

brational time scale. A possibly more appropriate choice for the frequency factor in the adiabatic limit is $k_b T/h$, which lowers the optically predicted rate constant by 1 order of magnitude giving $k_{12} \geq 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

In any case, given the estimates needed in calculating the two values for k_{12} , the agreement obtained is remarkable. Although further tests of this kind are essential, of the examples where CT transitions have been used to estimate thermal electron-transfer rate constants, the agreement obtained⁴ and the prospects for future experiments of the same kind in a variety of systems are very encouraging. In any given system, a detailed theoretical understanding of the full solvent and molecular contributions to E_{op} may be difficult. However, in principle, these details are contained intrinsically in the properties of the optical transition. As long as the optical and thermal processes are related, what can be measured optically

is also known for the thermal process. The possibility clearly exists that for a variety of CT-type transitions the properties of the optical absorption bands contain detailed information about the innate electron-transfer characteristics of the redox sites involved and that this information may be obtainable by a relatively simple deconvolution of CT absorption bands.

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Registry No. $\text{Fe}(\text{CN})_6^{3-}$, 13408-62-3; $\text{Fe}(\text{CN})_6^{4-}$, 13408-63-4; PQ^{2+} , 4685-14-7; PQ^+ , 25239-55-8.

Notes

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ESR Spectra of Low-Symmetry High-Spin Cobalt(II) Complexes. 7.¹ Trigonal-Bipyramidal Pentakis(picoline *N*-oxide)cobalt(II) Perchlorate

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We have recently started a program of characterization of the ESR spectra of high-spin cobalt(II) complexes and have found that octahedral^{1,2} and square-pyramidal³ complexes on one side and tetrahedral complexes^{4,5} on the other side are very sensitive to low symmetry components of the ligand field. In all the reported cases, the ESR spectra could be interpreted by using an $S = 1/2$ effective spin Hamiltonian. In particular tetrahedral complexes are characterized by g values ranging from 6.7 to 1.5, while square-pyramidal complexes can give g values higher and lower than these limits. Further the hyperfine splitting in tetrahedral complexes is in general small⁶⁻⁸ so that often it is not resolved, while it tends to be larger in octahedral and square-pyramidal complexes. Trigonal-bipyramidal complexes have an orbitally nondegenerate ground state,^{9,10} so that their ESR spectra should not be dissimilar from those of tetrahedral complexes. In order to verify if there is any possibility to discriminate between these two stereochemistries through ESR spectra, we wish to report

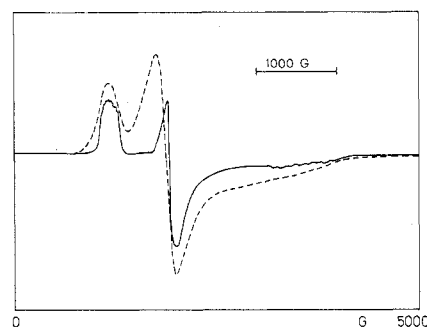


Figure 1. Polycrystalline powder ESR spectra of $\text{Co}(\text{picoline } N\text{-oxide})_5(\text{ClO}_4)_2$ (---) and of $(\text{Zn,Co})(\text{picoline } N\text{-oxide})_5(\text{ClO}_4)_2$ (—) recorded at 4.2 K at X-band frequency, in the range 0–5000 G.

Table I. Principal g Values and Direction Cosines for $\text{Co}(\text{picoline } N\text{-oxide})_5(\text{ClO}_4)_2$

g	crystallographic frame ^a			molecular frame ^b		
1.86 (3)	0.1825	0.1608	0.9700	0.1169	-0.0725	0.9905
3.53 (2)	0.9638	0.2245	0.1141	0.9904	-0.0662	-0.1217
5.67 (1)	0.1946	0.9611	-0.1960	0.0744	0.9951	0.0641

^a The crystallographic frame is a^*bc . ^b The molecular frame is centered on the metal atom with z parallel to the $\text{Co}-\text{O}_2$ bond direction and x parallel to a projection of the $\text{Co}-\text{O}_3$ bond direction in the plane orthogonal to z .

here the ESR spectra of pentakis(picoline *N*-oxide)cobalt(II) perchlorate which has been shown to contain fairly regular trigonal-bipyramidal CoO_3 chromophores^{11,12} and which has electronic spectra that have been characterized through a single-crystal polarized-light experiment.¹²

Experimental Section

The cobalt and zinc derivatives were obtained from ethanolic solutions of stoichiometric amounts of picoline *N*-oxide and the perchlorate of the metals. The needlelike crystals of pure and diluted complexes were grown in butanolic solutions with triethyl orthoformate in a slow stream of dry nitrogen. They were oriented by the Weissenberg technique, according to a previous report.¹²

ESR spectra down to 4.2 K were recorded with the apparatus described elsewhere.²

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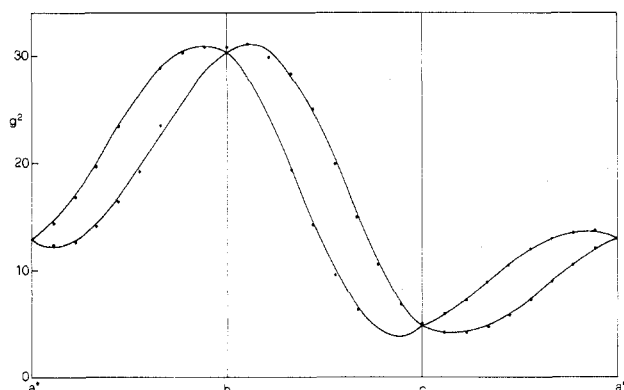


Figure 2. Angular dependence of the g^2 tensor in three rotations along the crystallographic axes c , a^* , and b . The curves correspond to the least-squares fit to experimental points.

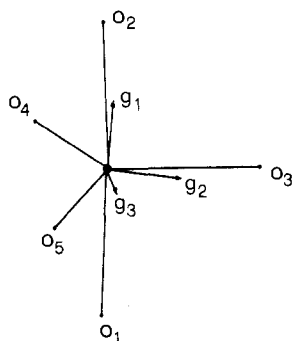


Figure 3. Principal directions of the g tensor within the molecular frame.

Table II. Angles (Deg) between the Principal g Directions and the Relevant Bond Directions

g_1 -Co-O ₂	5
g_2 -Co-O ₃	9

Results and Discussion

The polycrystalline powder ESR spectra of the pure and the magnetically diluted complexes recorded at 4.2 K are shown in Figure 1. The g values are practically identical in the two spectra: $g_1 = 1.86$, $g_2 = 3.52$, $g_3 = 5.67$. In the spectra of the complex diluted into the zinc lattice a hyperfine structure is resolved on g_1 and g_3 , yielding $A_1 = 97 \times 10^{-4} \text{ cm}^{-1}$, $A_2 < 20 \times 10^{-4} \text{ cm}^{-1}$, and $A_3 = 77 \times 10^{-4} \text{ cm}^{-1}$.

Due to the identity of the g values for the pure and the diluted complexes, single-crystal spectra only for the former were recorded, since they are simpler to interpret. The angular dependence of the g^2 values in three experimental rotations are shown in Figure 2. The principal g values and directions, obtained by the Schonland's method,¹³ are given in Table I. The orientation of the g tensor in the molecular frame is given in Figure 3, and the angles of the g directions with relevant bond directions are given in Table II. The lowest g value is found to be quite close to the "trigonal axis" of the bipyramid, while g_2 is almost coincident with the Co-O₃ bond direction. These directions correspond to those previously used in the interpretation of the electronic spectra, which was based on a C_{2v} symmetry.¹²

The data confirm that only the transition within the lowest Kramers doublet is seen. With use of the spin Hamiltonian approach,¹⁴ with the additional assumptions $g_x = g_y = g_{\perp}$ and D large, the following parameters are calculated: $g_{\parallel} = 2.03$, $g_{\perp} = 2.38$, $\lambda = E/D = -0.16$. These spin Hamiltonian pa-

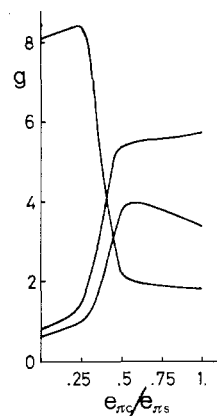


Figure 4. Dependence of calculated g values on varying the $e_{\pi c}/e_{\pi s}$ in the range 0-1. The other bond parameters are $B = 850 \text{ cm}^{-1}$, $\zeta = 533 \text{ cm}^{-1}$, $k = 0.85$, $e_{\sigma}^{\text{ax}} = 4725 \text{ cm}^{-1}$, $e_{\pi}^{\text{ax}} = 1185 \text{ cm}^{-1}$, $e_{\sigma}^{\text{eq}} = 5250 \text{ cm}^{-1}$, and $e_{\pi}^{\text{eq}} = 1315 \text{ cm}^{-1}$.

rameters can be reproduced also by using an angular overlap (AO) approach.⁵ The parameters which are required are e_{σ} , $e_{\pi s}$, and $e_{\pi c}$ for each ligand. However the three equatorial ligands show similar bond distances (197.7, 198.7, 198.9 pm) so that the same e_{λ} parameters were used for them. The two axial ligands have slightly different bond distances (210.4, 205.8 pm), but since they are almost on the same line passing through the cobalt atom, it is possible to use e_{λ} parameters which are the average of the e_{λ} values for the two individual ligands.

A detailed analysis of the electronic spectra yielded the AO parameters, in the assumption of isotropic π interactions. Using the same values for the calculations of g yielded as a best fit $g_1 = 1.896$, $g_2 = 3.532$, $g_3 = 5.680$ ($e_{\sigma}^{\text{ax}} = 4725 \text{ cm}^{-1}$, $e_{\pi}^{\text{ax}} = 1185 \text{ cm}^{-1}$, $e_{\sigma}^{\text{eq}} = 5250 \text{ cm}^{-1}$, $e_{\pi}^{\text{eq}} = 1315 \text{ cm}^{-1}$, $k = 0.85$, $B = 850 \text{ cm}^{-1}$, $\zeta = 533 \text{ cm}^{-1}$, $A_1 = 86 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 11 \times 10^{-4} \text{ cm}^{-1}$, and $A_3 = 68 \times 10^{-4} \text{ cm}^{-1}$ ($\kappa = 0.34$, $P = 235 \times 10^{-4} \text{ cm}^{-1}$).

Recently the magnetic susceptibility¹⁵ and ESR¹⁶ data of hexakis(pyridine *N*-oxide)cobalt(II) perchlorate have been reported and interpreted within the same AO formalism.¹⁵ In that case the observed large anisotropy in the magnetic susceptibility and g values could be reproduced only by using anisotropic e_{π} values; i.e., $e_{\pi x} \neq e_{\pi y}$ was assumed. In particular, on the basis of the assumption of sp^2 hybridized oxygen donors, $e_{\pi x} = 1/2 e_{\pi y}$ was assumed.¹⁷ The bond distances in the octahedral complex are very similar to those observed for the axial donors in the present case (206.0 vs. 208.1 pm),¹⁸ so that similar values of the e_{λ} parameters might be anticipated. Also the M-O-N angle is very close to 120° , in agreement with sp^2 hybridization.

We tried to fit the g and A values and the energies of the electronic transitions by using the same e_{λ} values for the axial donors as in the octahedral case and allowing for an increase of 10-15% for the equatorial ones. The results, however, were totally disappointing since both the electronic transitions and the g values were not reproduced. This result can be understood by looking at the variation of the $e_{\pi c}/e_{\pi s}$ ratio in the range 0-1, with the other parameters fixed at the values for which a good fit of g and A was found, as given in Figure 4. It is apparent that approaching the limit $e_{\pi x} = 1/2 e_{\pi y}$ determines

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a reduction of the anisotropy, and also the principal directions of g are rotated by large angles from the positions experimentally observed. Therefore, it is possible that $e_{\pi c} \neq e_{\pi s}$ also in the present case, but the anisotropy must be smaller than that suggested for sp^2 oxygen.

Our feeling is that anisotropic e_{λ} values are actually required for the interpretation of the spectral and magnetic properties of pyridine N -oxide complexes but that large significance cannot be given to prediction based on orbital hybridizations.

The g_z value observed in the present case is smaller than those observed for tetrahedral complexes,^{4,5} and also the hyperfine splitting is larger in the present case than usually observed for tetrahedral complexes, but more experimental data are required before any significant trend is obtained.

Registry No. Co(picoline N -oxide)₃(ClO₄)₂, 21460-56-0; Zn(picoline N -oxide)₃(ClO₄)₂, 74763-42-1.

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Induced Optical Activity in the Terbium(III) Complex of Pyridine-2,6-dicarboxylic Acid through Association with Resolved Tris(ethylenediamine)chromium(III)

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The observation of optical activity in a racemic mixture of a labile complex upon addition of a chiral compound is termed the Pfeiffer effect and serves as a useful means to study the chiroptical spectra of compounds that are too labile to be resolved into enantiomers.^{1,2} Almost all of the Pfeiffer-active systems have involved a racemic metal complex and some chiral organic molecule, but two studies have been reported in which the added chiral agent was a dissymmetric metal complex.³ In our present study, we wish to report the third Pfeiffer-active system, in which a chiral metal complex induces optical activity in another metal complex, and the first Pfeiffer-active system involving a lanthanide complex. The induced optical activity has been studied by means of circularly polarized luminescence (CPL) spectroscopy rather than circular dichroism (CD) spectroscopy, since the low absorptivity of Tb(III) complexes in the visible region makes any CD measurement of f - f optical activity difficult. On the other hand, the Tb(III) complexes tend to be strongly luminescent, and therefore the CPL technique is the preferable method to study lanthanide optical activity. The work presented here also represents the first measurement of a classical Pfeiffer effect by means of CPL spectroscopy.

Experimental Section

Tb(III) stock solutions were obtained by dissolving Tb₄O₇ (obtained as 99.9% pure, Kerr-McGee) in the minimum amount of 70% HClO₄, neutralizing to pH 3 with NaOH, and then diluting to the desired volume. Pyridine-2,6-dicarboxylic acid (which shall be abbreviated as DPA) was obtained from Aldrich and used as received. The Tb(DPA)₃³⁻ complex was prepared by mixing the Tb(III) and DPA stock solutions in a 1:3 mole ratio; this procedure yielded material which analyzed properly for Tb(DPA)₃³⁻. The tris(ethylenediamine)chromium(III) complex was prepared⁴ and resolved⁵ according to literature methods.

The CPL spectra were all taken at pH 8 and were recorded on a high-resolution spectrometer constructed in this laboratory. This

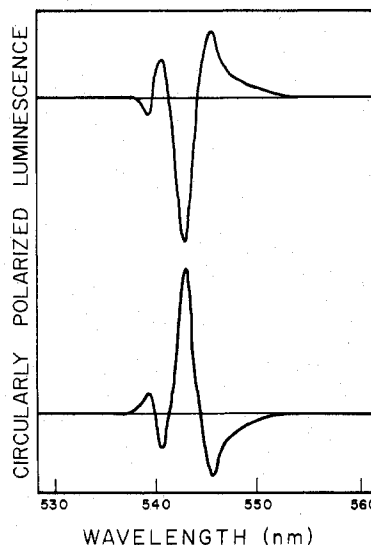


Figure 1. CPL spectra of Tb(DPA)₃³⁻/Δ-Cr(en)₃³⁻ (upper) and Tb(DPA)₃³⁻/Δ-Cr(en)₃³⁺ (lower). Both intensity scales are arbitrary.

apparatus has been described in detail.⁶ The Tb(DPA)₃³⁻ complex was excited at 290 nm, and the emitted light was analyzed by a grating monochromator whose resolution was set to a 10-Å band-pass. Further increases in resolution did not lead to any improvement of the spectral features. The induced optical activity was found to increase when excess Cr(en)₃³⁺ was added in solid form to an aqueous solution of Tb(DPA)₃³⁻ at pH 8.

Results and Discussion

The CPL spectra presented in Figure 1 clearly indicate that the racemic Tb(DPA)₃³⁻ complex can be partially resolved upon addition of either enantiomer of Cr(en)₃³⁺. The Tb(DPA)₃³⁻ complex is quite unique among lanthanide complexes in that the metal is observed to be 9-coordinate, and yet the complex possesses a C₃ axis and an approximate D₃ symmetry in solution.⁷ This molecular symmetry implies that the complex theoretically is resolvable into enantiomers, but the high degree of lability associated with Tb(III) ensures that only racemic mixtures of rapidly interconverting Δ and Λ enantiomers can be prepared.

The mirror-image relationship of the CPL spectra induced by the Δ and Λ forms of Cr(en)₃³⁺ strongly suggests that a definite isomer of the Tb(DPA)₃³⁻ is enriched in each case and that opposite enantiomers of the Tb(III) complex are enriched by opposite enantiomers of the Cr(III) complex.

During the course of CPL measurement, two observables are recorded. One is the mean total luminescence (TL) intensity, given by

$$I = \frac{1}{2}(I_L + I_R) \quad (1)$$

and the other is the differential luminescent intensity (CPL), given by

$$\Delta I = I_L - I_R \quad (2)$$

where I_L and I_R refer to the emitted intensities of left and right circularly polarized light, respectively. Since I and ΔI are normally measured in relative units, it is of value to calculate the luminescence dissymmetry factor:

$$g_{lum} = \Delta I / I \quad (3)$$

The g_{lum} factor is also of theoretical interest, since it is related to the dipole and rotational strength of the transition.⁸ We have calculated the values of g_{lum} for the major CPL component (found at 543 nm) in the Tb(DPA)₃³⁻ spectra and have

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