Electronic and Circular Dichroism Spectra of Some Tetradentate Schiff Base Complexes of Cobalt(II)[1]

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Abstract: Several complexes of the general formula N,N′-bis(7-X-salicylidene)-(−)-propylenediaminocobalt(II), Co[(7-X-sal)$_2$(−)pn], were prepared and their near-infrared and visible absorption spectra measured along with the associated circular dichroism. It was possible to assign the bands observed, to obtain the d orbital energy separations, and to correlate the magnitude of the circular dichroism observed in the near-infrared region with an equilibrium between the equatorial and axial conformations of the coordinated (−)pn methyl group. The sign of the circular dichroism observed in the near-infrared region associated with the low energy band may be rationalized by recourse to a right-handed octet rule similar to that proposed for octahedral cobalt(III) complexes.

Planar tetradentate Schiff base complexes of cobalt(II) have been known for some time.[3] Interest has been focused upon their behavior as oxygen carriers,[3,4] on their stereochemistry,[3-5] and on their magnetic properties.[3-6] Despite the relative abundance of these data, there have been few investigations of the ligand field spectra of such compounds,[5-9] and those which are reported concentrate on the near-infrared band, which is reputed to be indicative of low-spin planar cobalt(II) complexes of this type.[8] A study of the visible region of the ligand field spectrum of these complexes would seem to be of value, but this is hindered by the presence in this region of very intense bands of either charge transfer or intraligand origin.[8]

Several reports of the optical rotatory dispersion spectra of some optically active four-coordinate planar Schiff base complexes of cobalt(II)[10,11] and a recent treatment of the circular dichroism spectrum in the visible region of an analogous nickel(II) complex,[12] in which d–d bands, obscured in the isotropic absorption spectrum, are observed in the circular dichroism spectrum, have recently appeared. These suggest a method of determining the electronic energy levels and the provenance of the absorptions which are observed in the Co(II) systems.

Several complexes of the general formula N,N′-bis(7-X-salicylidene)-(−)-propylenediaminocobalt(II), Co[(7-X-sal)$_2$(−)pn] (Figure 1), have been prepared and their electronic and circular dichroism spectra in the near-infrared and visible regions measured. Circular dichroism was observed associated with the near-infrared "planar cobalt(II) band." This represents, to our knowledge, the first report of CD spectra of such planar systems in the near-infrared region, although studies in this region for other systems have been reported.[13] These data allow an assignment of the d–d bands associated with the metal chromophore as well as the metal–ligand charge transfer bands in the visible region and the first ligand $\pi \rightarrow \pi^*$ absorption. Information is also obtained suggesting the presence of a conformational equilibrium between the λ (methyl-pseudo-equatorial) and δ (methyl-axial) conformation of the (−)pn, similar to that observed in apically coordinated bidentate amino acid chelates[14] and in planar tetradentate nickel(II) and copper(II) Schiff base complexes.[15]

The isotropic absorption spectrum of the first $\pi \rightarrow \pi^*$ ligand transition in these complexes, along with the associated circular dichroism, indicates that the azomethane groups are coplanar with the cobalt(II) ion, and hence that there is little or no distortion from planarity as has been suggested for similar nickel(II) complexes.[15]

Experimental Section

Resolution of (+)- and (−)-Propylenediamine. The resolution of *dl*-propylenediamine was accomplished by methods described elsewhere.[16,17] Aqueous solutions of the resolved diamine, obtained from the distillation of the tartrate diastereoisomers,[17] were used for the preparation of the Schiff base ligands.

Preparations. The ligands were prepared by refluxing an aqueous solution (~10 ml) containing 0.01 mol of the resolved diamine with 0.02 mol of the appropriate 2-hydroxy ketone or aldehyde in 100 ml of methanol. After several hours of refluxing, 0.02 mol of triethylamine was added and the solution cooled to room temperature.

The ligand solutions were flushed with nitrogen and added slowly under a nitrogen atmosphere to 0.01 mol of $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml of 2,2-dimethoxypropane which had been flushed with nitrogen for an hour. The resulting dark brown solutions were then flushed with nitrogen and stirred until the desired complex separated from solution. The complexes were filtered under nitrogen and dried *in vacuo*. Once dry these complexes were stable in air. No

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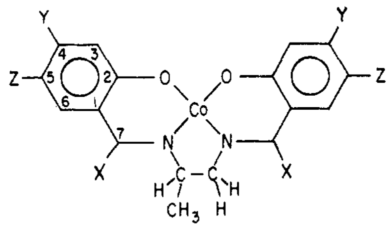

Figure 1. N,N′-Bis(7-X-salicylidene)-(−)-propylenediaminocobalt(II); Co[(7-X-sal)$_2$(−)pn].

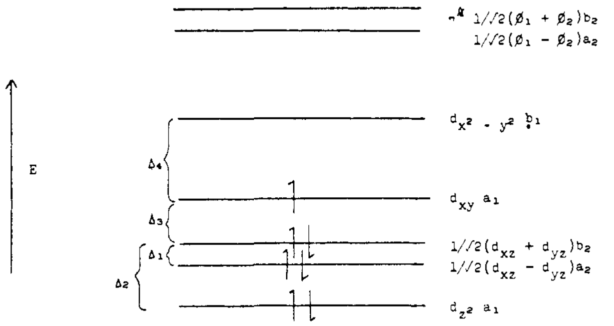

Figure 2. Orbital energy level diagram for a planar *cis*-Co^{II}N$_2$O$_2$ complex of C$_{2v}$ symmetry.

attempt at recrystallizations was made owing to their ease of oxidation.

Chemicals. Except for the *dl*-propylenediamine which was Eastman practical grade, all chemicals were reagent grade and used without further purification. The aldehydes and ketones were obtained from the Aldrich Chemical Co. Solvents were spectro grade and flushed with nitrogen before use.

N,N′-Bis(salicylidene)-(−)-propylenediaminocobalt(II). This compound was previously reported as reddish brown crystals.[10] This method gave a dark brown powder which was dried *in vacuo* at room temperature for 24 hr. *Anal.* Calcd for $C_{17}H_{16}N_2O_2Co$: C, 60.18; H, 4.72; N, 8.26. Found: C, 59.61; H, 5.05; N, 8.50.

N,N′-Bis(7-methylsalicylidene)-(−)-propylenediaminocobalt(II). This compound was reported earlier as a bright red powder.[11] It was obtained as a red powder and dried *in vacuo* for 24 hr at room temperature. *Anal.* Calcd for $C_{19}H_{20}N_2O_2Co$: C, 62.12; H, 5.45; N, 7.63. Found: C, 61.91; H, 5.48; N, 7.6.

N,N′-Bis(7-phenylsalicylidene)-(−)-propylenediaminocobalt(II). This compound was obtained as a bright orange powder which was dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{29}H_{24}N_2O_2Co$: C, 70.88; H, 4.89; N, 5.70. Found: C, 70.52; H, 5.08; N, 5.74.

N,N′-Bis(5-methoxy-7-methylsalicylidene)-(−)-propylenediaminocobalt(II). This complex was obtained as a dark red powder and dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{21}H_{24}N_2O_4Co$: C, 59.02; H, 5.62; N, 6.56. Found: C, 58.71; H, 6.35; N, 7.28.

N,N′-Bis(5,6-benzosalicylidene)-(−)-propylenediaminocobalt(II). This compound was obtained as a red-brown powder and dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{25}H_{20}N_2O_2Co$: C, 68.34; H, 4.55; N, 6.38. Found: C, 67.62; H, 4.41; N, 6.37.

N,N′-Bis(7-methylsalicylidene)-(+)-propylenediaminocobalt(II). This compound was prepared by a method analogous to that used for the other complexes. It was obtained as a red-orange hydrate and was dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{19}H_{22}N_2O_3Co$: C, 59.22; H, 5.71; N, 7.27. Found: C, 59.42: H, 5.46; N, 7.83.

N,N′-Bis(7-methylsalicylidene)ethylenediaminocobalt(II). This compound has been reported previously as a brown crystalline hydrate.[18] This method gave an orange-brown hydrate which was dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{18}H_{19}N_2O_{2.5}Co$: C, 59.67; H, 5.25; N, 7.73. Found: C, 59.46; H, 5.21; N, 7.71.

N,N′-Bis(7-methylsalicylidene)ethylenediaminozinc(II). This compound was prepared by a method analogous to that used for the cobalt(II) compounds. It gave a light yellow hydrate which was dried *in vacuo* for 24 hr. *Anal.* Calcd for $C_{18}H_{20}N_2O_3Zn$: C, 57.29; H, 5.31; N, 7.43. Found: C, 57.08; H, 5.19; N, 7.12.

Physical Measurements. The electronic absorption spectra of the complexes were obtained using a Cary Model 14 recording spectrophotometer. The solution spectra were measured in the visible region using 1-cm quartz cells and in the near-infrared region using 10-cm cells. The spectra of the solid complexes were obtained using a hydrocarbon mull (Kel-F grease) on quartz plates and Nujol on filter paper as a reference. The magnetic susceptibility measurements were carried out on a Faraday balance using Hg[Co(NCS)$_4$] as a calibrant. Diamagnetic corrections were calculated from a table of Pascal's constants.[19] The circular dichroism spectra in the visible and ultraviolet regions (700–300 mμ) were obtained on a Jasco Model ORD/VU-5 spectrometer, while the near-infrared circular dichroism spectra were measured on a spectrommeter designed originally for magnetic circular dichroism measurements and modified for the present purpose. The authors are indebted to Professor Martin Sage for the use of the instrument and assistance in obtaining the spectra Analytical data were obtained by Galbraith Laboratories, Knoxville, Tenn.

Results

Magnetic Data. The room temperature magnetic behavior of these complexes is typical of low-spin planar cobalt(II),[20] having moments of 2.2–2.5 BM, with one exception. The value of μ_{eff} for Co[(sal)$_2$(−)pn] at room temperature shows an anomalously high moment and considerable field dependence and is being further investigated.

Band Assignments. The energy level diagram expected for a planar *cis*-N$_2$O$_2$ complex with C$_{2v}$ symmetry is given in Figure 2. There are ten spin-allowed d–d bands expected from one electron transitions and these separate into two groups. Assuming reasonable values for the energy level separations, Δ_n,[21] one expects to find a group with seven components in the visible region, and a second group with three components in the near-infrared region. Providing that the separation Δ_1 is small and that Δ_2 is smaller than the half-width of the absorption band, one would expect in the near-infrared region one asymmetric absorption band. This result could be predicted since for an analogous nickel(II) complex[12] the transition ($d_{xz} \pm d_{yz}$) → $d_{x^2-y^2}$ is unsplit, and for a large number of planar transition metal complexes the d_{z^2} orbital is known to be close in energy to the d_{xz} and d_{yz} orbitals.[22]

The chloroform solution spectrum ofCo [(7-CH$_3$-sal)$_2$(−)pn] in the near-infrared region is given in Figure 3 along with the associated circular dichroism. This spectrum is representative of those exhibited by all the complexes discussed, and the data for all in this region are given in Table I. The isotropic absorption spectra (both in solution and mull) indicate one asymmetric band (Table I) in accordance with the predicted result. This band envelope has been suggested to be indicative of low-spin planar cobalt(II)[8] and assigned by different workers to spin-forbidden transitions[8] and to spin-allowed d–d transitions expected in low-spin planar cobalt(II) complexes of D$_{4h}$ symmetry.[21] Since the circular dichroism of this region which is given in Figure 3 shows that there are at least three components to the band, we assign it as ($d_{xz} \pm d_{yz}$), $d_{z^2} \rightarrow d_{xy}$.

Under the same conditions necessary to observe one asymmetric band in the near-infrared region, seven

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Table I. Spectral Data for Complexes in the Near-Infrared Region

	ν_{max}[a] CHCl$_3$	ν_{max}[a] Kel-F mull	$(\epsilon_l - \epsilon_r)_{max}$ in CHCl$_3$[c] $d_{z^2} \rightarrow d_{xy}$	$(d_{xz} + d_{yz}) \rightarrow d_{xy}$	$(d_{xz} - d_{yz}) \rightarrow d_{xy}$
Co[(7-CH$_3$-sal)$_2$(−)pn]	8170 (24.3)	8100 (8600 sh)	<8360 (+)[b]	8590 (−0.17)	9150 (−0.09 sh)
Co[(7-C$_6$H$_5$-sal)$_2$(−)pn]	8190 (23.6)	7950 (8500 sh)	<8400 (+)	8850 (−0.11)	9350 (−0.06 sh)
Co[(5-OCH$_3$,7-CH$_3$-sal)$_2$(−)pn]	8350 (19.9)	8220 (8520 sh)	<8530 (+)	8980 (−0.07)	9400 (−0.03 sh)
Co[(5,6-benzosal)$_2$(+)pn]	8360 (25.6)	8370 (8740 sh)	<8400 (+)	8970 (−0.05)	9500 (−0.025 sh)
Co[(sal)$_2$(−)pn]	8250 (16.8)	8150 (8550 sh)	<8600 (+)	8860 (−0.045)	9300 (−0.035 sh)

[a] ϵ in parentheses. [b] It was not possible to obtain the maximum of the positive component of the CD associated with these bands due to instrumental limitations. [c] Value of $\epsilon_l - \epsilon_r$ in parentheses.

bands are expected in the visible region. Referring to Figure 2 one expects at low energy the transition $d_{xy} \rightarrow d_{x^2-y^2}$, and at higher energies the transitions $d_{z^2} \rightarrow d_{x^2-y^2}$ and $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$. Both the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$ transitions are expected to be split by configuration interaction.[21] The former transition should have two components and, again assuming that Δ_1 is small, the latter transition should also have two components.

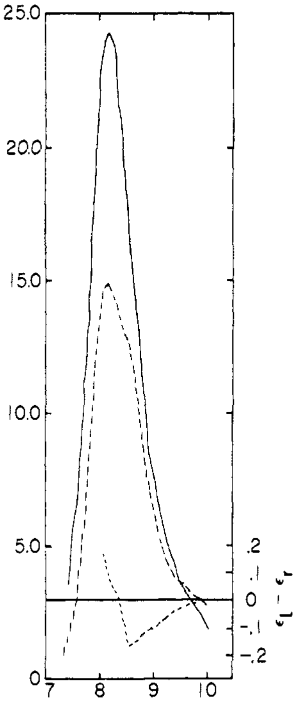

Figure 3. Near-infrared spectra of Co[(7-CH$_3$-sal)$_2$(−)pn]: (——) absorption spectrum in CHCl$_3$, (– – – – – –) absorption spectrum in a Kel-F mull, (-----) CD in CHCl$_3$ solution.

Using reasonable values of F_2 and F_4, and allowing configuration interaction, one expects the two components of the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$ transitions to be split by several thousand wave numbers. The lower energy component of each should occur below 20,000 cm^{-1}. This places the higher energy components beneath the intense bands starting at ~20,000 cm^{-1}.

The visible absorption spectra of these complexes in chloroform solution are shown in Figure 4. The very intense bands starting at ~20,000 cm^{-1}, which are assigned as metal to ligand charge transfer bands, prevent the location and assignment of the d–d bands expected in this region, since they occur only as weak shoulders on the major band envelope.

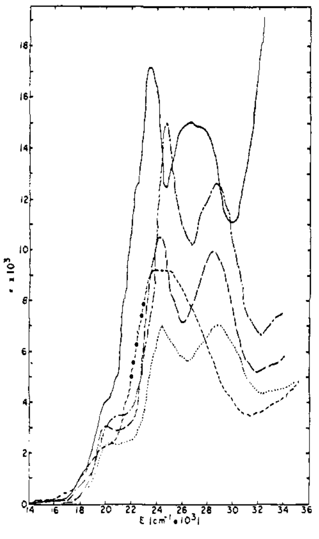

Figure 4. Visible region isotropic absorption spectrum of Co[(sal)$_2$(−)pn] (·-·-·-·-), Co[(7-CH$_3$-sal)$_2$(−)pn] (· · · ·), Co[(7-C$_6$H$_5$-sal)$_2$(−)pn] (– – – –), Co[(5-OCH$_3$,7-CH$_3$-sal)$_2$(−)pn] (----), Co[(5,6-benzosal)$_2$(−)pn] (——).

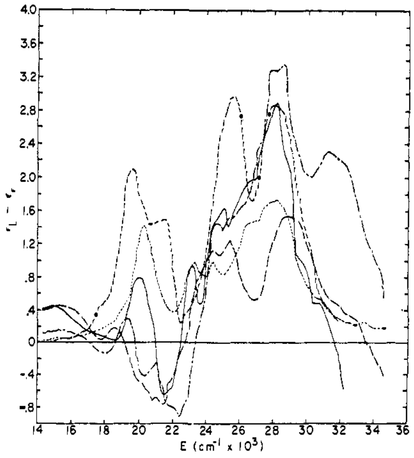

Figure 5. Visible region circular dichroism spectra of Co[(sal)$_2$-(−)pn] (· · · ·), Co[(7-CH$_3$-sal)$_2$(−)pn] (-·-·), Co[(7-C$_6$H$_5$ sal)$_2$(−)pn] (——), Co[(5-OCH$_3$,7-CH$_3$-sal)$_2$(−)pn] (– – –), Co[(5,6-benzosal)$_2$-(−)pn] (-----).

The circular dichroism associated with the visible spectra are shown in Figure 5, and here it is easier to distinguish the d–d bands from the overlapping charge transfer absorptions, at least in the lower energy region of the visible spectrum. Assigning a particular transi-

Table II. Visible Region Circular Dichroism Maxima, cm^{-1}

	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{z^2} \rightarrow d_{x-y^2}$	$(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$
Co[(7-CH_3-sal)$_2$(−)pn]	15,500 (+0.15)	18,100 (−0.12)	19,300 (+0.28)
Co[(7-C_6H_5-sal)$_2$(−)pn]	15,000 (+0.44)	17,500 (+0.10)	*a*
Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn]	15,400 (+0.45)	*a*	18,600 (+0.18)
Co[(5,6-benzosal)$_2$(−)pn]	15,500 (+0.04)	16,700 (+)[b]	17,800 (+)[b]
Co[(sal)$_2$(−)pn]	15,500 (+0.06)	17,500 (+)[b]	19,000 (+)[b]

[a] Not observed—obscured by charge transfer CD band of the same sign. [b] Observed, but an overlapping charge transfer band prevents an estimation of the CD magnitude.

tion to a given circular dichroism absorption is simplified by two factors. First, the lowest lying visible region CD absorption at ~15,500 cm^{-1} can be assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in agreement with work done on the analogous Ni[(sal)$_2$(−)pn][12] and the polarized spectrum of the similar *trans*-bis[N-methylsalicylaldimino]nickel(II) complex.[23] Also the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ is expected to exhibit a smaller circular dichroism (smaller dissymmetry factor)[24,25] in that, in the absence of configuration interaction, it should not possess magnetic dipole character. This transition may, however, mix with the $d_{xy} \rightarrow d_{x^2-y^2}$ transition under the influence of the C_{2v} field and acquire magnetic dipole character in this manner. Still, it seems reasonable to expect the $d_{z^2} \rightarrow d_{x^2-y^2}$ absorption to exhibit weaker circular dichroism.

Table II gives the relevant data concerning the d–d transitions in these complexes. In those cases where the d–d bands can be clearly observed, the second d–d band at ~17,500 cm^{-1} appears to have the weakest CD (smallest dissymmetry factor), and consequently is assigned to the low energy component of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The highest energy d–d band observed (~19,000 cm^{-1}) is then assigned to the lower energy component of the $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$ transition.

The apparent variation in energy of the CD bands assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$ transitions in this series of similar complexes may be rationalized by observing that there is some difficulty in estimating the extent of overlap of two CD bands of opposite sign and consequently the observed bands correspond only approximately to the real transition energy. In support of this it may be observed that the energy of the $d_{xy} \rightarrow d_{x^2-y^2}$ CD band (which is less extensively overlapped) is relatively constant throughout this series, as would be expected.

The remaining bands in the visible region are then either charge transfer or intraligand absorptions. To determine the provenance of these bands, the visible absorption spectra of N,N′-bis(7-methylsalicylidene)-ethylenediaminocobalt(II) and the analogous zinc(II) complex were examined. The visible absorption spectra of these complexes in chloroform, together with that of Co[(7-CH_3-sal)$_2$(−)pn], are shown in Figure 6. Note that the band envelope from 20,000 to 27,000 cm^{-1} present in both of the cobalt(II) complexes is missing in the zinc(II) complex. This suggests that these bands are charge transfer in character. A recent report dealing with Ni[(sal)$_2$(−)pn][12] treated the first empty ligand π orbitals as an essentially degenerate symmetric and antisymmetric combination (ψ_{b2}, ψ_{a2}) of empty π orbitals located on the two nitrogen atoms. This treatment fits well with our data (Figures 4 and 5). Thus the band at ~20,400 cm^{-1} corresponds to the transition $d_{xy} \rightarrow \psi_{a2}, \psi_{b2}$, the absorption at ~22,500 cm^{-1} to the transition $d_{z^2} \rightarrow \psi_{a2}, \psi_b$ (this band is not clearly observed in the isotropic absorption spectrum), and the $(d_{xz} \pm d_{yz}) \rightarrow \psi_{a2}, \psi_{b2}$ transition is assigned to the broad peak at ~24,500 cm^{-1} and the shoulder at ~26,000 cm^{-1}.

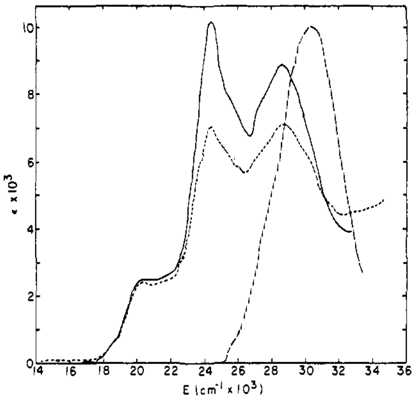

Figure 6. Visible absorption spectra in $CHCl_3$ of Co[(7-CH_3-sal)$_2$(−)pn] (— — —), Co[(7-CH_3-sal)$_2$en] (——), Zn[(7-CH_3-sal)$_2$en] (- - - -).

The remaining asymmetric band at ~28,500 cm^{-1}, which is observed in analogous zinc(II) complexes at slightly higher energy,[26] is thus assigned to a $\pi \rightarrow \pi^*$ ligand transition.

The energy level separations Δ_n may now be approximated. The energy of the transition $d_{xy} \rightarrow d_{x^2-y^2}$ corresponds to Δ_4, the energy separation between the d_{xy} $d_{x^2-y^2}$ orbitals, and is ~15,500 cm^{-1}.

The circular dichroism associated with the near-infrared band of Co[(7-CH_3-sal)$_2$(−)pn] (Figure 3) reveals at higher energy a negative band with a weak shoulder at ~9000 cm^{-1} and a stronger component at ~8500 cm^{-1}. Under the C_{2v} symmetry of the complexes considered, transitions which are of A_2 symmetry are not electric dipole allowed and thus are expected to have a smaller electric dipole moment. The $(d_{xz} - d_{yz})$ orbital which is a_2 is thus assumed to be slightly lower in energy than the $(d_{xz} + d_{yz})$ orbital, and the observed energy separation should correspond to Δ_1, which is ~500 cm^{-1}.

In order to estimate the energy level separations Δ_2 and Δ_3, the electronic repulsion terms must be evaluated explicitly. This was done using the Slater–Condon electronic repulsion parameters F_2 and F_4. The electronic repulsion term is more negative for the $d_{z^2} \rightarrow d_{xy}$

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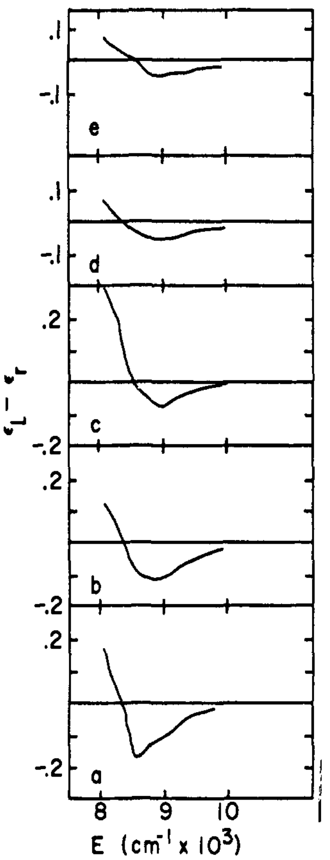

Figure 7. Near-infrared CD spectra of (a) Co[(7-CH_3-sal)$_2$(−)-pn], (b) Co[(7-C_6H_5-sal)$_2$(−)pn], (c) Co[(5-OCH_3,7-CH_3-sal)$_2$(−)-pn], (d) Co[(5,6-benzosal)$_2$(−)pn], (e) Co[(sal)$_2$(−)pn].

transition than for the $(d_{xz} \pm d_{yz}) \rightarrow d_{xy}$ transitions and consequently, for any reasonable value of F_2 and F_4 the d_{z^2} orbital is lower in energy then the $(d_{xz} \pm d_{yz})$ orbitals. Using values of the parameters $F_2 = 8F_4 = 900\ \text{cm}^{-1}$, which give the best fit for the d–d bands observed, results in $\Delta_2 \cong 1200$ and $\Delta_3 \cong 12{,}900\ \text{cm}^{-1}$.

These calculations, which ignore two-electron transitions as well as the low-lying ligand π orbitals of symmetry common to those of the d orbitals, are necessarily approximate, but they have merit in that they allow a qualitative determination of the orbital energy level separations which otherwise could not be obtained Spin–orbit coupling has also been neglected and the excited states arising from $(d_{xz} \pm d_{yz}) \rightarrow d_{xy}$ do mix under the influence of this coupling. Such an interaction between the two excited states would change slightly the estimate of Δ_1 but would not change the general conclusions.

Conformational Equilibrium. Recent reports of the circular dichroism associated with the d–d bands of tetradentate Schiff base nickel(II)[12,15] and copper(II)[15,27] complexes are consistent with an equilibrium between the methyl-axial and methyl-equatorial conformations of the coordinated propylenediamine. Increasing steric hindrance to the equatorial conformation due to substitution of a 7-CH_3 group for 7-H (Figure 1) causes the conformation of the pn to be inverted. This in turn leads to a change in the sign of the circular dichroism associated with the lowest energy d–d band. It has also been suggested[15] that another explanation of the sign inversion in the CD which does not require reversal in the conformation of the central chelate ring may be a distortion from planarity of the MN_2O_2 chromophore, which would induce helicity in the side chelate rings opposite to that of the central chelate ring.

A spectroscopic criterion for colinearity between the two azomethane groups in complexes of this type has been proposed on the basis of the circular dichroism associated with the $\pi \rightarrow \pi^*$ ligand transition.[12] The circular dichroism associated with this band, for all the complexes considered, is positive (Figure 5) and appears to be split into two components. This is in accord with the results expected for essentially colinear azomethane groups.[12] Thus, any distortion from planarity must occur through rotation of the plane of the side chelate rings about the C_1–C_7 bond axis (Figure 1). Evidence for any such distortion from planarity should be found in the difference in energy of the "low-spin planar cobalt(II)" band at ~8000 cm⁻¹ between these complexes and bis(salicylaldimino)cobalt(II)[8] where there should be considerably less steric strain involved in the planar environment. This latter complex, however, which is presumably *trans* planar, exhibits the near-infrared band at 8300 cm⁻¹ in methyl ethyl ketone, at about the same energy as do the complexes reported here (Table I). Recent work with a series of cobalt(II) complexes of N,N′-bis(salicylidene)polymethylenediamine ligands[28] suggests that the electronic absorption spectra and magnetic moments of complexes of this type are quite sensitive to distortion of the tetradentate ligands from planarity toward a tetrahedral structure. Thus it is not unreasonable to suggest that the origin of the asymmetry giving rise to the observed circular dichroism in these complexes occurs at the central chelate ring and not at the essentially planar side rings.

The circular dichroism associated with the lowest energy d–d band (in this case the near-infrared band) does not change sign for the cobalt(II) complexes on going from Co[(sal)$_2$(−)pn] to Co[(7-CH_3-sal)$_2$(−)pn] (Figure 7) and furthermore, the CD associated with the $d_{xy} \rightarrow d_{x^2-y^2}$ transition shows no sign reversal (Figure 5). This together with the change in magnitude of the CD associated with these two bands, which is in the order Co[(sal)$_2$(−)pn] $\leqq$ Co[(5,6-benzosal)$_2$(−)pn] < Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn] $\leqq$ Co[(7-C_6H_5-sal)$_2$(−)pn] < Co[(7-CH_3-sal)$_2$(−)pn] suggests that the λ, δ equilibrium is slightly in favor of the δ (methyl-axial) conformation for the least sterically hindered complex and increases as a function of the steric strain for the other complexes (Table III). In cases where the data are contradictory, Co[(7-CH_3-sal)$_2$(−)pn] and Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn], the near-infrared band has been chosen as more reliable since it is less extensively overlapped by other bands, and since the two components which contribute to the CD associated with this band are the same sign in all cases (Figures 5 and 7). Examination of atom models of these complexes suggests that this intrepretation is reasonable in that there appears to be significant steric interaction between the pn methyl in the equatorial position and the 7-H atoms in Co[(sal)$_2$-(−)pn] and Co[(5,6-benzosal)$_2$(−)pn], and that this interaction is much larger for Co[(7-C_6H_5-sal)$_2$-(−)pn] and still greater for Co[(7-CH_3-sal)$_2$(−)pn].

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Table III. Circular Dichroism Associated with the $1/\sqrt{2}(d_{xz} + d_{yz}) \rightarrow d_{xy}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions[a]

	$1/\sqrt{2}(d_{xz} + d_{yz}) \rightarrow d_{xy}$	$d_{xy} \rightarrow d_{x^2-y^2}$
Co[(7-CH_3-sal)$_2$(−)pn]	8590 (−0.17)	15,500 (+0.15)[b]
Co[(7-C_6H_5-sal)$_2$(−)pn]	8850 (−0.11)	15,000 (+0.44)
Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn]	8980 (−0.07)	15,400 (+0.45)
Co[(5,6-benzosal)$_2$(−)pn]	8970 (−0.05)	15,500 (+0.04)
Co[(sal)$_2$(−)pn]	8860 (−0.045)	15,500 (+0.06)

[a] In cm^{-1}. The values of $\epsilon_l - \epsilon_r$ are given in parentheses. [b] This low value may be rationalized by referring to Table II, where it may be seen that the next higher energy transition has negative CD for this case.

Substitution on the 5 position would seem to have no steric effect.

Further evidence for this intrepretation is seen in the sign of the CD associated with the visible region isotropic absorption spectrum of N,N′-bis(7-methylsalicylidene)-(+)-propylenediaminocobalt(II). This complex, which (if the pn methyl is axial) must have a central chelate ring λ conformation, should in *the absence of any other source of optical activity* be enantiomeric to the analogous (−)pn complex. The CD spectrum of Co[(7-CH_3-sal)$_2$(−)pn] and Co[(7-CH_3-sal)$_2$(+)pn] in chloroform are shown in Figure 8 along with the isotropic absorption spectrum of the (−)pn derivative. It appears that, within experimental error, Co[(7-CH_3-sal)$_2$(−)pn] and Co[(7-CH_3-sal)$_2$(+)pn] are enantiomers.

The magnitude of the CD associated with the near-infrared band is of some significance. In accordance with the suggestion that the CD of metal d-d bands arises from the mixing of these transitions with totally allowed electronic transitions of the same symmetry[29–32] (charge transfer bands), one would expect that the interaction should be dependent upon the energy separation between the transitions involved, and hence, that the CD associated with the near-infrared band should be smaller than that associated with the visible region d-d bands. This is the observed result (Table III). There is some difficulty in determining the actual magnitude of the CD of any given transition in the presence of other nearby transitions with CD of the opposite sign,[31,32] and therefore no more quantitative treatment of this difference in magnitude was attempted.

The sign of the circular dichroism associated with the low energy d-d band (in the near-infrared region) or that of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition could then be rationalized by recourse to a right-handed octet rule similar to that proposed for octahedral cobalt(III).[33] With the coordinated (−)pn in the reference position for mono-bidentate complexes,[33a] the δ conformation of the central chelate ring would place C_2 of the propylene skeleton in a positive octet, while C_1 would lie near the *xy* plane in a negative octet. The atoms of the side rings would presumably also lie in the *xy* plane. Thus, with a shift in the λ, δ equilibrium in favor of the δ conformation as a function of steric hindrance to the λ conformation, one would expect, on the basis of this octet rule, an increasing positive sign for the Cotton effect associated with the low energy band.

As has been recently pointed out,[34] octet rules are of limited validity, especially when used to predict the sign of the Cotton effects exhibited by all of the d-d bands of an optically active complex. Despite this, however, it seems possible, at least in the case of these ligands, where few chelate ring atoms are out of the plane of coordination and one center of optical activity is present, to obtain some useful information about the conformation of the coordinated pn by measuring the sign and magnitude of the CD associated with the low energy band.

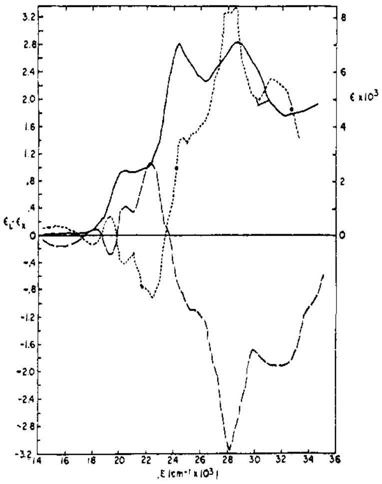

Figure 8. Circular dichroism of Co[(7-CH_3-sal)$_2$(−)pn] (---) and Co[(7-CH_3-sal)$_2$(+)pn] (- - - -), and the absorption spectrum of Co[(7-CH_3-sal)$_2$(−)pn] (——).

On the basis of the variation of sign shown by the CD of the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $(d_{xz} \pm d_{yz}) \rightarrow d_{x^2-y^2}$ transitions, as well as the CD of the charge transfer bands, in complexes which are quite similar in electronic environment, a simple rule correlating the displacement of chelate ring atoms from planarity with the observed Cotton effects would seem to be fortuitous. Nevertheless, the positive CD associated with the $d_{z^2} \rightarrow d_{xy}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions in these complexes seem to be consistent with such a rule.

Ring Substituent Effects. The band envelope from 20,000 to 32,000 cm^{-1} in Co[(7-CH_3-sal)$_2$(−)pn] containing the first three charge transfer absorptions and the ligand $\pi \rightarrow \pi^*$ band may be observed to shift to lower energies in Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn] and Co[(5,6-benzosal)$_2$(−)pn] (Figure 4). This shift, which is also observed in a wide variety of four- and five-substituted ethylenediamine analogs of these complexes[35]

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Table IV. Band Maxima for Electronic Absorption Spectra and Associated Circular Dichroism of the First Ligand $\pi - \pi^*$ Transition

Complex	Isotropic absorption spectrum	Circular dichroism
Co[(7-CH_3-sal)$_2$(−)pn]	28,750 (7100)[a]	28,150 (3.4);[b] 31,200 (2.3)
Co[(7-C_6H_5-sal)$_2$(−)pn]	28,300 (10,000)	28,200 (2.9); 29,900 (0.9)
Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn]	24,500 (9300)	25,300 (1.3); 28,900 (1.5)
Co[(5,6-benzosal)$_2$-(−)pn]	26,500 (15,000); 27,400 (14,800)	25,600 (3.0); 27,900 (2.9)
Co[(sal)$_2$-(−)pn]	27,500 (11,500); 28,600 (12,600)	26,600 (1.5); 28,260 (1.7)

[a] The values of ϵ_{max} are given in parentheses. [b] The values of $(\epsilon_l - \epsilon_r)_{max}$ are given in parentheses.

indicates that the substituents on the aryl ketone ring have a considerable effect on the energy of the empty π orbitals which are involved in the charge transfer absorptions.

Concomitant with this shift in the energy of the charge transfer and ligand bands, the CD associated with the $\pi \rightarrow \pi^*$ band varies in magnitude as a function of the substituent at the 4 or 5 position (Table IV). More detailed studies of the effects of substituents on the positions and magnitudes of the bands are in progress.

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Water Exchange between Solvent and Aquoamminenickel(II) Complexes

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Abstract: Water exchange rates with $Ni(H_2O)_5NH_3^{2+}$, $Ni(H_2O)_4(NH_3)_2^{2+}$, and $Ni(H_2O)_3(NH_3)_3^{2+}$ are reported. The k_1 (for a particular water molecule) values at 25° are 2.5 (±0.2) × 10^5, 6.1 (±0.2) × 10^5, and 2.5 (±0.2) × 10^6 sec^{-1}, respectively. The corresponding $\Delta H^{\ddagger}$ values are 10.6 ± 0.5, 7.8 ± 0.3, and 10.2 ± 0.5 kcal/mol. Scalar coupling constants for ^{17}O (A/h) in the same order are 2.5 (±0.2) × 10^7, 1.9 (±0.2) × 10^7, and 2.6 (±0.2) × 10^7 cps. T_{1e} for $Ni(H_2O)_3(NH_3)_3^{2+}$ is estimated to be 1.1 (±0.5) × 10^{-12} sec. Some discussion of ligands which do and do not labilize remaining water molecules is given.

Using ^{17}O nmr measurements, water exchange kinetics in labile aquo and substituted aquo ions can be studied. Such studies are of interest because of their relations to substitution mechanisms in general as well as providing information on effects caused by ligands adjacent to coordinated water molecules. A previous report has given results for several Ni(II) complexes.[2] In general, the remaining water molecules appear to be labilized as the extent of substitution by other ligands increases. A different result has been reported for the terpyridyl complexes.[3] This paper reports a detailed study on the mono-, di-, and triammine complexes which can be compared with previous studies, especially with ethylenediamine as ligand.[2]

Experimental Section

The nmr equipment and conditions used have been described previously.[2,4] A Varian 24.6-kG magnet was employed and the ^{17}O resonance in water observed at *ca.* 14.19 MHz. The water used was enriched to *ca.* 7% in ^{17}O. It was distilled from alkaline permanganate and redistilled *in vacuo* before each use. Other chemicals used were Mallinckrodt A R $Ni(NO_3)_2 \cdot 6H_2O$, NH_4NO_3, and 58% NH_4OH. Solutions were prepared in 2 *M* NH_4NO_3 by addition of known amounts of all reagents. Some pH measurements were made to provide estimates of species concentrations used in a computer program which calculated the equilibrium concentrations.[2] Values used for the acidity constant of NH_4^+ and the nickel-ammine complexes were those of Bjerrum[5] for 2 *M* NH_4NO_3. Enthalpy of formation values were those of Spike, as listed in ref 6. Since the equilibria do shift slightly with temperature, solution compositions were calculated as a function of temperature. Some typical results are shown in Table I for the solutions employed.

Treatment of Data and Results

A fairly detailed discussion of data treatment has been given.[2] Line broadenings and chemical shifts are observed in the free water species produced by the various nickel species over a wide range of temperature. The line broadenings are reported in terms of the defined quantity $T_{2p}' = 2M(Ni)/\gamma\Delta'$, where M(Ni) refers to the total molarity of all Ni(II) species, γ is 3628 G^{-1} sec^{-1}, and Δ' is $W_{obsd} - W_0$. The quantity W_{obsd} is the full line width for the Ni(II) solutions (in G) mea-

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[1] To whom inquiries may be addressed. This work supported by U. S. A. E. C. Contract AT(45-1)-2040 and is Report No. RLO-2040-16.

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