$Zn(C_5H_7O_2)_2$, 190°,[22] and $Cr(C_5H_7O_2)_3$, 250°.[23] Consequently, in view of their demonstrated chelating ability, they may prove of value in improving the thermal stability of our chelated coordination polymers.[1]

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[22] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

[23] J. von Hoene, R. G. Charles, and W. W. Hickam, *ibid.*, **62**, 1098 (1958).

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Optical Activity of Pseudotetragonal Coordination Compounds. The Dissymmetric Ligand Field in Diacidobis(*l*-propylenediamine)cobalt Complexes

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The circular dichroism and absorption spectra of $Co(l\text{-pn})_2Cl_2^+$ and $Co(l\text{-pn})_2(NO_2)_2^+$ are reported. The assignments are discussed. Point charge and molecular orbital models are proposed for the molecules. Electric moments calculated from the circular dichroism indicate that virtually all of the intensity in the absorption spectra is vibronic in origin.

Optical activity and in particular circular dichroism is beginning to provide new information about molecular and electronic structure of coordination compounds. Recent attention has centered on predominantly d–d transitions of trigonal complexes such as $Co(en)_3Cl_3$ in both experimental studies[1,2] and theoretical analyses.[2,3] Complexes with pseudotetragonal symmetry are relatively unstudied but for the early experimental work of Mathieu[4] and a recent proposal of assignments for electronic transitions of *trans*-$Co(l\text{-pn})_2Cl_3$ based on circular dichroism and magnetic selection rules.[5]

Experimental

Preparation of Compounds. *l*-**Propylenediamine.**—Propylenediamine was resolved by recrystallization of the *d*-tartrate[6] until there was no appreciable change in the optical rotation; $[\alpha]_D$ −30.1°.

Anal. Calcd. for $C_{11}H_{22}N_2O_{12}\cdot 2H_2O$: C, 32.20; H, 6.39; N, 6.83. Found: C, 31.95; H, 6.33; N, 6.91.

Solutions of *l*-pn were prepared by reaction of the dihydrate with the calculated amount of $Ba(OH)_2\cdot 8H_2O$ in a minimum amount of water, followed by cooling at ice temperature and filtering.

trans-$[Co(l\text{-pn})_2Cl_2]ClO_4$ was prepared by dropwise addition of concentrated perchloric acid to a cold, concentrated, aqueous solution of crude *trans*-$[Co(l\text{-pn})_2Cl_2]Cl\cdot HCl\cdot 2H_2O$,[7] followed by filtration and a rapid recrystallization by the same procedure.

Anal. Calcd. for $[Co(C_3H_{10}N_2)_2Cl_2]ClO_4$: C, 19.09; H, 5.30; total Cl, 28.18. Found: C, 18.89; H, 5.39; total Cl, 28.37.

trans-$[Co(l\text{-pn})_2(NO_2)_2]ClO_4$ was prepared by the method of O'Brien, McReynolds, and Bailar.[8]

trans-$[Co(l\text{-pn})(d\text{-pn})Cl_2]ClO_4$ was prepared by treating a saturated methyl alcohol solution of the racemic chloride[7] with concentrated $HClO_4$ and washing with methyl alcohol and then ether. A second crop was obtained by cooling the filtrate to 0°. Interestingly, the recrystallization procedure used with the optically active compound was not useful because of lower solubility. Instead, the perchlorate was converted to the chloride by shaking with an excess of Dowex 2 anion-exchange resin in the chloride form, followed by reprecipitation of the perchlorate with concentrated perchloric acid and washing with methyl alcohol and then ether.

Anal. Found: C, 18.97; H, 5.38.

Spectral Measurements.—Visible and ultraviolet spectra were determined using a Cary Model 14 spectrophotometer. The circular dichroism was determined using a Roussel–Jouan Dichrographe with a spectral range of 2000–6000 Å. Methanol was used as a solvent. The spectra are given in Figures 1 and 2. The decadic extinction coefficient in M^{-1} cm.$^{-1}$ (ϵ) is used. $\Delta\epsilon$ is the circular dichroism $\epsilon_l - \epsilon_r$.

Assignments

Before making assignments, we need to be certain our recorded spectra were obtained from solutions free of solvolysis products. We used methanol solutions because such solutions of *trans*-$Co(en)_2Cl_2^+$ are known to be stable to solvolysis and isomerization.[9] In water this cation hydrolyzes with isomerization; the half-time is 3.57 hr. at 30°.[10] We have followed the hydrolysis of *trans*-$Co(l\text{-pn})_2Cl_2^+$ at 27° using the circular dichroism at 6000 Å.; this cation disappears with a half-life of 3.5 hr., in good accord with Mathieu's result.[11] Our

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[1] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

[2] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

[3] A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

[4] J.-P. Mathieu, *Ann. Phys.*, [11] **19**, 335 (1944).

[5] J. H. Dunlop and R. D. Gillard, *Mol. Phys.*, **7**, 493 (1964).

[6] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

[7] A. Werner and A. Frohlich, *Ber.*, **40**, 2228 (1907).

[8] T. D. O'Brien, J. P. McReynolds, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **70**, 749 (1948).

[9] D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

[10] J.-P. Mathieu, *Bull. soc. chim. France*, **3**, 2152 (1936).

[11] As the hydrolysis proceeds a new band appears at 4780 Å. which may be assigned to *cis* hydrolysis products. At no point in the hydrolysis could we reproduce the results of ref. 5; see Figure 1.

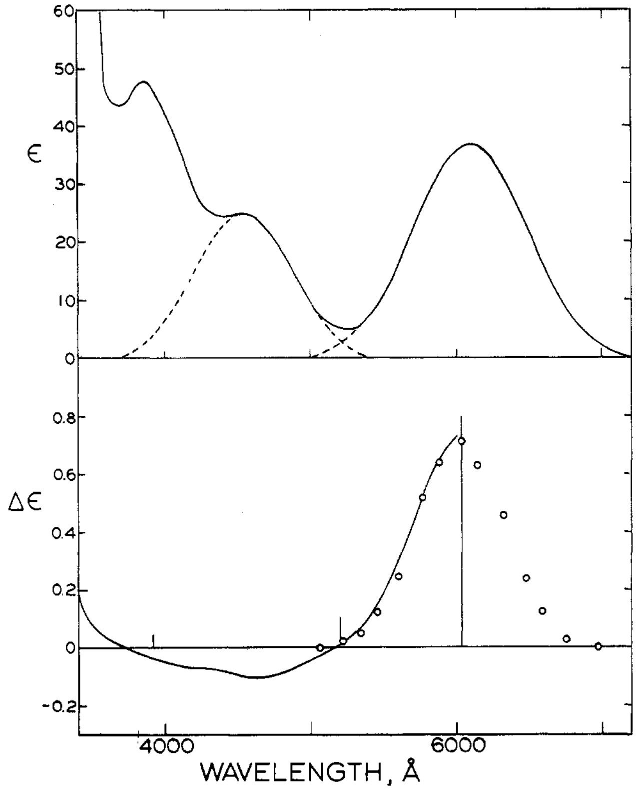

Figure 1.—Absorption spectrum (above) and circular dichroism (below) of *trans*-$Co(l\text{-}pn)_2Cl_2ClO_4$ in methanol solution. The vertical lines represent the dichroism maxima reported in ref. 5. The circles are data of Mathieu.[4]

initial dichroism curves in water as well as those in methanol are in good agreement with Mathieu's points in the wave length region shared by the two measurements; see Figure 1. These observations assure us of the absence of solvolysis products.

The first two transitions in the spectrum of Co(III) in an octahedral field in order of increasing energy are ${}^1A_1 \rightarrow {}^1T_1$ and ${}^1T_2$ which split in a tetragonal field into ${}^1A_2 + {}^1E^a$ and ${}^1B_2 + {}^1E^b$ components, respectively (we omit g subscripts throughout for simplicity). It has generally been assumed that the first two bands in the spectra of dihalotetraamminecobalt compounds are assigned to the ${}^1E^a$ and ${}^1A_2$ levels in order of increasing energy. The splitting of the ${}^1T_2$ band has been thought to be small or obscured in the spectrum by the onset of charge transfer in the near-ultraviolet. A detailed analysis of energy levels in both crystal field and molecular orbital models has been given by Yamatera.[12] He has shown that the ${}^1A_2$ band for *trans*-$CoA_4X_2^+$ should have roughly the same energy as the ${}^1T_1$ band of CoA_6^{3+}. In Table I, we record an absorption band at 22,100 cm.$^{-1}$ which compares favorably with the value of 21,400 cm.$^{-1}$ found in this laboratory for $Co(pn)_3^{3+}$. Furthermore, for axial ligands X which are lower in the spectrochemical series than A, ${}^1E^a$ should be lower in energy than ${}^1A_2$. Accordingly the band at 16,400 cm.$^{-1}$ has been assigned to ${}^1A_1 \rightarrow {}^1E^a$.

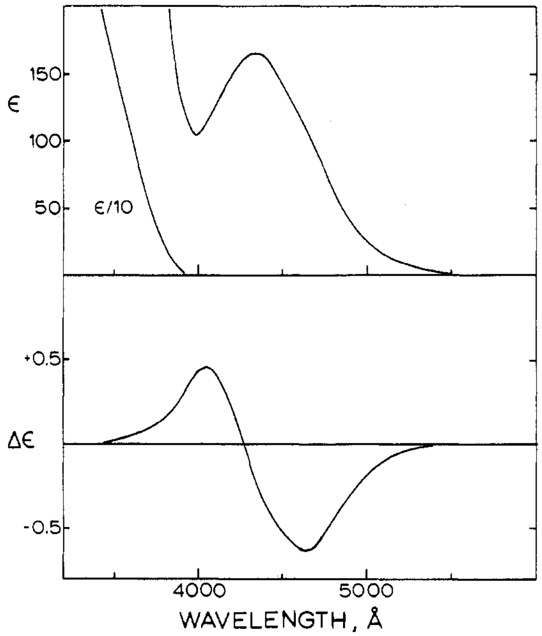

Figure 2.—Absorption spectrum (above) and circular dichroism (below) of *trans*-$Co(l\text{-}pn)_2(NO_2)_2ClO_4$ in water.

TABLE I

ABSORPTION AND CIRCULAR DICHROISM DATA FOR *trans*-$Co(l\text{-}pn)_2Cl_2^+$ AND *trans*-$Co(l\text{-}pn)_2(NO_2)_2^+$

	Absorption spectra		Circular dichroism		
	Max., cm.$^{-1}$ × 10^{-3}	ϵ_{max}	Max., cm.$^{-1}$ × 10^{-3}	$\Delta\epsilon_{max}$	Excited state
$Co(l\text{-}pn)_2Cl_2^+$ [a]	16.4	37	16.6[c]	+0.71	${}^1E^a$
	22.1	25	21.7	−0.10	${}^1A_2$
	...	...	24.0[d]	−0.07[d]	[e]
	26.0	47	...	...	[e]
$Co(l\text{-}pn)_2(NO_2)_2^+$ [b]	23.1	165	21.7	−0.62[f]	${}^1A_2$
			24.5	+0.44[f]	${}^1E^a$

[a] Measured in methanol. [b] Measured in water. [c] Data of Mathieu.[4] [d] Shoulder. [e] Assignment uncertain, see text. [g] Because of finite band width and overlap these maximum and Δε values cannot be taken as characteristic of the separate tetragonal components.

Further support for these assignments is provided by data for $Co(l\text{-}pn)_2(NO_2)_2^+$. Since the axial substituent lies higher in the spectrochemical series than propylenediamine, the crystal field model leads us to expect the ${}^1E^a$ band to be at higher energy than the ${}^1A_2$ band at 21,700 cm.$^{-1}$. The circular dichroism does reveal these bands although the absorption spectrum does not provide clear evidence for any tetragonal splitting; see Figure 2. We expect the sign of Δε of each transition to be independent of axial substituent and therefore to carry over from those of the chloro compound. This expectation is borne out by the circular dichroism curves.

Unfortunately the crystal field model does not make a clear-cut prediction of the splitting of the ${}^1T_2$ level. Transitions to the ${}^1B_2$ component of this level in D_{4h} are magnetically forbidden while transitions to the component ${}^1E^b$ become allowed by admixture of ${}^1E^a$ character (all traionsitns become active in the D_2 field,

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[12] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958). Additional treatments of various aspects of this problem have been given by: J. S. Griffith and L. S. Orgel, *J. Chem. Soc.*, 4981 (1956); C. J. Ballhausen and W. Moffit, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956); D. S. McClure in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillian Co., New York, N. Y., 1961, p. 498.

which should be considerably weaker than the D_{4h} field). In the circular dichroism there appears to be a weak negative shoulder at about 24,000 cm.$^{-1}$ which may be partially obscured by the positive band in the near-ultraviolet. Whether this shoulder is due to the $^1E^b$ level—the more likely possibility taking the magnetic selection rules as a guide—or whether it is due to the $^1B_2$ level made active by spin–orbit coupling cannot be decided at this point.

The Ligand Field

An optically active molecule is one whose mirror image is not superimposable with itself. Alternately we may say that the molecule lacks improper symmetry operations: center of symmetry, plane of symmetry, and rotatory-reflection axis. Such molecules are often referred to as asymmetric or dissymmetric. The latter term is favored because the former indicates that the molecule possesses no symmetry at all, whereas it may possess simple rotation axes and yet be enantiomorphous. Unfortunately the implications of the term dissymmetric are equally unclear from the word itself. Now the total Hamiltonian will be dissymmetric. However, in crystal field theory we can distinguish between dissymmetric contributions to the potential and other parts of higher symmetry. For greater clarity in referring to the various contributions to the intensity, we will use the word amirrocentric, rather than dissymmetric, to refer to those terms lacking improper symmetry operations.

Consider the complex *trans*-Co(pn)$_2$XY$^+$, and let us find a point charge model to represent the ligand field retaining only those atoms in the first coordination sphere; that is, in particular we neglect the NH dipoles, the ring and its methyl groups. The atomic positions from the crystal structure[13] of *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl·HCl·2H$_2$O will serve as an excellent guide. The site symmetry at cobalt is C_2 with this axis parallel to the Cl–Co–Cl axis and the methyl groups *trans* to each other. The nitrogen atoms are displaced above and below the *xy* plane. In Figure 3, we have displayed the arrangements of the "in-plane" nuclei which give rise to the enantiomorphous isomers. Note that when X = Y the ion has D_2 symmetry.

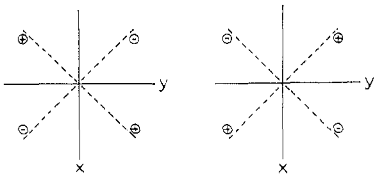

Figure 3.—Enantiomorphous point charge distributions of D_2 symmetry. The dashed lines are 45° lines. Encircled signs indicate the direction of equivalent small displacements above and below the *xy* plane.

However, regardless of the small displacements of the nitrogen atoms, the crystal field remains predominantly tetragonal, and those terms in the crystal field potential proportional to Y_2^0, Y_4^0, and $Y_4^{+4} + Y_4^{-4}$ will determine the relative energies of the split components of the d orbitals. These perturbations will not change the g character of the orbitals and d–d transitions will be forbidden.

If X $\neq$ Y there will be a very large perturbation proportional to Y_1^0 due to the acentric axial field. This field will mix excited odd (u) functions into the d orbitals, making d–d transitions allowed; for example p_z will mix strongly with d_{z^2}. However, this contribution to the acentric field will not make the transitions optically active because the X–Co–Y grouping possesses planes of symmetry and $C_{\infty v}$ local symmetry.

Now consider the contributions to the field of the four displaced point charges providing local symmetry D_2 about the metal ion. The first odd term in the potential expansion which will contribute in this symmetry is proportional to $Y_3^{+2} - Y_3^{-2}$. This term contributes to both the intensity and the optical activity; it is amirrocentric in contrast to the Y_1^0 term which is merely acentric. The contribution to the intensity of this higher order term will be considerably smaller than that of Y_1^0, provided X and Y are well separated in the spectrochemical series. Accordingly, in Co(pn)$_2$XY$^+$ compounds it will be impossible to gauge the amirrocentric intensity from the absorption spectrum. The difference in intensity between the centric ion Co(*d*-pn)(*l*-pn)X$_2^+$ and Co(*l*-pn)$_2$X$_2^+$ would gauge the amirrocentric contribution, provided it were not obscured by the vibronic contributions. The circular dichroism is a very powerful tool for obtaining the amirrocentric intensity since the vibronic mechanism is ineffective in circular dichroism.[14]

Analogous considerations arise in molecular orbital models. We would propose displaced ligand nuclei as in Figure 3 with their σ-orbitals directed toward the metal ion. Molecular orbitals would be calculated in some approximation and the electric moment could then be expressed in terms of the various atomic orbitals. Acentric and amirrocentric contributions would be readily identified on symmetry grounds. An amirrocentric electron distribution might also arise from ligand σ-orbitals skew to the bond axis.[3] Since, as we shall see, the amirrocentricity in these molecules is very small, it will be quite difficult to get conclusive experimental evidence on relative contributions of these various models.

The Rotational Strength

The rotational strength of a transition 0 → n is given by

$$R = Im(0|\mathbf{Q}|n)\cdot(n|\mathbf{L}|0)e^2/2mc$$

while the dipole strength is

$$D = (0|\mathbf{Q}|n)\cdot(n|\mathbf{Q}|0)e^2$$

where **Q** and **L** are the coordinate and angular momentum operators. Matrix elements of the first two transitions of a d^6 metal ion in a strong tetragonal field may be written in terms of empirical parameters *l* and *q*.

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[13] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

[14] W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

$$({}^1A_1|\mathbf{L}|{}^1A_2) = -il_{\|}\hbar\mathbf{k}$$
$$({}^1A_1|\mathbf{L}|{}^1E^a{}_{x,y}) = -il_{x,y}h(\mathbf{i},\mathbf{j})$$

and

$$({}^1A_1|\mathbf{Q}|{}^1A_2) = q_{\|}\mathbf{k}$$
$$({}^1A_1|\mathbf{Q}|{}^1E^a{}_{x,y}) = q_{x,y}(\mathbf{i},\mathbf{j})$$

We will assume that the angular momentum parameters are isotropic and identical with gas phase values, an approximation which cannot be in error by more than 20–50%.[1,2] Then

$$l_{\|} = l_{\perp} = 2\sqrt{2}$$

This is readily proven from the fact that the sum of the squared matrix elements of the angular momentum for $t_2{}^6 \rightarrow t_2{}^5e$ is $24\hbar^2$ in the approximation that the matrix elements are not appreciably different from those of the parent octahedral excited state, ${}^1T_1$. The rotational strengths for the transition in question are then

$$R({}^1A_1 \rightarrow {}^1A_2) = 2\sqrt{2}q_{\|}\hbar e^2/2mc$$
$$R({}^1A_1 \rightarrow {}^1E^a) = 4\sqrt{2}q_{\perp}\hbar e^2/2mc$$

where $q_{\perp}$ represents the small difference in rotatory strength of the two components of the perpendicular band.

Recalling, however, that the rotational strength is obtained experimentally from the expression

$$R = 22.9 \times 10^{-40}\int(\Delta\epsilon/\lambda)\mathrm{d}\lambda$$

Empirical values of $q_{\|}$ and $q_{\perp}$ are readily obtained from the experimental integrated circular dichroism and equations given above. These parameters in conjunction with the theoretical expression for dipole strength and the equation

$$D = 3.982 \times 10^{-20}e^2\int(\epsilon/\lambda)\,\mathrm{d}\lambda$$

allow computation of a quasi-theoretical value for the integrated band intensity of a transition. A comparison with the experimental value will then aid in deducing the intensity mechanism for an optical transition.

In Table II we list experimental rotational strengths and integrated band intensities for the transitions ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1E^a$ for $Co(l\text{-pn})_2Cl_2{}^+$. The rotational strength of the transition ${}^1A_1 \rightarrow {}^1A_2$ was computed with the assumption that the entire negatively rotating component was due to this transition, while that of the transition ${}^1A_1 \rightarrow {}^1E^a$ was computed from Mathieu's data from 6000 Å. to longer wave lengths, and our own data at shorter wave lengths. Integrated band intensities were obtained from a resolution assuming symmetry about the band maximum.

We also include in Table II empirical values of $q_{\|}$ and $q_{\perp}$ and the quasi-theoretical values for the integrated band intensities. Note that the empirical q values are one to two orders of magnitude less than those found for the presumed electronically allowed transitions in $Co(en)_3{}^{3+}$.[2] Note also the large disparity between experimental and theoretical integrated band intensities. Both of these facts point to small electric moments effective in the circular dichroism and thus the mechanism of absorption band intensity must be preponderantly vibronic.

TABLE II

SPECTRAL DATA FOR *trans*-$Co(l\text{-pn})_2Cl_2{}^+$ IN METHANOL SOLUTION

Transition	Rotational strength, c.g.s. $\times 10^{40}$	q, mÅ.	Integrated intensity, ϵ unit Exptl.	Calcd.[a]
${}^1A_1 \rightarrow {}^1E^a$	+2.10	+0.835	5.71	3.52×10^{-3}
${}^1A_1 \rightarrow {}^1A_2$	−0.424	−0.337	4.27	2.86×10^{-5}

[a] Calculated from the circular dichroism; *i.e.*, dissymmetric contribution only.

Further confirmation is found in a comparison of the intensities of the corresponding transitions of the centric molecular ion *trans*-$Co(l\text{-pn})(d\text{-pn})Cl_2{}^+$.[15] The extinction coefficients (and integrated band intensities) are 37 (4.27) for ${}^1A_2$ and 25 (5.73) for ${}^1E^a$. Clearly the amirrocentric contribution to the intensity is negligible compared to the vibronic portion. This raises the question as to the validity of the assumption that all of the intensity of $Co(en)_3{}^{3+}$ is due to electronically allowed transitions. However, in this case it is clear that only a moderate fraction of the intensity can be vibronic in view of the fair but by no means exact comparisons of q values from absorption band intensities and optical activity data. Larger q values for the trigonal complexes could be accounted for in terms of larger ligand–ligand repulsions resulting in larger displacements of ligand nuclei from the octahedral points.

To conclude, we comment on the rotational strength of $Co(l\text{-pn})_2(NO_2)_2{}^+$. We cannot readily interpret signed contributions to the integrated circular dichroism (+0.0256 and −0.0700 ϵ unit) because of serious band overlap. However, from dichroism maxima in Table I it would appear that rotational strengths here are considerably larger than for the corresponding dichloro compound (as is the integrated band intensity, 31 ϵ units). The simple crystal field and molecular orbital models we have described above predict that the dissymmetric electric moments ought to be constants characteristic of the diamine whatever the axial substituents. The apparent breakdown of this approximation suggests that more detailed models should include contributions to the electric moment from axial groups.[16]

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(15) Y. Komiyama and Y. Saito, unpublished work; S. Kirschner, Ed., "Advances in The Chemistry of The Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p. 562.

(16) The nitro group is not an ideal group for such a study because of the complications involved in rotational freedom about the Co–N axis, the unsymmetrical π bond, and low-energy charge-transfer states.