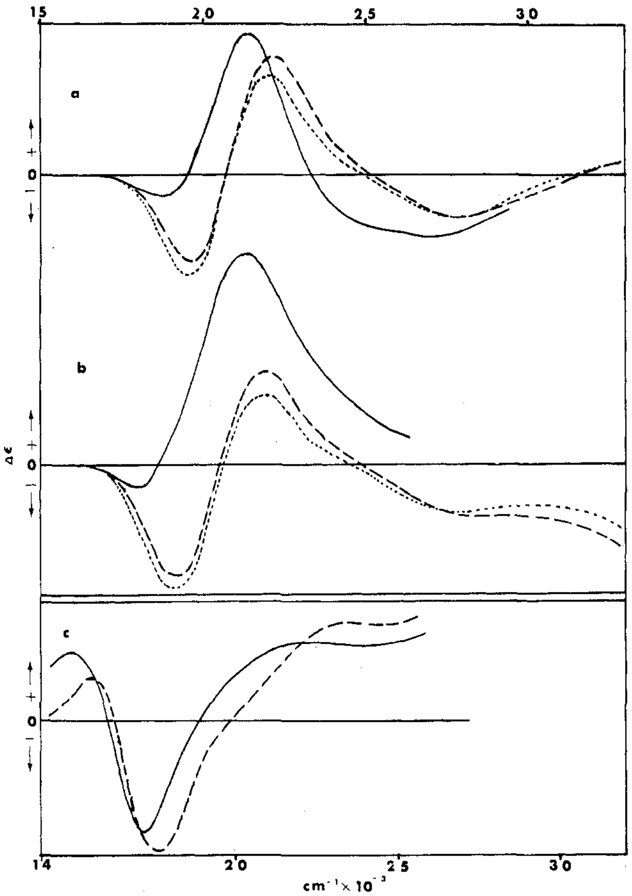

Figure 4. Circular dichroism spectra. (a) Λ-$Co(Hbgd)_3Br_3{\cdot}H_2O$: (—) KCl disk, (---) water solution, (···) methanol solution. (b) Λ-$Co(bgd)_3{\cdot}2H_2O$: (—) KCl disk, (---) methanol solution, (···) Me_2SO solution. (c) Δ-$Co(acac)_3$: (—) KCl disk, (---) cyclohexane solution.

E component could not be expected to be completely independent of direction in these low-symmetry crystals.

The following resolution procedure was followed. In the crystals examined, the molecular threefold axes are symmetrically disposed with respect to one of the crystallographic axes and describe a relatively small angle with respect to it. Following Piper, we call this angle the polar angle, θ, the crystallographic axis involved, z, and the plane perpendicular to z, the xy plane. There is no crystallographically unique way of choosing the two E components and so they were arbitrarily chosen so that one, E_α, was parallel to the xy plane and the other was in the plane defined by the z axis and the molecular threefold axis, E_β. Then if a polarized spectrum is taken with the propagation vector of the light beam parallel to the xy plane and the polarization vector parallel to the z axis, we have

$$A(\parallel) = (\cos^2\theta)A(A_2) + (\sin^2\theta)A(E_\alpha) \tag{1}$$

where A is absorbance. When both the propagation vector and the polarization vector of the light beam are in the xy plane we have

$$A(\perp) = (\sin^2\phi\,\sin^2\theta)A(A_2) + (\sin^2\phi\,\cos^2\theta)A(E_\alpha) + (\cos^2\phi)A(E_\beta) \tag{2}$$

where ϕ is the angle between the propagation vector and the projection of the molecular threefold axis onto the xy plane.

If the above analysis is meaningful, spectra taken with the propagation vector in different directions in the xy plane with the polarization vector parallel to z should be identical. This was found to be true within experimental error for crystals of Λ-$[Co(Hbgd)_3]Br_3{\cdot}H_2O$. Thus, any parallel spectrum and two perpendicular spectra at different values of ϕ should be sufficient for the decomposition of the spectrum.

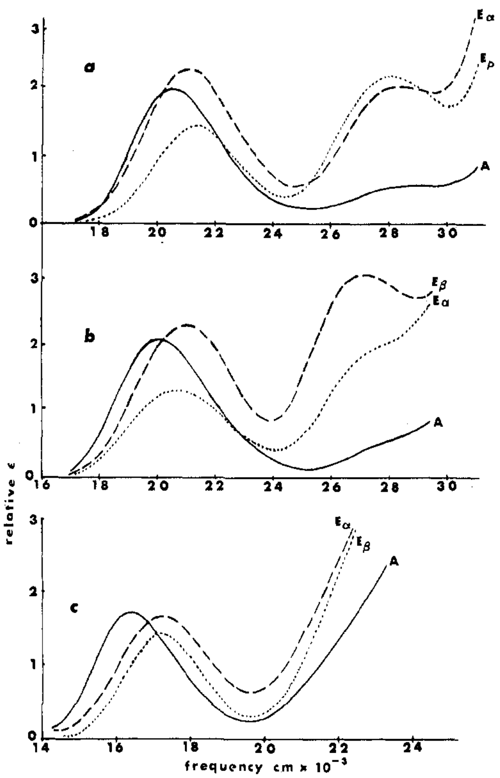

Figure 5. Calculated plane-polarized spectral components. The A components are parallel to the threefold axis of the complexes and the E components are perpendicular to the threefold axis: (a) Λ-$Co(Hbgd)_3Br_3{\cdot}H_2O$; (b) *rac*-$Co(bgd)_3{\cdot}2H_2O$; (c) *rac*-$Co(acac)_3$.

The results of a single-crystal study of Λ-$[Co(Hbgd)_3]Br_3{\cdot}H_2O$ are given in Figure 5a. In this crystal, the parallel direction is the crystallographic c axis, and $\theta = 12.15°$. The two perpendicular spectra were taken with the beam incident on the (010) face of the crystal ($\phi = 69.83°$) and on the (100) face of the crystal ($\phi = 20.17°$). The transformation matrix for this orientation is

$$\begin{matrix} A(A_2) \\ A(E_\alpha) \\ A(E_\beta) \end{matrix} = \begin{vmatrix} 1.0486 & 0.0076 & -0.0562 \\ 0 & 1.1560 & -0.1560 \\ -0.0486 & -0.1636 & 1.2122 \end{vmatrix} \times \begin{vmatrix} A(\parallel) \\ A(\perp)(100) \\ A(\perp)(010) \end{vmatrix} \tag{3}$$

The results for the $Co(bgd)_3{\cdot}2H_2O$ crystal are shown in Figure 5b. For this crystal, the parallel direction is the b axis, and $\theta = 19.74°$. In this crystal, the naturally occurring crystallographic faces parallel to b were not suitable for spectrographic purposes and so the crystals were cut and polished into two laminae with $\phi = 90°$ and $\phi = 11.2°$. For these orientations the transformation matrix is

$$\begin{matrix} A(A_2) \\ A(E_\alpha) \\ A(E_\beta) \end{matrix} = \begin{vmatrix} 1.1477 & 0 & -0.1477 \\ 0 & 1.0392 & -0.0392 \\ 0 & -0.1477 & 1.1477 \end{vmatrix} \times \begin{vmatrix} A(\parallel) \\ A(\perp)(11.2°) \\ A(\perp)(90°) \end{vmatrix} \tag{4}$$

The results for the $Co(acac)_3$ crystal are shown in Figure 5c. In this crystal, the parallel direction is the b axis and $\phi = 30.56°$. For the spectrum taken through the (100) face $\phi = 67.32°$ and through the (001) face $\phi = 14.28°$. These angles were calculated using the crystallographic data of Kruger and Reynhardt.[21]

$$\begin{matrix} A(A_2) \\ A(E_\alpha) \\ A(E_\beta) \end{matrix} = \begin{vmatrix} 1.5353 & 0.1007 & -0.6360 \\ 0 & 1.0770 & -0.0770 \\ -0.5353 & -0.2888 & 1.8241 \end{vmatrix} \times \begin{vmatrix} A(\parallel) \\ A(\perp)(001) \\ A(\perp)(100) \end{vmatrix} \tag{5}$$

Table IV. Summary of Spectral Properties (Band Maximum ν, cm^{-1} × 10^3; $\Delta\epsilon$, M^{-1} cm^{-1})

	ν ($\Delta\epsilon$)				
Spectral type	Λ-Co(Hbgd)$_3^{3+}$	Λ-Co(bgd)$_3$	Δ-Co(acac)$_3$	Λ-Co(Ox)$_3^{3-}$	Λ-Cr(Ox)$_3^{3-}$
Absorption (soln)	21.05^{d,e} 28.29^{d,e}	20.83^{d} 27 (sh)^{d}	16.89^{d,f}	16.61^{a} 23.70^{a}	17.51^{a} 27.30^{a}
CD (soln)	19.61 (−3.53)^{d,e,i} 22.12 (+4.74)^{d,e,i} 27.93 (−1.88)^{d,e,i}	19.53 (−4.7)^{d,h,j} 21.93 (+3.8)^{d,h,j} 27.78 (−2.1)^{d,h,j}	15.53 (+2.68)^{d,f,h,k} 17.70 (−8.38)^{d,f,h,k} 23.5 (+sh)^{d,f,k}	16.21 (+3.30)^{a,i}	15,87 (−0.58)^{d,i} 18.18 (+2.83)^{a,i} 24.10 (−0.56)^{a,i}
	19.53 (−4.1)^{d,j} 22.03 (+4.0)^{d,j} 27.78 (−1.7)^{d,j}	19.23 (−5.2)^{d,h,l} 21.83 (+2.9)^{d,h,l} 27.8 (+sh)^{d,h,l}	15.4 (−2.3)^{g,m} 17.4 (+6.1)^{g,m}		
Powder CD (KCl disk)	18.73 (−0.13)^{d,h} 21.37 (+0.88)^{d,h}	17.99 (−0.14)^{d,h} 21.28 (+1.30)^{d,h}	14.93 (+0.28)^{d,h} 17.12 (−0.86)^{d,h}	16.4 (+)^{b}	
CD (single cryst)	20.3 E (+)^{d}			16.1 E (+)^{a}	17.8 E (+)^{a} 24.4 E (−)^{a}
Plane polarized	20.5 A^{d} $\left.\begin{matrix}21.0\\21.3\end{matrix}\right\}E^{d}$	20.0 A^{d} $\left.\begin{matrix}20.6\\20.9\end{matrix}\right\}E^{d}$	16.4 A^{d} $\left.\begin{matrix}17.1\\17.2\end{matrix}\right\}E^{d}$	15.50 A^{c} 16.35 E^{c}	17.32 A^{c} 17.62 E^{c}

[a] Reference 15. [b] Reference 10. [c] Reference 5. [d] Present work. [e] Reference 36. [f] Reference 19. [g] Λ isomer: I. Jonas and B. Norden, *Inorg. Nucl. Chem. Lett.*, **12**, 43 (1976). [h] Relative intensities; sh = shoulder. [i] Water solvent. [j] Methanol solvent. [k] Cyclohexane solvent. [l] Me$_2$SO solvent. [m] Isopentane/ether (4/1) solvent.

An examination of these curves seems to indicate that the electronic selection rules appear to hold well enough that at least in a qualitative sense we have one "A-like" curve and two "E-like" curves. Certainly the behavior in the region of the $^1A_1 \rightarrow {}^1T_2$ (octahedral) transition, where the A_1 transition is electronically forbidden, would seem to indicate that a real separation has been achieved. However, the differences between the two E curves in each case would seem to be sufficiently large that the conventional characterization of the A_2–E separation in terms of a single trigonal parameter should not be used.

Single-Crystal CD Spectra. It is well-known that single-crystal CD spectra of low-symmetry crystals are difficult to obtain because of the presence of linear dichroism and birefringence. However, it was decided to attempt such a measurement. In the present case, if a satisfactory CD spectrum could be obtained with the propagation vector of the beam along the *c* axis of the Λ-[Co(Hbgd)$_3$]Br$_3$·H$_2$O crystal, the resulting spectrum should consist almost entirely of the E components because the molecular axis of the complex lies only about 12° from this axis. Thus, such a spectrum should lead to an unambiguous assignment of the signs of the rotational strengths of the trigonal components.

An analysis of the response of a conventional Grosjean and Legrand type circular dichroism spectrometer when a thin slice of an anisotropic crystal is placed in the beam[38] indicates that if a thin slice of Λ-[Co(Hbgd)$_3$]Br$_3$·H$_2$O with the faces of the slice perpendicular to the *c* axis is placed in the instrument with the *c* axis parallel to the propagation vector of the beam, eq 6 should hold, where CD is circular dichroism, LD is linear

$$\text{pen deflection} = P_{\nu\phi} \simeq \frac{\text{CD} + E(S\sin 2\phi - \text{LD}\cos 2\phi)}{1 + (\text{CD}^2 + \text{LD}^2)/2 + F(S\sin 2\phi - \text{LD}\cos 2\phi)} \qquad (6)$$

dichroism ($A_a - A_b$), S = [(LD)(CB) − (CD)(LB)]/2 (CB is circular birefringence, and LB is linear birefringence), ϕ is the angle between the *a* crystal axis and the electric vector of the plane-polarized light in the instrument, and E and F are numerical constants characteristic of the particular instrument but independent of wavelength.

Equation 6 suggests several possible procedures for the determination of CD. The procedure adopted was to measure $P_{\nu\phi}$ at 10° intervals from 0 to 360° and least-squares fit eq 6 with CD, LD, and S as adjustable parameters at each wavelength. The resulting "calculated" CD spectrum in the region of interest is given in Figure 6. The results are not given at frequencies greater than 25 × 10^3 cm^{-1}, because at higher frequencies both LD and S become very much larger than CD and the experimental measurements were not accurate enough to give meaningful results for the CD.

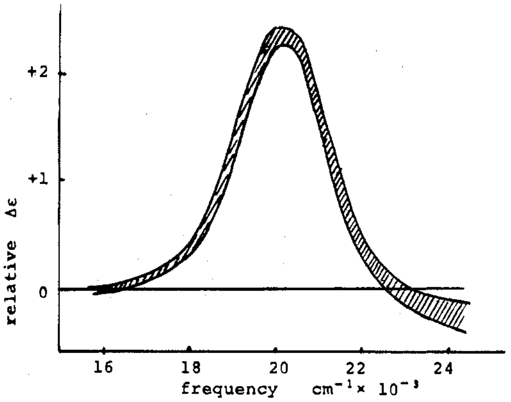

Figure 6. Calculated CD spectrum parallel to the *b* axis of Λ-Co(Hbgd)$_3$Br$_3$·H$_2$O. The band covers the scatter of the calculated points.

Figure 6 should not be considered to be more than semiquantitative. A check on the procedure was made by independently measuring the LD of the crystal used and comparing it with the LD calculated by the above procedure. The calculated and measured LD values agree within 10% which is probably within experimental error considering the well-known experimental difficulties associated with this type of measurement. It is difficult to make a realistic estimate of the possible error in our calculated CD values. However, Figure 6 should be reliable enough to unambiguously assign the E trigonal component to the positive CD band.

Discussion

The relevant spectral data for all of the cobalt(III) and chromium(III) symmetrical tris-bidentate complexes containing essentially planar unsaturated ligands for which both structural and spectral information are available are summarized in Table IV, and the relevant structural parameters are given in Table V.

It would seem that the assignment of the A_2 and E bands in the CD spectrum can be made with considerable confidence in all of these species. Λ-Co(Hbgd)$_3^{3+}$, Λ-Co(Ox)$_3^{3+}$, and

Table V. Structural Parameters Describing the MX_6 Unit[a]

Parameter	$Co(Hbgd)_3^{3+}$		$Co(bgd)_3$[d]	$Co(acac)_3$[e]	$Co(Ox)_3^{3-}$[f]	$Cr(Ox)_3^{3-}$[g]	Octahedron
a, Å	1.91[b]	1.92[c]	1.89	1.92	1.92	1.96	
b, Å	2.68[b]	2.68[c]	2.64	2.81	2.58	2.59	$2^{1/2}a$
s/*h*	1.221[b]	1.229[c]	1.265	1.153	1.301	1.295	1.225
τ, deg	58.4[b]	58.3[c]	57.0	67.3	54.1	50.5	60
β, deg	89.2[b]	88.9[c]	87.0	96.6	84.3	82.4	90
π, deg	54.6[b]	54.8[c]	55.6	53.1	56.4	56.1	54.7
λ, deg	129.1[b]	130.0[c]	127.3	123.4	111.5	110.5	

[a] Parameters as defined in Figure 3. [b] Reference 20. [c] Reference 32. [d] This work. [e] Reference 21. [f] Reference 41. [g] Reference 42.

Λ-$Cr(Ox)_3^{3-}$ can be assigned directly from the single-crystal CD results. We were unable to grow active single crystals of Λ-$Co(bgd)_3$, but the very great similarities between Λ-$Co(bgd)_3$ and Λ-$Co(Hbgd)_3^{3+}$ in all of the measured properties would seem to leave little doubt that the assignment of the CD band should be the same.

We were unable to obtain usable single-crystal CD spectra for Δ-$Co(acac)_3$, and so we are forced to rely on the assignment from the linear dichroism spectrum. In principle, the room-temperature band maxima in the absorption and CD spectra would not be expected to coincide exactly even if one could compensate for the extensive mutual cancelation which takes place in the CD spectrum. The quite different intensity mechanisms in the two types of spectra make this conclusion almost inevitable. Theoretical intensity equations support this conclusion.[39,40] However, an examination of the theoretical equations and of the very few experimental cases, where both single-crystal CD and LD are known accurately, indicates that the band maxima will probably not differ by more than 300–400 wavenumbers. The A_2–E separation in the linear-polarized spectrum of Λ-$Co(acac)_3$ is ~800 cm^{-1} with the A_2 component at lower energy. This rather large separation would seem to make it highly probable that the A_2 component will also be at lower energy in the CD spectrum. Therefore, we assign the lower energy positive band to the A_2 transition and the higher energy negative band to the E transition in Δ-$Co(acac)_3$ in agreement with previous workers.[19]

Our assignments indicate that, with the exception of $Co(Ox)_3^{3-}$, all of the species in Table IV show essentially the same CD behavior in the region of interest. For the Λ absolute configuration, they have an A_2 of negative sign at lower energy and an E component of positive sign at higher energy. The situation is not as clear in the case of $Co(Ox)_3^{3-}$ because the A_2 component was apparently not observed. The simplest explanation for this nonappearance is the assumption that the A_2 and E bands are so close together that the somewhat more strongly rotating E band completely hides the A_2 band. This explanation is supported by the small separation seen in the linear dichroism and also in the corresponding $Cr(Ox)_3^{3-}$ spectra. Some caution is necessary in the interpretation of the results with the oxalate complexes, because the spectral results and the structural results were not obtained on material of the same crystal structure. However, the very similar structural parameters obtained for $Co(Ox)_3^{3-}$ and $Cr(Ox)_3^{3-}$ in very different crystals, together with the very short bite and planar nature of the chelated oxalate ion, would seem to leave little doubt that these complexes would have similar structural parameters when incorporated into $KMgAl(Ox)_3{\cdot}9H_2O$ where the spectral studies were made.

The energy order $A_2 < E$ is usually associated with an elongation along the threefold axis of the complex,[5,43] but an examination of the structural parameters in Table V shows that the situation here is not so simple. The *s*/*h* ratio indicates that $Co(acac)_3$ is markedly elongated, $Co(Hbgd)_3^{3+}$ has very little axial distortion, $Co(bgd)_3$ is somewhat compressed, and the oxalate complexes are both markedly compressed. However, in the oxalate complexes $A_2 \simeq E$ while all of the others have $A_2 < E$ in energy. This is in sharp contrast to the situation with bidentate saturated ligands where the usual situation is small axial compressions and the energy order $A_2 > E$ applies.

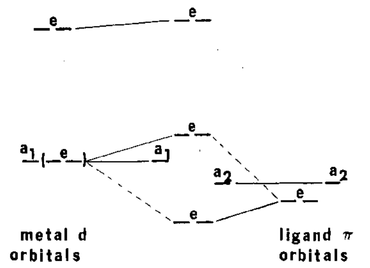

Figure 7. Interaction of the filled metal d orbitals and the highest energy filled π orbitals of the ligands.

It is possible to make a simple qualitative molecular orbital argument which leads to the conclusion that the filled π orbitals on the ligands should increase the energy of the E transition relative to the A_2 transition. If we consider the individual ligands to be planar with C_{2v} symmetry, then the highest energy occupied π orbital for all of the ligands considered here is of b_1 symmetry with relatively large coefficients on the ligating atoms. This can be demonstrated by simple Hückel calculations, and a MINDO/3 calculation on the biguanide gives the same result.

When three of these b_1 (C_{2v}) orbitals are combined in the D_3 symmetry of the complex, the overall ligand π orbitals are of a_2 and e symmetry. These e ligand orbitals will then interact with the e (D_3) metal d orbitals arising from the octahedral t_{2g} orbitals (Figure 7). The net effect of this interaction will be to raise the energy of the e (t_{2g}) metal orbitals relative to the a_1 (t_{2g}) orbital. Now if we examine the wave functions for the excited states,[44] we see that in the A_2 excited state the "hole" in the t_{2g} (O_h) orbitals is entirely in the e (D_3) orbitals. Thus, the net qualitative effect of increasing the energy of the e (t_{2g}) orbitals is to decrease the energy of both the A_2 and E transitions with A being decreased approximately twice as much as E. Thus, we would expect that an essentially undistorted octahedron would give the order $A_2 < E$ when the ligands contain π bonds. Experimentally, this is what we observe, and only in the markedly compressed oxalates do we have $A_2 \simeq E$.

It would seem as though the effect of any orbital mismatch (bond bending)[44] between the ligand and the metal should be relatively small in the species considered here. The effect of such mismatch is to make the "electronic" distortion "seen" by the metal atom different from the geometrical distortion as determined by x-ray results. If we assume that the "unstrained" metal–ligating atom–carbon angle λ should be 120°, the effect cannot be particularly large. The mismatch would tend to make the biguanide complexes slightly more compressed and the oxalate complexes slightly less compressed than the simple *s*/*h* ratio would indicate, while the $Co(acac)_3$ would be virtually unaffected. The overall changes would almost certainly be too small to affect the general conclusions about the effects of π bonding and geometrical distortions given above.

The complexes considered here all have strongly allowed rotatory bands in the ultraviolet region at much lower energies than the corresponding complexes containing saturated ligands which should facilitate intensity borrowing from the allowed bands.[45] The fact that these complexes show considerable rotatory strength in the region of the second d–d band, $A_1 \rightarrow T_2$, would seem to support such a mechanism. On the other hand, the identity of the near-UV CD bands is not known, so a quantitative calculation cannot be made.

The observed signs of the trigonal components of the CD spectra do not seem to be amenable to a simple theoretical explanation. For a given absolute configuration, the A_2 and E bands do not change sign in going from the strongly axially elongated ($s/h < 1.225$) azimuthally expanded ($\tau > 60°$) Co(acac)$_3$, through the almost undistorted Co(Hbgd)$_3^{3+}$, to the strongly axially compressed, azimuthally contracted oxalate complexes. In all cases, the Λ isomer gives rise to a negative A_2 band and a positive E band. This does not seem to be in accord with the theoretical predictions of either the static one-electron model[5,44–46] or the dynamic-coupling model[47] for the optical activity. It also seems to differ from the limited experimental results for complexes with saturated ligands.[7]

There should be no conformational contribution to the activity due to chiral puckering of the chelate rings in the species under consideration here because in all cases the ligand rings are essentially planar. Thus, the activity should be entirely of a configurational nature. The nonligating atoms should contribute very little to the activity because of their relatively great distance from the metal. Thus, the activity should arise largely from the displacement of the ligating atoms from the octahedral positions.[47] To a first approximation, we should be able to predict the signs of the components by considering only the locations of the ligating groups.

In this approximation Λ ($\tau > 60°$) and Δ ($\tau < 60°$) will lead to the same signs for the components in either the static one-electron model or the dynamic-coupling model when the ligating atoms are considered to be isotropic about the bond axis. Clearly, the experimental results are not in agreement with this prediction. Thus, it would seem that a theoretical treatment which recognizes the anisotropic nature of the ligating atoms is going to be necessary to explain these results.

Our results clearly indicate that the common practice of attributing differences in relative intensities in the solid state and in solution to differences in conformation of the chelate rings or chiral hydrogen bonding should be viewed with caution. We observe quite marked changes in relative intensities in going from the solid state to various solutions which clearly cannot arise from either of these effects.

CD Spectra and Absolute Configuration. The search for simple reliable correlations which would enable one to relate the absolute configuration of a complex and its CD spectrum in the d–d region has been a frustrating one, and the situation has been confused by many absolute configuration assignments in the literature which rest on questionable grounds. The structure–spectra question here can be broken into two parts: (1) Given the CD spectrum of a complex (solution, KBr, or single crystal), is it possible to unambiguously assign the absolute configuration? (2) Given the absolute configuration and the structure, is it possible to predict the CD spectrum using one of the available theoretical models? We conclude that both of these questions must currently be answered in the negative.

When confronted with the CD spectrum for a tris-bidentate d^3 or d^6 complex of D_3 or C_3 symmetry, the first problem is to decide which band is A_2 and which is E. As mentioned above, apparently the only completely reliable method of doing this is the single-crystal CD spectrum. However, various other methods have been used, all of which have led to at least one incorrect assignment. The simplest of these is the empirical rule that the E band is the more intense,[15] but the numerous exceptions[48] make this rule of doubtful utility. Note that rules concerning the net rotation[49,50] can be included here.

The oxyanion "gegenion" procedure[51] has had some success, but it seems to give misleading results in at least two cases.[20,43] The hydrogen bonding proposed to explain this effect undoubtedly affects the CD spectrum,[10] but the details do not seem to be well enough understood to support predictions. In addition, the enhancement of the A_2 bands of Co(bgd)$_3$ and Co(Hbgd)$_3^{3+}$ in various solutions reported above must arise from a different cause.

As was discussed above, the A_2–E energy order in the CD spectrum can probably be predicted from the order in the LD spectrum provided that the separation is fairly large (greater than about 400 cm^{-1}), but the uncritical acceptance of a separation of 180 cm^{-1} in the LD spectrum[52] has led to an incorrect assignment for Co(mal)$_3^{3-}$.[10]

Unfortunately, even the correct assignment of the A_2 and E bands does not completely solve the spectrum-to-absolute configuration problem. It has been stated[9] that a positive E band implies a Λ configuration and negative E band implies a Δ configuration, but this is not in accord with most theoretical models[5,44,47] or with the experimental results on Co(tn)$_3^{3+}$.[43]

In view of the above discussion, we feel that all assignments of absolute configurations made solely on the basis of d–d CD spectra must be viewed with caution.

The situation with respect to the structure-to-spectrum question does not seem to be much better. A detailed knowledge of the geometry of the complex is necessary to apply most of the theoretical models, but even this information does not seem to permit a completely satisfactory interpretation of all of the observed spectra. The models of Karipides and Piper[5] and Mason and Seal[47] seem to correctly predict the spectra of complexes containing saturated diamines and similar ligands. On the other hand, as was discussed above, none of the available models seem adequate to explain the results reported here for planar unsaturated ligands where the spectrum appears to be affected by the π electrons on the ligands. For example, we have been unable to explain the experimental observation that Δ-Co(tn)$_3^{3+}$ and Λ-Co(acac)$_3$ both of which are axially elongated and azimuthally expanded have qualitatively very similar spectra using any of the available theoretical models.

Results which seem to be qualitatively similar to ours have been reported for other ligands where π bonding would be expected to be a factor.[10,53] However, we feel that there are probably still too few cases involving ligand π bonding for which accurate structures and absolute configurations are known to support any generalizations.

Acknowledgment. The help of the Office of Computer Services, Georgia Institute of Technology, is appreciated. We thank Dr. E. M. Burgess for making the MINDO/3 calculation on biguanide.

Registry No. *rac*-Co(bgd)$_3$·2H$_2$O, 65832-83-9; Λ-Co(Hbgd)$_3$Br$_3$, 65802-31-5; Λ-Co(bgd)$_3$, 65831-51-8; Δ-Co(acac)$_3$, 50600-77-6.

Supplementary Material Available: A listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) S. F. Mason, "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism", Ciardelli and Salvatory, Ed., Heyden and Son Ltd., London, 1973, Chapter 3.6.
(2) Y. Saito, *Coord. Chem. Rev.*, **13**, 305 (1974), and references therein.
(3) D. J. Caldwell and H. Eyring, "The Theory of Optical Activity", Wiley-Interscience, New York, N.Y., 1971.
(4) S. Mason, *Q. Rev., Chem. Soc.*, **17**, 20 (1963).

(5) A. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).
(6) R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, **49**, 433 (1976).
(7) R. R. Judkins and D. J. Royer, *Inorg. Chem.*, **13**, 945 (1974).
(8) B. Bosnich, "Fundamental Aspects and Recent Developments in Optical Dispersion and Circular Dichrosim", Ciardelli and Salvatory, Ed., Heyden and Son Ltd., London, 1973, Chapter 3.7.
(9) R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, and C. F. Weich, *J. Chem. Soc., Dalton Trans.*, 1385 (1974).
(10) K. R. Butler and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 251 (1976).
(11) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).
(12) P. G. Beddoe, M. J. Harding, S. F. Mason, and P. G. Peart, *Chem. Commun.*, 1283 (1971).
(13) R. Kuroda, J. Fujita, and Y. Saito, *Chem. Lett.*, 225 (1975).
(14) Single-crystal CD spectra of eight cobalt(III) and chromium(III) complexes have been reported: ref 6, 15, 43; H. P. Jensen and F. Galsbøl, *Inorg. Chem.*, **16**, 1294 (1977).
(15) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).
(16) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).
(17) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **33**, 98 (1960).
(18) R. Dingle and C. J. Ballhausen, *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **35**, No. 12 (1967).
(19) R. B. Von Dreele and R. C. Fay, *J. Am. Chem. Soc.*, **93**, 4936 (1971).
(20) M. R. Snow, *Acta Crystallogr., Sect. B*, **30**, 1850 (1974).
(21) G. J. Kruger and E. C. Reynhardt, *Acta Crystallogr., Sect. B*, **30**, 822 (1974).
(22) D. Karipides and W. C. Fernelius, *Inorg. Synth.*, **8**, 56 (1963).
(23) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **16**, 621 (1939).
(24) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941).
(25) B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, **5**, 188 (1957).
(26) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1965, p 99.
(27) J. A. Bertrand, E. Fujita, and P. G. Eller, *Inorg. Chem.*, **13**, 2067 (1974).
(28) P. W. R. Clearfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(29) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(30) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(31) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(32) N. C. Moucharafieh, Ph.D. Thesis, Georgia Institute of Technology, 1976.
(33) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, **11**, 434 (1972).
(34) K. R. Dymock and G. J. Palenik, *Inorg. Chem.*, **14**, 1220 (1975).
(35) A. Avdeef and J. P. Fackler, Jr., *Inorg. Chem.*, **14**, 2002 (1975).
(36) K. Michelsen, *Acta Chem. Scand.*, **19**, 1175 (1965).
(37) T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).
(38) D. J. Royer, *Inorg. Chem.*, **17**, 512 (1978).
(39) S. H. Lin, *J. Chem. Phys.*, **55**, 3546 (1971).
(40) C. O. Hill and S. H. Lin, *Trans. Faraday Soc.*, **67**, 2833 (1971).
(41) K. R. Butler and M. R. Snow, *J. Chem. Soc. A*, 565 (1971).
(42) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **5**, 499 (1952).
(43) R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).
(44) A. D. Liehr, *J. Chem. Phys.*, **68**, 665 (1964).
(45) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).
(46) G. Hilmes and F. S. Richardson, *Inorg. Chem.*, **15**, 2582 (1976).
(47) S. F. Mason and R. H. Seal, *Mol. Phys.*, **31**, 755 (1976).
(48) In addition to the work reported here, other examples are given in ref 6, 10, and 55. Also see M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **27**, 2187 (1971); H. Toftlund and E. Pedersen, *Acta Chem. Scand.*, **26**, 4019 (1972); and S. S. Isied, G. Kuo, and K. N. Raymond, *J. Am. Chem. Soc.*, **98**, 1763 (1976).
(49) F. S. Richardson, *J. Phys. Chem.*, **75**, 692 (1971).
(50) F. S. Richardson, *Inorg. Chem.*, **11**, 2366 (1972).
(51) S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 307 (1966), and references therein.
(52) W. E. Hatfield, *Inorg. Chem.*, **3**, 605 (1964).
(53) K. Abu-Dari and K. N. Raymond, *Inorg. Chem.*, **16**, 807 (1977).

Contribution from the Laboratoire de Polarographie Organique Associé au CNRS (LA 33), Université de Dijon, 21000 Dijon, France,
the Département de Recherche Fondamentale (EOA), Equipe de Recherche Associée au CNRS (ERA 675),
Centre d'Etudes Nucléaires de Grenoble, 38041 Grenoble Cedex, France, and the Laboratoire de Cristallographie,
Equipe de Recherche Associée au CNRS (ERA 162), Université de Nancy I, 54037 Nancy Cedex, France

Peroxotitanium(IV) Porphyrins. Synthesis, Stereochemistry, and Properties

ROGER GUILARD,*[1a] JEAN-MARC LATOUR,[1b] CLAUDE LECOMTE,[1c] JEAN-CLAUDE MARCHON,*[1b]
JEAN PROTAS,*[1c] and DENIS RIPOLL[1a]

Received July 22, 1977

Reaction of hydrogen peroxide with several oxotitanium(IV) porphyrin complexes $PTi^{IV}O$ under mild conditions affords the corresponding peroxotitanium(IV) complexes $PTi^{IV}(O_2)$. The structures of 2,3,7,8,12,13,17,18-octaethylporphinatoperoxotitanium(IV), OEPTi(O_2), and 2,3,7,8,12,13,17,18-octaethylporphinatooxotitanium(IV), OEPTiO, have been determined from three-dimensional x-ray diffraction data. The peroxo complex crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 14.603$ (6) Å, $b = 23.266$ (8) Å, $c = 9.793$ (3) Å, and $\beta = 105.0$ (2)°. The structure was solved by direct methods. Least-squares refinement has led to a final value of the conventional R index of 0.064 based on 3415 reflections. The titanium atom is hexacoordinated to the four nitrogen atoms and to the two oxygen atoms. The latter are bonded to the metal in a symmetrical fashion and eclipsed with respect to two nitrogen atoms. The O–O bond length is 1.445 (5) Å, the two Ti–O bond lengths are 1.827 (4) and 1.822 (4) Å, and the average Ti–N bond distance is 2.109 (4) Å. The titanium atom lies at 0.620 (6) Å out of the mean plane of the four nitrogen atoms toward the dioxygen ligand. The oxo complex OEPTiO crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 14.407$ (6) Å, $b = 23.126$ (8) Å, $c = 9.793$ (3) Å, and $\beta = 104.2$ (2)°. The structure was solved assigning the fractional coordinates found for the OEPTi(O_2) complex to the titanium, nitrogen, and carbon atoms. Least-squares refinement has led to a final value of the conventional R index of 0.067 based on 3570 reflections. The titanium atom is pentacoordinated to the four nitrogen atoms and to the oxygen atom. The Ti–O bond length is 1.613 (5) Å and the average Ti–N bond distance is 2.114 (6) Å. The titanium atom is found to be 0.555 (6) Å out of the plane of the four nitrogen atoms toward the oxygen atom. ^1H and ^{13}C dynamic nuclear magnetic resonance studies on OEPTi(O_2) and TPPTi(O_2) (TPP is 5,10,15,20-tetraphenylporphinato) show that these are fluxional molecules. At room temperature and down to about −50 °C, the peroxo ligand undergoes fast exchange between two equivalent sites where the two oxygen atoms eclipse the two equivalent pairs of opposite nitrogen atoms. The barrier to rotation of the peroxo group at the coalescence temperature T_c is 10.8 ± 0.5 kcal mol^{-1} ($T_c = -50$ °C) for TPPTi(O_2) and 9.9 ± 0.5 kcal mol^{-1} ($T_c = -65$ °C) for OEPTi(O_2). Peroxotitanium(IV) porphyrin complexes undergo three successive electron-transfer reactions at a platinum cathode in dichloromethane solution. The first step is bielectronic and irreversible and leads to the corresponding oxotitanium(IV) complex by reductive cleavage of the O–O bond.

Dioxygen complexes of the transition-metal porphyrins are the focus of active current research.[2] These complexes can be considered as synthetic analogues of the hemoproteins which are involved in the transport and activation of molecular oxygen. Much work has been devoted to such model compounds toward a better understanding of the bonding and reactivity of the dioxygen ligand in the biological systems. A major breakthrough was obtained in the isolation and x-ray structure determination of the dioxygen adduct of a ferrous "picket fence" porphyrin.[3] Dioxygen adducts have also been obtained with cobalt(II),[4] chromium(II),[5] and manganese(II) porphyrins.[6] The bonding of O_2 in these complexes is best

0020-1669/78/1317-1228$01.00/0