Stereochemistry and Electronic Structure of Low-Spin, Square-Planar Cobalt(II) Chelates with Tetradentate Schiff Base Ligands

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Abstract: The ground-state electronic configurations of N,N'-bis(o-aminobenzylidene)-(R)-($-$)-propane-1,2-diaminocobalt(II), Co(aba)$_2$($-$)pn, N,N'-bis(o-aminobenzylidene)-(R,R)-($-$)-cyclohexane-1,2-diaminocobalt(II), Co(aba)$_2$($-$)chxn, and N,N'-bis(2-pent-2-en-4-ono)-(R)-($-$)-propane-1,2-diaminocobalt(II), Co(acac)$_2$($-$)pn, have been established to be $(xy)^2(z^2)^1$ (hole formalism) by electron spin resonance measurements in frozen glasses and in ordered nematic phases. Agreement between the calculated and theoretical P and κ values provides the primary basis for the ground-state assignments. The complete ligand field spectra of these complexes, obtained by isotropic absorption and circular dichroism spectroscopy, are presented for the first time. Transition energies, calculated from single orbital energies and interelectronic repulsion parameters (including configuration interaction), are in agreement with the observed spectra and are consistent with the observed esr parameters. The ordering of the 3d orbitals is found to be: $(xy) > (z^2) > (yz) > (x^2 - y^2) > (xz)$. The failure of Co(aba)$_2$($-$)pn and Co(aba)$_2$-($-$)chxn to react with oxygen in contrast to the highly oxygen-sensitive Co(acac)$_2$($-$)pn is attributed to the stabilization of the 3d$_{z^2}$ orbital by the stronger in-plane ligand field present in the N$_4$ complexes. The signs of the Cotton effects in the CD spectra are dependent on the conformation of the central chelate ring and reveal that the methyl group in Co(aba)$_2$($-$)pn prefers a pseudoaxial position.

There has been considerable interest[3-16] in the nature of tetradentate Schiff base complexes of cobalt(II) owing to the capability of several complexes of this type to undergo reversible oxygenation–deoxygenation.[5-7,12,13] This oxygen-carrying property is usually manifest in the presence of a nitrogenous base donor so that the cobalt(II) ion is in a five-coordinate, square-pyramidal environment. In this five-coordinate geometry, cobalt(II) complexes have been shown almost universally to have an $(xy)^2(z^2)^1$ electronic configuration as the ground state.[6,7,13] The ground-state configuration of planar, four-coordinate Co(II) is much more variable, and several different descriptions have been proposed for different complexes.

Cobalt(II) porphyrins[17] and phthalocyanines,[18,19]

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(3) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jap.*, **37**, 8 (1964).
(4) A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).
(5) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).
(6) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 61 (1970).
(7) D. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Commun.*, 467 (1970).
(8) S. A. Cockle, H. A. O. Hill, and R. J. P. Williams, *J. Inorg. Nucl. Chem. Lett.*, **6**, 131 (1970).
(9) S. Koda, A. Misono, and Y. Uchida, *Bull. Chem. Soc. Jap.*, **43**, 3143 (1970).
(10) C. Busetto, C. Neri, N. Palladino, and E. Perrotti, *Inorg. Chim. Acta*, **5**, 129 (1971).
(11) L. M. Engelhardt, J. D. Duncan, and M. Green, *Inorg. Nucl. Chem. Lett.*, **8**, 725 (1972).
(12) E.-I. Ochiai, *J. Chem. Soc., Chem. Commun.*, 489 (1972).
(13) E.-I. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 1727 (1973).
(14) C. Busetto, F. Cariati, P. C. Fantucci, D. Galizzioli, and F. Morazzoni, *Inorg. Nucl. Chem. Lett.*, **9**, 313 (1973).
(15) C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973).
(16) B. M. Hoffman, F. Basolo, and D. Diemente, *J. Amer. Chem. Soc.*, **95**, 6497 (1973).
(17) F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).
(18) J. M. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, **87**, 207 (1965).
(19) J. M. Assour, *J. Amer. Chem. Soc.*, **87**, 4701 (1965).

trans-dimesitylbis(diethylphosphine)cobalt(II),[20] and bis(dithio-2,4-pentanedionato)cobalt(II)[21] have been shown to have the $(xy)^2(z^2)^1$ hole configuration analogous to the square-pyramidal case. On the other hand, Co(mnt)$_2$$^{2-}$ has been shown rather conclusively to have an $(xy)^2(yz)^1$ ground state,[22] and, more recently, the same ground state has been established for the bis-(cyclopentadienedithiocarboxylate)cobalt(II) complex.[23] In the case of tetradentate Schiff base complexes of the type reported here, preliminary communications have suggested the $(xy)^2(x^2 - y^2)^1$ ground state for N,N'-bis(o-aminobenzylidene)ethane-1,2-diaminocobalt(II) and related derivatives[11] and the $(xy)^2(z^2)^1$ configuration for Co(acac)$_2$en[14,16] and N,N'-bis(salicylidene)ethane-1,2-diaminocobalt(II) (Co(sal)$_2$en).[14] A complete description of the electronic configuration and spectra of Co(sal)$_2$en and derivatives has recently been published.[15]

The two types of complexes which are the subject of the present study exhibit markedly different reactivities toward oxygen. Co(acac)$_2$($-$)pn is extremely oxygen sensitive and in the presence of an additional donor forms an oxygen adduct essentially identical with that reported for Co(acac)$_2$en.[6] The electronic description of Co(acac)$_2$en·py·O$_2$ is a coordinated superoxide with a bent ($\sim$120°) cobalt-oxygen bond.[6] In contrast to this behavior, Co(aba)$_2$($-$)pn and Co(aba)$_2$($-$)chxn are unreactive toward oxygen in solution or in the solid state and, further, show no tendency to increase their coordination number in the presence of additional

(20) R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *J. Chem. Soc. A*, 3003 (1970).
(21) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).
(22) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).
(23) B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, **12**, 2997 (1973).

Table I. Microanalytical and Magnetic Susceptibility Data for the Cobalt(II) Complexes

| Compound | %C | | %H | | %N | | μ_{eff}, |
	Calcd	Found	Calcd	Found	Calcd	Found	BM
Co(acac)₂(−)pn	52.85	52.72	6.82	6.80	9.49	9.31	2.57
Co(aba)₂(−)pn	60.54	60.50	5.38	5.28	16.62	16.47	2.10
Co(aba)₂(−)chxn	63.65	63.91	5.88	5.87	14.85	14.72	2.38

donors.[11,24,25] Attempts have been made to rationalize this difference in behavior by suggesting different electronic configurations for the CoO_2N_2 and CoN_4 systems.[11,26]

Low-spin, square-planar cobalt(II) complexes exhibit a characteristic electronic spectrum[3] and several attempts have been made to assign the observed bands.[15,27,28] A detailed transition assignment by Hipp and Baker[27] is apparently incorrect since these authors failed to observe the d → d transitions <6000 cm⁻¹ and their assumption of a $(xy)^2(x^2 - y^2)^1$ ground state is not supported by recent esr data. The circular dichroism spectra of the complexes reported here reveal additional bands not observed in the absorption spectra. From an examination of both the isotropic absorption and circular dichroism spectra, the complete ligand field spectrum of the square-planar complexes is presented for the first time. A relatively simple ligand field calculation including configuration interaction yields transition energies in good agreement with the observed values and consistent with the excited-state parameters derived from the esr measurements. The circular dichroism data also provide information about the detailed stereochemistry of the cobalt(II) chelates.

Experimental Section

Materials. The complexes Co(acac)₂(−)pn, Co(aba)₂(−)pn, and Co(aba)₂(−)chxn were prepared in an analogous manner to the methods reported for Co(acac)₂en⁶.[29] and Co(aba)₂en.[24] The (R)-(−)-propane-1,2-diamine and (R,R)-(−)-cyclohexane-1,2-diamine employed in the syntheses were resolved by literature methods: for R(−)pn, $[\alpha]_D^{21}$ −34.0° (benzene) (lit.[30] −34.2°); for R,R(−)chxn, $[\alpha]_D^{21}$ −39.2° (benzene) (lit.[31] −36.0°), mp 41–44° (lit.[31] 42.7°). Tetrachloroethylene employed as a spectral solvent was dried over molten sodium and distilled in a nitrogen atmosphere. Dichloromethane was deaerated with a stream of nitrogen gas at room temperature for 1 hr. Toluene was distilled under an anydrous nitrogen atmosphere and stored over 4-A molecular sieves for several weeks prior to sample preparation. All syntheses and sample preparations were carried out under a rigorously anhydrous and oxygen-free atmosphere of nitrogen.

Physical Measurements. Magnetic susceptibilities (Table I) were determined for solid-state samples by the Faraday method. Diamagnetic corrections were calculated from a table of Pascal's constants. Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer. Spectra in the near-infrared region (3800–7000 cm⁻¹) were measured for the complexes dissolved in tetrachloroethylene solution or in Fluorolube (Fisher Scientific) mulls. Circular dichroism spectra in the range 8300–14,000 cm⁻¹

were obtained with a Shimadzu photoelectric spectrophotometer (Type QV-50) equipped with the circular dichroism accessory (Type VCD-1). A Cary Model 60 recording spectropolarimeter fitted with a Model 6001 CD accessory was employed for CD measurements in the range 14,300–40,000 cm⁻¹. X-Band electron spin resonance spectra were determined with a Varian V-4502-19 spectrometer in conjunction with a Magnion proton oscillator gauss meter and a Hewlett-Packard frequency meter to obtain accurate measurements of the magnetic field and microwave frequency. Esr spectra were measured at 100°K by employing a Varian variable temperature control apparatus with liquid nitrogen as the coolant. Second-order corrections were employed where possible to correct for the perturbation of the Zeeman transitions resulting from the hyperfine interactions. Esr spectra in ordered nematic phases were determined with a Varian E-3 spectrometer together with a Varian E-4540 variable temperature unit. The spectrometer was calibrated with standards of known g and A values. Galbraith Laboratories, Knoxville, Tenn., provided the microanalytical data (Table 1).

Results and Discussion

The three optically active complexes reported in this study, Co(acac)₂(−)pn, Co(aba)₂(−)pn, and Co(aba)₂-(−)chxn, exhibit essentially identical physical properties to the achiral analogs which have been described previously.[6,24,32] The tetradentate Schiff base ligands produce an approximately square-planar geometry about the cobalt(II) ion and the magnetic susceptibility measurements indicate a low spin electronic configuration. The compounds exhibit good solubility in a variety of nonpolar solvents with the exception that solutions of the aba complexes in chloroform deposit black crystals, presumably chloroform solvates of the complexes. For this reason solution studies of the aba complexes were not carried out on chloroform solutions. The complexes were prepared and handled in a rigorously oxygen-free atmosphere, although Co(aba)₂(−)pn or Co(aba)₂(−)chxn showed no sensitivity toward oxygen in solution or in the solid state.

Ground-State Configuration of the Complexes. Precise X-band esr measurements of the cobalt(II) complexes in frozen glasses and in frozen ordered nematic phases provided the basis for the determination of the ground-state configurations of the complexes. The values of the magnetic tensor elements measured from frozen toluene glass spectra are summarized in Table II. In order to provide a basis for the assignment of the g

Table II. Esr Parameters of Low-Spin Square-Planar Schiff Base Cobalt(II) Complexes

Compound	g_{xx}	g_{yy}	g_{zz}	A_{xx}^{Co}, G	A_{yy}^{Co}, G	A_{zz}^{Co}, G
Co(acac)₂(−)pn	3.1619	1.8968	2.0117	75.5	33.4	37.6
Co(aba)₂(−)pn	2.6985ᵃ	1.9764	2.0703ᵃ	20ᵇ	30.90	−
Co(aba)₂(−)chxn	2.7369	1.9867	2.1316	21.3	30.8	23.1

ᵃ Assigned at the point of maximum intensity of the asymmetric absorption peaks. ᵇ Estimated from one-eighth of the maximum line width of the absorption peak at the base line.

(24) M. Green and P. A. Tasker, *J. Chem. Soc. A*, 3105 (1970).
(25) Recently evidence has been obtained for the coordination of oxygen by Co(aba)₂en; *cf.* E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nucl. Chem. Lett.*, 9, 151 (1973).
(26) M. Green, J. Smith, and P. A. Tasker, *Discuss. Faraday Soc.*, 47, 172 (1969).
(27) C. J. Hipp and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, 92, 792 (1970).
(28) Y. Nishida and S. Kida, *Bull. Chem. Soc. Jap.*, 45, 461 (1972).
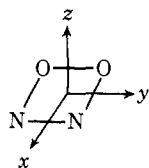(29) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Amer. Chem. Soc.*, 77, 5820 (1955).
(30) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 81, 290 (1959).
(31) F. M. Jaeger and L. Bijkerk, *Kon. Akad. Wetensch. Amsterdam, Proc.*, 40, 12 (1937).

(32) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 92, 55 (1970).

tensors to a coordinate system,[33] the esr spectra of the complexes were obtained in frozen oriented nematic phases. This technique[34-36] is based on the property of nematic liquid crystals to be aligned in a magnetic or electric field with the long axis of the liquid crystal molecules parallel to the applied field. A planar solute molecule is aligned sympathetically with its long axis parallel to the nematic solvent long axis and this alignment is maintained as the sample is frozen. Since only the long axis of the molecule is aligned with the nematic mesophase, all rotational orientations about this axis will also be found in the frozen ordered sample. In the original orientation, with the long axis of the molecule parallel to the magnetic field (0° orientation), the out of plane g tensor $(g_{||})$ of an axially symmetric complex will be perpendicular to the applied magnetic field regardless of its rotational orientation and its absorption of microwave radiation will be suppressed. The in-plane g tensor $(g_{\perp})$ will have some component parallel to the field at the 0° placement and will give rise to an absorption band. Rotation of the sample tube by 90° will bring some component of $g_{||}$ into a parallel orientation with respect to the field and its absorption will be observed. A concomitant decrease in the $g_{\perp}$ signal is usually observed at 90°. This type of axial behavior has been reported for Cu^{2+} and VO^{2+} complexes with planar Schiff base ligands.[34] For a rhombic complex in an ordered nematic mesophase, the orientation of all three g tensors with respect to the field must be considered. In the 0° orientation, all of the possible orientations of the out of plane (g_{zz}) tensor will be perpendicular to the field, and no signal is possible. The g_{xx} and g_{yy} tensors will exhibit absorptions provided that they have some component parallel to the field direction. At 90° orientation, the g_{zz} signal will be enhanced at the expense of the in-plane signals. Ordered samples of $Co(aba)_2(-)pn$ and $Co(aba)_2(-)$-chxn (Figure 1) exhibit only a single unique absorption in the 0° orientation. This signal must arise from the g tensor coincident with the long axis of the molecule (g_{yy}). The failure to observe a second signal also reveals that g_{xx} is aligned in a perpendicular direction to the field in the 0° orientation. In the 90° orientation, these CoN_4 complexes exhibit strong absorptions for both the g_{xx} and g_{zz} tensors which now have components parallel to the field.

A different orientation pattern occurs for $Co(acac)_2$-$(-)pn$. Two signals, which must correspond to g_{xx} and g_{yy}, are observed at 0° orientation, and the unique absorption, g_{zz}, becomes apparent at the 90° placement. Two explanations are possible for the observation of both g_{xx} and g_{yy} at the 0° orientation. Both signals could be observed if (1) the magnetic tensors are not coincident with the x and y coordinates[33] or (2) if the

Figure 1. Toluene glass and frozen nematic phase esr spectra of $Co(aba)_2(-)pn$ (A) and $Co(acac)_2(-)pn$ (B).

molecules is not aligned with the y axis parallel to the nematic solvent axis. It is not possible to distinguish between these two explanations at the present time, and the assignments of g_{xx} and g_{yy} for $Co(acac)_2(-)pn$ are made by analogy to the CoN_4 systems. The assignments of the g tensors, which are based on the nematic mesophase spectra, are given in Table II. In light of the nematic mesophase spectra reported here, a recent report[14] which arbitrarily assigns the lowest g value $(g \sim 1.9)$ for $Co(acac)_2en$ to g_{zz} is apparently incorrect.

In order to confirm the proposed orientation of these cobalt(II) chelates in the nematic mesophase, the spectra of the orientated copper(II) derivatives were also examined. In all cases, the out of plane absorption of the nearly tetragonal copper(II) complexes was suppressed at the 0° orientation and $g_{\perp}$ was diminished at 90°.

The method described by Maki, et al.,[22] is used to determine which metal ion 3d orbital contains the lone

(33) The coordinate scheme for the complexes is

$$z$$
$$O \begin{array}{c} | \\ \end{array} O$$
$$N \diagdown N \rightarrow y$$
$$x$$

(34) J. P. Fackler, Jr., J. D. Levy, and J. A. Smith, J. Amer. Chem. Soc., 94, 2436 (1972).
(35) A. Saupe, Angew. Chem., Int. Ed. Engl., 7, 97 (1968).
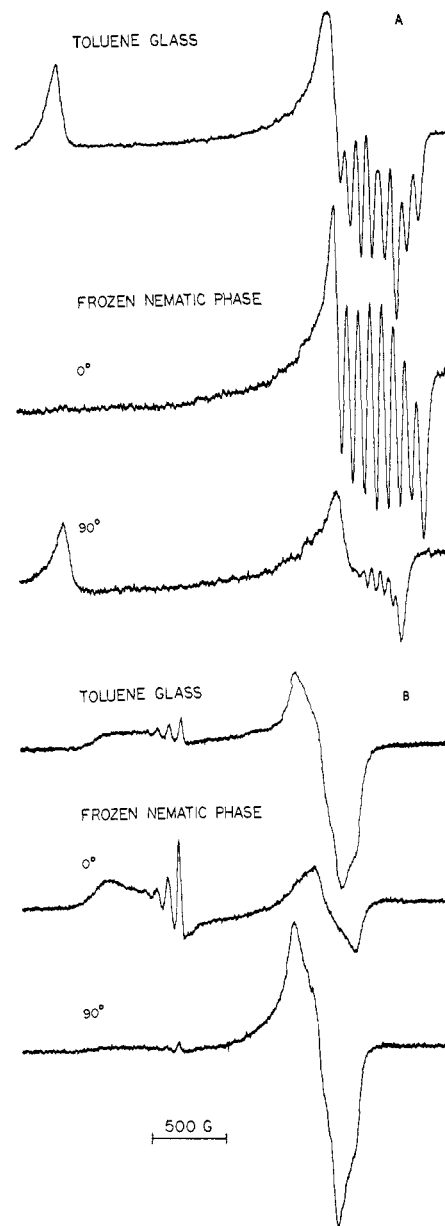(36) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, J. Chem. Phys., 43, 3442 (1965).

unpaired electron in these low symmetry complexes. This procedure was derived for complexes of D_{2h} symmetry[37] and is applied to the present complexes without modification. For the various possible electronic ground states, the six observable spin Hamiltonian parameters are calculated theoretically using a basis set of d orbitals. By comparing the experimental and theoretical values, it is possible to reject some ground-state configurations. For example, the ground-state configuration $(xy)^2(z^2)^1$ has a truncated first-order ground-state doublet of the form

$$\psi_{\pm} = N_b|(xy)^2(z^2)^{\pm 1}\rangle \pm \frac{i3}{2}b_1|(xy)^2(yz)^{\pm 1}\rangle \pm$$

$$\frac{3}{2}b_2|(xy)^2(xz)^{\pm 1}\rangle$$

For this ground state, the expressions for the spin Hamiltonian parameters are

$$g_{xx} = 2.0023 - 6b_1$$

$$g_{yy} = 2.0023 - 6b_2$$

$$g_{zz} = 2$$

and

$$A_{xx} = P\left[-6b_1 - \kappa - \frac{2}{7} - \frac{3}{7}b_2\right]$$

$$A_{yy} = P\left[-6b_2 - \kappa - \frac{2}{7} - \frac{3}{7}b_1\right]$$

$$A_{zz} = P\left[-\kappa + \frac{4}{7} + \frac{3}{7}(b_1 + b_2)\right]$$

where b_1 and b_2 are equal to the effective spin-orbit coupling constant divided by the energy difference between the ground state and the appropriate excited state. $P = 2g_N\beta_e\beta_N \overline{r^{-3}}$ and κ refers to the Fermi hyperfine coupling energy in units of P.

For Co(aba)₂(−)chxn, where all three hyperfine values are resolved experimentally, the above theoretical expressions for the A terms become

$$A_{xx} = P[+0.450 - \kappa]$$

$$A_{yy} = P[-0.246 - \kappa]$$

$$A_{zz} = P[+0.519 - \kappa]$$

Solving A_{xx} and A_{yy} for P and κ, we obtain $P = 0.008$ cm⁻¹ and $\kappa = 0.11$. These values of P and κ are reasonable and are internally consistent since they yield a calculated value of $A_{zz} = 32.8 \times 10^{-4}$ cm⁻¹ as compared to 22.9×10^{-4} cm⁻¹ experimentally. Although the observed P value is low compared to the free ion value[38] of 0.0254 cm⁻¹, none of the other ground-state configurations yielded P values of even the right order of magnitude and were rejected on this basis.

A similar procedure for Co(acac)₂(−)pn did not yield a straightforward assignment of the ground state. A suitable fit was obtained for both the $(xy)^2(x^2 - y^2)^1$ configuration with P and κ values of 0.010 cm⁻¹ and

(37) The real symmetry of the present chelates is C_2 for the Co(aba)₂-(−)chxn and C_1 for Co(aba)₂(−)pn and Co(acac)₂(−)pn. The choice of D_{2h} as a pseudo-symmetry places the d_{z^2} orbital as the out-of-plane orbital and allows a comparison with other complexes which have been studied.

(38) B. R. McGarvey, J. Phys. Chem., 71, 51 (1967).

0.160, respectively, and $(xy)^2(z^2)^1$ with P and κ equal to 0.012 cm⁻¹ and −0.07, respectively. On the basis of the esr results it is not possible to choose between these two ground-state configurations, although other configurations can be rejected.

Further considerations must be made in order to establish the ground-state configuration of Co(acac)₂-(−)pn. The strong similarity in both the isotropic absorption and esr spectra of the CoO₂N₂ and CoN₄ chelates suggests that both types of complexes have the same ground state, i.e., $(xy)^2(z^2)^1$, which has been determined for the CoN₄ complexes. Secondly, the b_n parameters which result from the assumption of an $(xy)^2(x^2 - y^2)^1$ configuration yield totally unrealistic energy differences between ground and excited states. On the other hand, the $(xy)^2(z^2)^1$ case yields b_n values which allow a consistent correlation between the absorption spectrum and the esr parameters which is described below. For these reasons, we conclude that the best description of the ground state for Co(acac)₂-(−)pn is that with the unpaired electron in the $3d_{z^2}$ orbital.

Electronic Spectra of the Cobalt(II) Chelates. The detailed electronic spectra of the cobalt(II) chelates (Figure 2) was obtained by the combined application of isotropic absorption (Table III) and circular dichroism spectroscopy (Table IV). Both the CoO₂N₂ and CoN₄

Table III. Isotropic Absorption Spectra of Low-Spin Square-Planar Schiff Base Cobalt(II) Complexes[a]

Compound	$\bar{\nu}$, cm⁻¹ (ϵ_{max})
Co(acac)₂(−)pn	3970 (96), 4300 sh (57), 4870 sh (23), 5550 (16), 8500 (20), 20,600 sh (360), 22,000 sh (~1100), 26,800 (6500), 30,000 (6150), 34,000 (13,000)
Co(aba)₂(−)pn	5100 (18), 6250 (22), 6900, 11,050 (73), 11,900 sh (48), 16,670 sh (~370), 18,900 (5000), 23,150 (22,000), 26,900 (15,500)
Co(aba)₂(−)chxn	5100,[b] 5750,[b] 6900,[b] 10,870 (74), 16,400 sh (~360), 18,940 (5100), 23,260 (18,400), 26,250 (15,450)

[a] Spectra obtained in tetrachloroethylene solutions except where noted. [b] Spectra obtained using Fluorolube mulls.

Table IV. Circular Dichroism Spectra of Low-Spin Square-Planar Schiff Base Cobalt(II) Complexes

Compound	$\bar{\nu}$, cm⁻¹ ($\Delta\epsilon$)
Co(acac)₂(−)pn	15,630 (+0.003), ~18,000 sh (−0.33), ~19,500 (+),[a] 20,700 (−2.27), 22,400 (−1.50), 25,450 (+2.14), 28,400 (+4.55), 32,250 (+32.4), 35,700 (15.60)
Co(aba)₂(−)pn	10,740 (+0.62), 11,360 (−0.09), 15,430 sh (+0.24), 16,890 (+1.62), 20,000 (+3.75), 21,690 (+3.25), 23,260 (3.39), 25,970 (+5.19), 30,300 (+7.20)
Co(aba)₂(−)chxn	10,360 (−0.68), 10,990 (+0.48), 16,130 (+0.30), 17,180 (−1.20), 20,100 (−2.49), 21,980 (−2.0), 23,100 (−3.53), 25,500 (−2.1), 27,400 (+3.22), 29,850 (−7.40)

[a] Observed but the overlapping bands prevent an estimation of the magnitude of $\Delta\epsilon$.

chromophores exhibited similar ligand field spectra. In addition to the characteristic near-infrared band (8.3 kK for the CoO₂N₂ chelate, 10.7 kK for the CoN₄ chelates), the absorption spectra obtained for tetrachloroethylene solutions of the complexes revealed several, previously

unreported, low energy electronic transitions in the range 3.9–7.0 kK. These transitions appear to be general for low-spin square-planar Co(II) complexes; we have observed analogous transitions for [N,N'-bis(3-isopropylsalicylidene)-1,2-ethanediamino]cobalt-(II),[39] a similar CoO_2N_2 chromophore. In the present chelates these bands are ascribed to d → d transitions, since there are no comparable absorptions for the corresponding copper(II) or nickel(II) chelates. This observation rules out the possibility that the low energy bands could be overtones of vibrational transitions.

Further detail is added to the ligand field spectra from the CD measurements (Table IV). Several additional transitions are observed in the CD spectra of all of the chelates in the visible region of the spectrum just prior to the onset of the intense charge transfer or intraligand bands. These are assigned as d → d transitions on the basis of their energy and low intensity (they are so weak that they are obscured in the absorption spectra by the more intense transitions). For the CoN_4 chelates the CD of the near-infrared band at ~10 kK was also obtained and revealed the additional degeneracy in the band which could be anticipated from its asymmetric nature in the absorption spectra. Two well-defined components of this band are defined in the CD spectra with a third transition apparently lying beneath the high energy component. A similar definition of three components within this near-infrared band envelop by CD has been reported for $Co(sal)_2(-)pn$.[27] CD spectra could not be obtained for the near-ir band of $Co(acac)_2(-)pn$ or for the transitions below 7 kK in the present study because of the wavelength limitation of the CD instrument.

The complete ligand field spectrum of low-spin, square-planar cobalt(II) consists of several transitions in the region 3.9–7.0 kK, a complex band multiplet at 8.3–11.0 kK encompassing three transitions, and several transitions in the visible region (14.0–20.0 kK). For a d^7 complex where the low symmetry has completely removed the degeneracy of the d manifold, a total of ten d → d transitions are expected if configuration interaction is included. For the present chelates, nine of these bands have been resolved. An assignment of these ligand field transitions is given in the following section.

Calculation of Electronic Transition Energies. The energy of each electronic configuration is given by

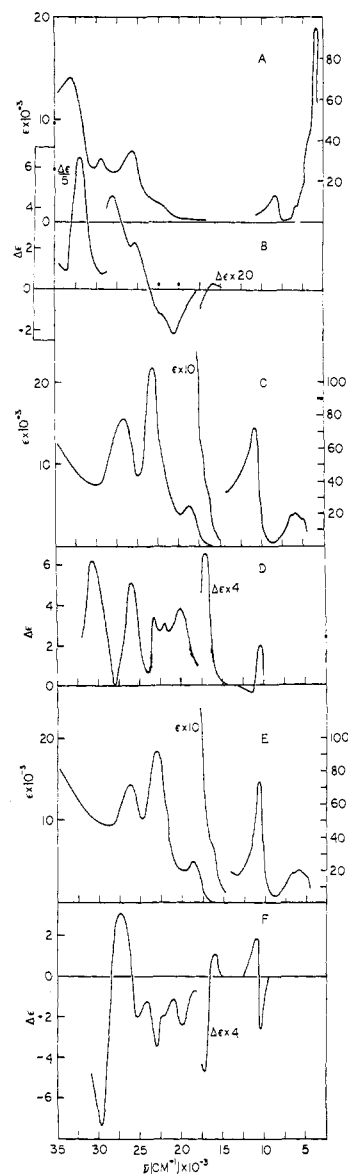$$E(\psi) = \sum_i \epsilon_i + \left\langle \psi \left| \frac{1}{r_{12}} \right| \psi \right\rangle$$

where $\sum_i \epsilon_i$ is the sum of the single d orbital energies and

$$\left\langle \psi \left| \frac{1}{r_{12}} \right| \psi \right\rangle = \sum_{k > i = 1} \left[\left\langle \phi_k(1)\phi_i(2) \left| \frac{1}{r_{12}} \right| \phi_k(1)\phi_i(2) \right\rangle - \left\langle \phi_k(1)\phi_i(2) \left| \frac{1}{r_{12}} \right| \phi_i(1)\phi_k(2) \right\rangle \right]$$

which gives the interelectronic interaction energies in terms of the Coulomb and exchange integrals. The interelectronic interaction energies for the configurations which are not subject to configuration interaction are determined directly in terms of the Condon–Shortley parameters F_0, F_2, and F_4.[40,41] Orbital excited-state

(39) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, 10, 2667 (1971).
(40) D. A. Brown, *J. Chem. Phys.*, 28, 67 (1958).

Figure 2. Isotropic absorption and circular dichroism spectra of $Co(acac)_2(-)pn$ (A and B), $Co(aba)_2(-)pn$ (C and D), and $Co(aba)_2(-)chxn$ (E and F).

configurations with single electrons in three different orbitals will have different energies depending on the spin occupancy of each orbital which results in a different number of exchange integrals for the various transitions.[41] We have treated this configuration interaction as a first-order perturbation[42] energy with the perturbation function e^2/r_{ij} averaged over configurations of like symmetry. Our calculations show that the nondegenerate configurations of this type are separated by several kilokaysers. Inclusion of this configuration interaction results in the prediction of ten spin-allowed electronic transitions for square-planar d^7 complexes. We have neglected the quartet excited states in our transition assignment since their intensity will be considerably less than the spin-allowed bands.

A set of single d orbital energies, ϵ_i, was determined which reproduced the observed electronic transitions

(41) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 76.
(42) L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill, New York, N. Y., 1935, Chapter 6.
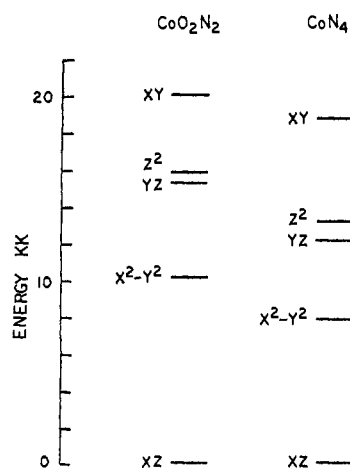
Figure 3. Single-electron d orbital energies calculated for the N_2O_2 and N_4 cobalt(II) chelates.

when the interelectronic interaction parameters were included. The choice of ϵ_i was not arbitrary but was subject to several constraints. The highest energy orbital was required to be $3d_{xy}$, which is directed at the ligand donor atoms in our coordinate scheme.[33] The $3d_{z^2}$ must be the second highest orbital to fit the ground-state assignment. The energies of the $3d_{yz}$ and $3d_{xz}$ are related to the observed values of g_{xx} and g_{yy} by the equations[22]

$$b_1 = \frac{\xi}{(xy)(xy)(z^2) \rightarrow (xy)(xy)(yz)}$$

$$b_2 = \frac{\xi}{(xy)(xy)(z^2) \rightarrow (xy)(xy)(xz)}$$

With a reasonable value of the spin orbit coupling constant, ξ (reduced from the free ion value[22] of $-515\,\mathrm{cm}^{-1}$), the energies of the $3d_{yz}$ and $3d_{xz}$ must be chosen so as to yield values of b_1 and b_2 which are comparable to those values obtained from the esr data.

Since g_{yy} is reduced below a value of 2.0,[43] the b_2 parameter is always positive and cannot be used to predict the energy of the $(xy)(xy)(z^2) \rightarrow (xy)(xy)(xz)$ transition. In any event, the proximity of g_{yy} to a value of 2.0 suggests that b_2 will be quite small relative to the b_1 parameter and the corresponding orbital separation will be large. We have accordingly assigned the $(xy)(xy)(z^2) \rightarrow (xy)(xy)(xz)$ transition to the highest energy d $\rightarrow$ d transition which was observed. The electronic transition energies calculated by this procedure are compared with the observed spectra in Table V. The single d orbital energies are shown in Figure 3.

Several features of this assignment of electronic transitions and orbital arrangement require further comment. The assignments for both the CoO_2N_2 and CoN_4 chelates are similar as would be anticipated from the similarity in the electronic and esr spectra of these compounds. It is necessary to predict unobserved transitions $<3200\,\mathrm{cm}^{-1}$ in order to produce a complete correlation between the optical spectra and the esr parameters. The large in-plane anisotropy observed in the esr spectra of these complexes yields a large value for the b_1 parameter. With a value of ξ approximately 70% of the free ion value, the observed values of b_1 re-

(43) The value of g_{yy} can be reduced below 2.0 by inclusion of second-order terms in the theoretical expressions for the g tensors.

Table V. Calculated and Experimental Ligand Field Spectra for the Cobalt(II) Complexes[a]

State (hole configuration)	Inter-electronic inter-action terms[b]	$\Sigma\epsilon_\kappa$[c]	Calcd transition[d]	Obsd transition
Co(acac)₂(—)pn[e]				
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{z^2})$	−3620	4,300	0	
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{yz})$	−1620	4,800	2,500	f
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{yz})$	−5178	9,100	3,242	3,970
$(\overset{+}{xy})(\overset{-}{z^2})(\overset{+}{z^2})$	−3620	8,600	4,300	4,300
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{yz})$	−3062	9,100	5,358	5,550
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{x^2 - y^2})$	−5720	14,343	7,943	8,300
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{x^2 - y^2})$	−2520	14,343	11,143	8,900
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{x^2 - y^2})$	+4380	10,043	13,743	15,630
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{xz})$	−1620	20,300	18,000	18,000
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{xz})$	−5178	24,600	18,742	19,500
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{xz})$	−3062	24,600	20,858	20,600
Co(aba)₂(—)chxn[e]				
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{z^2})$	−3620	5,700	0	
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{yz})$	−1620	6,700	3,000	f
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{yz})$	−5178	12,400	5,142	5,100
$(\overset{+}{xy})(\overset{-}{z^2})(\overset{+}{z^2})$	−3620	11,400	5,700	5,700
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{yz})$	−3062	12,400	7,258	6,900
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{x^2 - y^2})$	−5720	16,800	9,000	10,870
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{x^2 - y^2})$	−2520	16,800	12,200	12,190
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{x^2 - y^2})$	+4380	11,100	13,400	13,400
$(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{xz})$	−1620	19,000	15,300	15,300
$(\overset{+}{xy})(\overset{+}{z^2})(\overset{-}{xz})$	−5178	24,700	17,442	16,600
$(\overset{-}{xy})(\overset{+}{z^2})(\overset{+}{xz})$	−3062	24,700	19,558	19,220

[a] All energies are expressed in cm^{-1}. [b] Condon–Shortley parameters used were $F_2 = 700\,\mathrm{cm}^{-1}$ and $F_4 = 60\,\mathrm{cm}^{-1}$. [c] ϵ_κ is the single electron orbital energy (hole configuration) with respect to d_{xy}. [d] The calculated transition is obtained from the sum of the interelectronic interaction terms and the single electron orbital energies minus the ground-state energy. [e] The specific assignment within the bracketed transitions may vary owing to the approximate nature of the calculation. [f] Not observed.

quire optical transitions in the region 2500–3000 cm^{-1}. Our transition assignment readily accounts for the asymmetry observed in the characteristic near-infrared band of these complexes in terms of splitting produced by configuration interaction. These calculations over-emphasize this interaction, however, and the predicted splitting is much larger than is observed.

The calculated orbital scheme predicts that $(\mathrm{aba})_2$-$(-)\mathrm{pn}^{2-}$ and $(\mathrm{aba})_2(-)\mathrm{chxn}^{2-}$ produce a stronger ligand field about the cobalt(II) ion than does $(\mathrm{acac})_2(-)\mathrm{pn}^{2-}$. If the separation between the d_{xy} and $d_{x^2-y^2}$ orbitals is taken to represent Δ_1, then for $\mathrm{Co(aba)_2}(-)\mathrm{pn}$ $\Delta_1 =$

11,100 cm^{-1} and for Co (acac)$_2$($-$)pn $\Delta_1 = 10,043$ cm^{-1}. The CoN$_4$ chelates also produce a larger separation between the d$_{xy}$ and d$_{z^2}$ orbitals. The increased stabilization of the single electron in the d$_{z^2}$ orbital could account for the failure of the CoN$_4$ chelates to react with oxygen. In the formation of a cobalt–oxygen bond the unpaired d$_{z^2}$ electron is transferred to the oxygen molecule to form a coordinated superoxide ion.[6] In most examples of reversible oxygen carriers, the cobalt(II) ion is in a five-coordinate geometry which greatly destabilizes the d$_{z^2}$ orbital and makes this electron accessible for transfer to the oxygen. The reverse process is operative in the CoN$_4$ systems where the stabilization of the d$_{z^2}$ electron renders the chelates inert to oxygen.

Stereochemistry of the Chelates. In addition to the greater resolution of the electronic spectra, further details of the stereochemistry of these cobalt(II) chelates are revealed by the circular dichroism spectra. The complexes Co(aba)$_2$($-$)pn and Co(aba)$_2$($-$)chxn exhibit CD spectra which are virtually mirror images despite the fact that both parent diamines have the same absolute configuration. This relationship between the ($-$)pn and ($-$)chxn derivatives is a result of the metal ion complexation; the free ligands produce essentially superimposable CD spectra.[44] We have observed similar behavior previously with copper(II),[45] nickel(II),[46] and oxovanadium(IV) complexes[47] with Schiff base ligands derived from ($-$)pn and ($-$)chxn. As we originally proposed,[45–47] this effect can be explained by a consideration of the conformational preference of the central gauche chelate ring. In the

($-$)chxn derivative the requirement that the cyclohexyl group have a trans equatorial arrangement fixes the central chelate ring into a λ conformation.[48] The ($-$)pn derivative, however, is conformationally mobile and can adopt either a λ conformation, with the methyl substituent in a pseudoequatorial position, or a δ conformation, with the methyl group axial. The δ conformation is strongly preferred since it minimizes the steric interaction between the (pn)methyl group and substituents attached to the azomethine carbon. The reversal in the CD spectra observed between Co(aba)$_2$-($-$)pn and Co(aba)$_2$($-$)chxn can therefore be attributed to the opposite conformations of the chiral central chelate ring which are present in these complexes.

A further source of chirality has been observed in the Zn(II),[49] Cu(II),[45] and VO(IV)[47] complexes of this type in the form of a slight pseudotetrahedral distortion of the donor atom array. This contribution is characterized by the presence of a CD exciton couplet[49] corresponding to nondegenerate $\pi \rightarrow \pi^*$ transitions localized in the azomethine chromophores. In the present cobalt(II) chelates it is not possible to identify with certainty two CD components corresponding to azomethine excitations owing to the complexity of the CD spectrum in this region arising from charge transfer bands. Since the CD behavior of the cobalt(II) chelates is similar to the other metal ion derivatives, it is likely that a chiral pseutotetrahedral distortion is operative here also.

(44) R. S. Downing, Ph.D. Thesis, Case Western Reserve University, 1969.

(45) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **91**, 5977 (1969).

(46) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **92**, 5861 (1970).

(47) R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **9**, 2562 (1970).

(48) Proposed IUPAC nomenclature, *Inorg. Chem.*, **9**, 1 (1970).

(49) B. Bosnich, *J. Amer. Chem. Soc.*, **90**, 627 (1968).