Figure 6. Dependence of k_5 on varying concentrations of H₂L and H⁺. $k_5/[H_2L]$ at constant [H⁺] is invariant in the range 0.05 M < [H₂L] < 1.00 M.

reacting systems with no spectral evidence of significant ester formation and no kinetic evidence in the present study nor in studies of HMBA and MA. H_2CrO_4 ([H⁺] > 0.5 M) and $Cr_2O_7^{2-}$ (Cr(VI) > 10⁻³ M) are the only other forms of Cr(VI) that affect reaction rates—both as less reactive or inert forms of Cr(VI) in equilibrium with $HCrO_4^-$.

The magnitude of k_L/k_H or k_L/k_0 is smaller for mandelic acid than for lactic acid, with mandelate ion being the weaker base for assisting α-H transfer. The fact that a mandelic acid molecule can be oxidized by 3 equiv removes the need for a $[Cr^{VI}(MA)_2]^+$ active complex to effect a three-electron oxidation and indicates that the second MA molecule in the activation process functions as a general acid and not as an electron donor (Table VI).

This study presents compelling evidence that monitoring chromium(V) intermediates is essential to mechanistic studies of chromate oxidations. General-acid catalysis of chromium(VI) oxidations is suggested: $d[Cr(VI)]/dt = [HCrO_4^-][S](k_0 + \sum k_{HX}[HX])$ includes the substrate in HX if it is an acid. Three chromium(V) lactates undergo internal redox to form products. $CrO_2L(H_2O)_2^-$ and $CrOL(OH_2)_2^+$ are comparable to chromium(VI) ($CrO_2L(OH)(OH_2)^-$) in reactivity. $CrOL_2^-$ is inert but reacts with radicals after Cr(VI) is consumed.

EPR Properties of a Cobalt(II) Complex Containing a Low-Symmetry Porphyrin-like Ligand

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The single-crystal EPR spectrum of the low-spin, strongly rhombic (hemiporphyrazinato)cobalt(II) (Co(hp)) diluted into the isomorphous Ni(II) complex gives $g_x = 3.567$, $g_y = 1.821$, $g_z = 1.728$, $A_x = 247.6 \times 10^{-4}$ cm⁻¹, $A_y \simeq 4 \times 10^{-4}$ cm⁻¹, and $A_z = 33.5 \times 10^{-4}$ cm⁻¹. With respect to the related porphyrin and phthalocyanine complexes, loss of the axial symmetry strongly affects the spectrum but does not change the ground-state orbital, which remains $(x^2 - y^2)^2(z^2)$. An extended Hückel MO calculation predicts the correct ground state; the right ordering of the excited states can be obtained from a ligand field type calculation. Fitting of the spin-Hamiltonian parameters indicates that, among these low-lying excited states, two doublets and one quartet give important contributions to the ground-state wave function. The quartet state lies at a few hundred wavenumbers from the doublet ground state. Model calculations predict that a ground-state inversion may occur upon small structural changes. Experimentally this is confirmed by the EPR spectra of Co(hp) diluted in a range of nonisomorphous host lattices. A rationalization of the different ground states possible for Co(II) complexes is given in terms of simple MO arguments.

Introduction

A large amount of work, both theoretical and experimental, has been reported in the past years with the aim to clarify the electronic properties of planar low-spin Co(II) complexes.[1-6] The main problem in these compounds is that several doublet and quartet states are clustered together at low energies and strongly interact with each other through spin–orbit coupling.

However, careful EPR and ENDOR studies have allowed determination of the ordering of the levels in a number of cases. The general result is that two spin doublets, namely $(x^2 - y^2)^2(yz)$ and $(x^2 - y^2)^2(z^2)$, are lowest in energy and possible candidates for the ground state. The EPR spectrum is strongly influenced by the energy separation of these two states, but definitive assignment of the ground state is not unambiguous. In spite of this,

detailed analysis of the theoretical g-value expressions has shown that the actual ground state can be obtained from the relative values of the g_z and g_y components.[1,7]

This criterion, which seems to be generally valid, requires single-crystal data to be available for a definitive assignment of the magnetic axes.

The results reported up to now show that high-symmetry compounds, such as the D_{4h} porphyrin and phthalocyanine derivatives[8] or the quasi-D_{4h} complexes with bidentate S-containing

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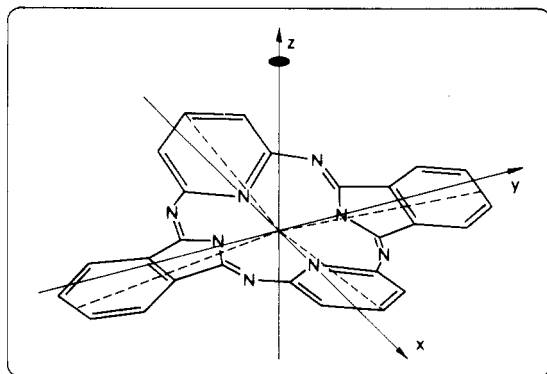† ITSE-CNR.
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Figure 1. Molecular geometry of Ni(hp). The coordinate system used throughout the text is indicated.

Figure 2. X-band, single-crystal EPR spectrum of Co/Ni(hp) at 110 K. The external magnetic field is in the $g_y g_z$ plane at ca. 20° from g_y. $\Delta M_I \neq 0$ lines are indicated by asterisks.

ligands,[9,10] invariably display a $(x^2 - y^2)^2(z^2)$ ground state. Conversely, in the absence of axial ligands, an $(x^2 - y^2)^2(yz)$ ground state has always been found for low-symmetric systems, such as the C_{2v} Schiff base complexes.[1] For these latter compounds variation of the donor atoms set from N_2O_2 to N_4, N_2S_2, and N_2Se_2 has been shown to leave essentially unchanged this basic trend.[3]

In this context the electronic properties of the recently reported (hemiporphyrazinato)cobalt(II),[11] Co(hp) (Figure 1), are interesting because this compound is a derivative of a porphyrin-related ligand but lacks the fourfold symmetry typical of these macrocycles. Structural and chemical information has shown that the four inner nitrogens of the ligand are strongly inequivalent, giving rise to a large rhombic component of the ligand field.[12,13]

Therefore, we measured the EPR spectrum of Co(hp), diluted into single crystals of the isomorphous Ni(hp), to see whether a substantial decrease in symmetry, other things being roughly equal, might affect the ground-state level and the ordering of the excited states.

Rationalization of the experimental results has been attempted on the basis of a ligand field description.

Experimental Section

Co(hp) and Ni(hp) were prepared with use of reported procedures.[11] Doped single crystals (nominal Co concentrations ca. 5%) were grown by vacuum sublimation at 450 °C and 10^{-2} torr or, better, by controlled cooling of nitrobenzene solutions sealed under vacuum. The needlelike crystals obtained in this way are quite small, but they can reach reasonable dimensions if supersaturated solutions are used and several cooling cycles are performed. The identity of the crystals was checked by measuring the unit cell dimensions from oscillation and zero-layer photographs taken with Cu Kα radiation.

The EPR measurements were carried out at 110 K, at the X-band frequency, with a Varian E-9 spectrometer equipped with a standard variable-temperature accessory, a Systron-Donner 6246A frequency counter, and a Bruker BNM-20 gauss meter. The spectra were recorded at 10° intervals in the three planes defined by the monoclinic axis system of the host compound. The deviation of this frame from orthogonality is small (β = 92.8°) and was ignored during subsequent analysis of the spectra. Details of the procedures for data collection and analysis have been reported elsewhere.[14] Spectra were also measured in the plane of lowest magnetic anisotropy to check the precise location of g_z and g_y.

In agreement with X-ray data[12] the spectra showed the presence of a single magnetic site. Typical line widths were about 1 mT. The spectrum of a polycrystalline sample was recorded at the Q-band frequency (cf. Figure 3). All the model calculations were carried out at the computing center of the University of Fribourg on an IBM 4341/1 computer.

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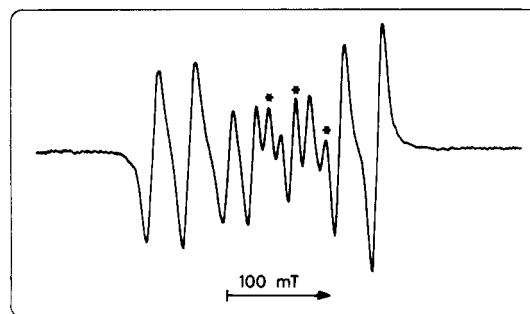(14) Attanasio, D.; Bellitto, C.; Flamini, A. *Inorg. Chem.* **1980**, *19*, 3419.
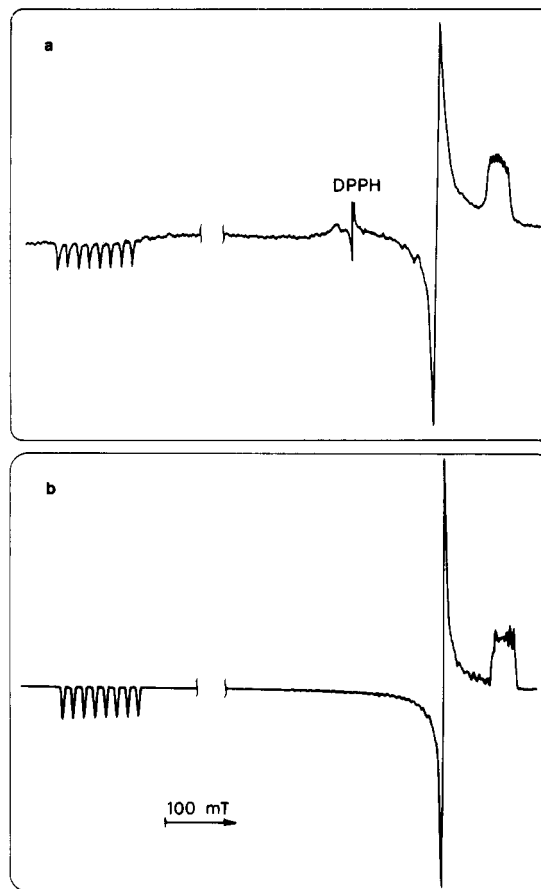

Figure 3. Experimental (a) and simulated (b) polycrystalline, Q-band EPR spectra of Co/Ni(hp) at 110 K. The simulation parameters are those reported in Table I. The line width is 2 mT. The simulation program is described in ref 23.

Results and Discussion

EPR Spectra. Co(hp) and Ni(hp) are isomorphous. The crystal and molecular structure of the latter, which dates back to 1953,[12] has been confirmed by a recent redetermination.[15]

Ni(hp) crystallizes in the monoclinic space group $C2/c$ with $Z = 4$, $a = 23.55$ Å, $b = 3.781$ Å, $c = 21.97$ Å, and $\beta = 92.8°$. The hemiporphyrazinato anion is largely nonplanar, with the isoindole and pyridine rings tilted out of the equatorial plane by about 25°, to give a pronounced saddle conformation (Figure 1).

The overall symmetry of the complex is not higher than C_2. However, the Ni(II) ion and the four inner nitrogens are closely coplanar and do not show appreciable deviations from D_{2h} symmetry. The isoindole and pyridine nitrogens are strongly inequivalent, their bonding distances being 1.90 and 1.985 Å, respectively.

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Table I. Single-Crystal (9.1-GHz) and Powder (35-GHz) Spin-Hamiltonian Parameters of Co(hp) Doped into Ni(hp) at 110 K[a]

	principal values[b]	direction angles,[b] deg			diluted-powder params
		a	b	c	
g_x	3.567	44.5	90	134.5	3.57
g_y	1.821	134.5	89.8	45.5	1.83
g_z	1.729	89.8	0.2	90	1.725
A_x	247.6	44.3	90.4	134.2	250
A_y	3.8	43.7	91.1	44.3	unresolved
A_z	33.5	89.9	1.2	90.4	32
Q^c	0.9				
η^c	0.2				

[a] Hyperfine and quadrupole parameters are in units of 10^{-4} cm^{-1}. [b] Estimated errors on single-crystal parameters are $\Delta g_i = \pm 0.005$ and $\Delta A_i = \pm 1 \times 10^{-4}$ cm^{-1}. For the direction angles the error is about 2°. [c] $Q = {}^3/_2 P_1$; $\eta = (P_2 - P_3)/2$.

Representative single-crystal and powder spectra of Co/Ni(hp) are reported in Figures 2 and 3. The final spin-Hamiltonian eigenvalues and eigenvectors are listed in Table I. In the proximity of the y direction the effective hyperfine and quadrupole coupling constants have comparable magnitudes and the spectra show strong second-order effects (see Figure 2). A detailed study of these effects has not been attempted, and therefore, the lowest a^{Co} value and the quadrupole coupling parameters are not expected to be very accurate.

Comparison of our results with those reported for axially symmetric low-spin Co(II) complexes illustrates the extreme sensitivity of these EPR spectra to the overall symmetry of the complexes. Porphyrin and phthalocyanine derivatives of Co(II) give $g_\parallel < 2$, $g_\perp \geq 3$, and large hyperfine values with $a_\perp > a_\parallel$.[8] These features can be interpreted as due to an $(x^2 - y^2)^2(z^2)$ ground state, strongly interacting with the e_g orbitals (xz) and (yz), which give first-order spin–orbit contributions respectively to the y and x components of g. Loss of the axial symmetry ($D_{4h} \rightarrow D_{2h}$) splits the e_g doublet, leaving only one low-lying state, namely the $^2B_{3g}$ $(x^2 - y^2)^2(yz)$. Therefore, g_y, in the absence of large first-order contributions, drops to values comparable with the free-electron g value, whereas g_x remains much larger than g_e, reversing the general appearance of the spectrum. Higher order contributions are important in determining the detailed behavior of the g and a values but do not change this basic picture.

Reversal of the ^2A_g and $^2B_{3g}$ states gives an $(x^2 - y^2)^2(yz)$ ground state but does not affect dramatically the spectrum, which, at first approximation, depends only on the energy separation between the two states. However, in the case of Co(hp) the presence of an $(x^2 - y^2)^2(z^2)$ ground state is strongly suggested by the fact that the experimental g_y value is larger than g_z.

In C_2 symmetry we expect one principal direction of the magnetic tensors to be collinear with the C_2 axis. This is observed experimentally, since both g_z and a_z coincide with C_2 within the experimental error. The orientation of the other two tensor components is symmetry unrestricted. However, in line with the gross D_{2h} symmetry present in the first coordination sphere of the metal ion, they lie approximately along the Co–N bond directions.

Ligand Field Description of the EPR Parameters. Ligand Field Levels. The symmetry of a molecular site in a Ni(hp) host lattice is C_2, and hence, (z^2), $(x^2 - y^2)$, and (xy) on one hand and (xz) and (yz) on the other hand are allowed to mix together in this low-symmetry field. In order to estimate these mixing coefficients and also to obtain a crude description of the electronic structure of Co(hp), we have carried out an extended Hückel calculation. Charge iteration on the central Co atom has been performed. The valence orbital ionization potentials used were those given by Basch et al.[16] "Single-ζ" STO's were used for the ligand orbitals and "double-ζ" STO's for the metal 3d orbitals.[17] The geometry of the Ni(hp) host was taken from the X-ray structure analysis.[12] The coordinate system we used is shown in Figure 1.

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Only MO's with dominant metal character are of interest. Four of the five d orbitals, i.e. (z^2), (xy), (xz), and (yz), interact weakly with the ligand system and remain relatively close to the d-orbital Coulomb energy (-11.63 eV) as is seen by inspection of Table II. The fifth one, i.e. $(x^2 - y^2)$, interacts strongly with the σ orbitals of the four ligating nitrogen atoms and lies about 1.5 eV above the other four d orbitals. It is remarkable to point out that this calculation predicts correctly the ground state, (z^2) is singly occupied, in agreement with the observed EPR parameters (vide infra).

Ground-State Wave Function for the Description of the Magnetic Parameters. A qualitative analysis of the observed g values, i.e. $g_x > g_y > g_z$, suggests that the ground state of Co(hp) is predominantly $(x^2 - y^2)(z^2)$.[1] The admixture of one or several low-lying excited states is suspected because of the large anisotropy of the magnetic tensors. The parent "hole" configurations and the first-order energies of the states that are allowed to mix with the ground state by spin–orbit coupling are depicted in Table III. Inspection of this table shows that all states, except the doublet $(x^2 - y^2)^2(xy)$, have similar energies and should therefore be taken into account for the description of the magnetic parameters. Nevertheless, it turned out during practical calculations with a trial wave function including all these states that the last two quartets in Table III were irrelevant for the description of the observed EPR parameters. Therefore, we base our description upon the ground-state Kramers doublet

$$|0\alpha\rangle = C_{1+}^\alpha |\Phi_1+\rangle + C_{1-}^\alpha |\Phi_1-\rangle + \dots + C_{5-}^\alpha |\Phi_5-\rangle \quad (1)$$

where $|0\alpha\rangle$ denotes the two components of the Kramers doublet and where

$$|\Phi_1 \pm\rangle = |(75)^2(\overset{\pm}{76})|$$

$$|\Phi_2 \pm\rangle = i|(75)^2(\overset{\pm}{78})|$$

$$|\Phi_3 \pm\rangle = \mp|(75)^2(79)|$$

$$|\Phi_4 \pm\rangle = \pm i/3^{1/2}\{|(\overset{\mp}{75})(\overset{\mp}{76})(\overset{\mp}{78})| + |(\overset{\mp}{75})(\overset{\pm}{76})(\overset{\mp}{78})| + |(\overset{\mp}{75})(\overset{\mp}{76})(\overset{\pm}{78})|\}$$

$$|\Phi_5 \pm\rangle = \pm i|(\overset{\pm}{75})(\overset{\pm}{76})(\overset{\pm}{78})|$$

The spin orbitals

$$(\overset{+}{75}), (\overset{-}{75}), \text{etc.}$$

are those given in Table II. The coefficients $C_{i\pm}$ are obtained by diagonalization of the CI matrix (cf. Table IV), and selection of the doublet with lowest energy. The full diagonalization of the CI matrix is necessary because of the presence of an almost (accidentally) degenerate ground state as suggested by the unusually large anisotropy of the g and a tensors.[1]

Electronic g Tensor. The Zeeman splitting of the ground state is obtained by calculation of the matrix elements of the Zeeman operator

$$\vec{H}_{Ze} = \beta_e \vec{H}(k\vec{L} + g_e\vec{S}) \quad (2)$$

with the Kramers doublet $|0\pm\rangle$ (cf. eq 1). This matrix $\langle \pm|\vec{H}_{Ze}\pm\rangle$ is equal to the Zeeman matrix of the spin Hamiltonian, $\langle \pm|\beta_e H\widetilde{g}\vec{S}|\pm\rangle$, evaluated over the components of the effective spin, and one yields for the components of the g tensor expressed in the coordinate system of Figure 1

$$g_{\mu x} = 2\text{Re}\langle +|H_{Ze},\mu|-\rangle \quad (3a)$$

$$g_{\mu y} = 2\text{Im}\langle +|H_{Ze},\mu|-\rangle \quad (3b)$$

$$g_{\mu z} = 2\langle +|H_{Ze},\mu|+\rangle \quad (3c)$$

where $\mu = x, y, z$ and Re and Im denote the real and imaginary parts of the complex matrix element. For low symmetries, monoclinic and triclinic, the g and a tensors are usually asym-

Table II. EHMO Calculation of Co(hp): MO's with Dominant Metal Character

MO	occ	energy, eV	population, % Co	3d orbital mixing[a]				
				d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
75	0	−10.08	54	0.0687	0.9976	0.0017	0.0	0.0
76	1	−11.43	88	0.9599	−0.0666	0.2722	0.0	0.0
77	2	−11.46	89	−0.2716	0.0171	0.9622	0.0	0.0
78	2	−11.51	93	0.0	0.0	0.0	0.0954	0.9954
79	2	−11.56	94	0.0	0.0	0.0	0.9954	−0.0954

[a] These ligand field mixing coefficients are the orthonormalized "extended Hückel" coefficients of the corresponding MO, the ligand contribution being neglected.

Table III. Ground and Excited States of Co(hp)

parent confign	spin multiplicity	first-order energy[a]
$(d_{x^2-y^2})^2(d_{z^2})$	doublet	0
$(d_{x^2-y^2})^2(d_{yz})$	doublet	$\Delta_1 + 5B$
$(d_{x^2-y^2})^2(d_{xy})$	doublet	$\Delta_2 + 20B$
$(d_{x^2-y^2})^2(d_{xz})$	doublet	$\Delta_3 + 5B$
$(d_{x^2-y^2})(d_{z^2})(d_{yz})$	quartet	$\Delta_4 + \Delta_1 - 4(B + C)$
$(d_{x^2-y^2})(d_{z^2})(d_{xy})$	quartet	$\Delta_4 + \Delta_2 - 4(B + C)$
$(d_{x^2-y^2})(d_{z^2})(d_{xz})$	quartet	$\Delta_4 + \Delta_3 - 4(B + C)$

[a] The symbols Δ_i (i = 1–4) denote the ligand field splitting energies, i.e. $d_{z^2} - d_{yz}$, $d_{z^2} - d_{xy}$, $d_{z^2} - d_{xz}$, and $d_{x^2-y^2} - d_{z^2}$, respectively. B and C are the Racah parameters.

metric; i.e. $g_{\mu\nu} \neq g_{\nu\mu}$.[18,19] From the EPR spectra only the symmetrized form

$$G_{\mu\nu} = 2\{\langle+|H_{Ze,\mu}|+\rangle\langle+|H_{Ze,\nu}|+\rangle + \text{Re}\langle+|H_{Ze,\mu}|-\rangle\langle-|H_{Ze,\nu}|+\rangle\} \quad (4)$$

can be determined. The "principal values" of the **g** tensor are then obtained by diagonalization of G

$$g_i = G_i^{1/2} \quad (5)$$

and the directions of the "principal axes" correspond to those of G.

Hyperfine Tensor. For the calculation of the hyperfine coupling, three contributions have to be considered, (i) the Fermi contact term $H_{hf}{}^F = {}^8/_3\pi g_e\beta_e g_{Co}\beta_N[\delta(\vec{r})]\vec{S}\cdot\vec{I}$; (ii) the "electron spin–nuclear spin" dipolar coupling $H_{Hf}{}^{DD} = g_e\beta_e g_{Co}\beta_N[3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r}) - r^2(\vec{S}\cdot\vec{r})]/r^5$, and (iii) the "nuclear spin–orbital momentum" coupling $H_{hf}{}^L = 2g_e\beta_e\beta_N\vec{I}[\vec{\nabla}(r^{-1})]\vec{P}$, where g_{Co} = gyromagnetic value of the Co nucleus, β_N = nuclear magneton, $\delta(r)$ = Dirac's delta, $\vec{r}$ = coordinates of the electron, $\vec{I}$ = nuclear spin operator, and $\vec{P}$ = linear momentum of the electron.

The calculation of the matrix elements of this operator is more conveniently performed with use of the method of the operator equivalents[20]

$$\vec{H}_{hf}\vec{I} = P\left\{\vec{L} + \left[\frac{2l(l+1)}{(2l-1)(2l+3)} + K\right]\vec{S} - \frac{3}{(2l-1)(2l+3)}[(\vec{L}\cdot\vec{S})\vec{L} + \vec{L}(\vec{L}\cdot\vec{S})]\right\}\cdot\vec{I} \quad (6)$$

where $P = 2g_{Co}\beta_e\beta_N\langle r^{-3}\rangle$ (here we approximate g_e = 2), and where $KPS\cdot I$ describes the Fermi contact interaction. The calculation of the hyperfine tensor elements $A_{\mu\nu}$ is performed in the same way as for the $G_{\mu\nu}$ elements:

$$A_{\mu\nu} = 2\{\langle+|H_{hf,\mu}|+\rangle\langle+|H_{hf,\nu}|+\rangle + \text{Re}\langle+|H_{hf,\mu}|-\rangle\langle-|H_{hf,\nu}|+\rangle\} \quad (7)$$

The "principal values" and the "principal axes" of the **a** tensor are obtained as before by diagonalization of A and

$$a_i = A_i^{1/2} \quad (8)$$

Interpretation of the EPR Parameters. In the model described previously, the values of the **g** and **a** tensors depend upon six adjustable parameters, i.e.: Δ_1/ξ, the energy of the $(75)^2(78)$ state in units of the spin–orbit coupling constant; Δ_2/ξ, the energy of the $(75)^2(79)$ state in units of the spin–orbit coupling constant; Δ_3/ξ, the energy of the $(75)(76)(78)$ state in units of the spin–orbit coupling constant; k, the orbital reduction factor in eq 2; P, the radial part in eq 6; K, the Fermi contact contribution in eq 6.

Therefore, we can use the three g values and the three a values to fix these six parameters. A perfect fit (the number of independent parameters is equal to the number of independent data points) is thus obtained with the following set of parameters: Δ_1/ξ = −1.191; Δ_2/ξ = −16.53; Δ_3/ξ = 0.830; k = 0.776; P = 158.7 × 10^{-4} cm⁻¹; K = −0.305.

The lowest excited state is the quartet $(x^2 - y^2)(yz)(z^2)$, which lies at only a few hundred wavenumbers from the ground state. The vicinity of the quartet accounts for the ground-state inversion observed upon small structural changes imposed by the use of nonisomorphous hosts. Thus a quartet ground state has been previously reported[11] when Co(hp) is doped into the free ligand, i.e. H_2hp, or into Zn(hp). A similar result has also been obtained with Zn(hp)·H_2O, which contains axially coordinated water.

This behavior can be easily understood by considering the first-order expression for the energy separation between this low-lying quartet and the $(x^2 - y^2)^2(z^2)$ ground-state doublet

$$\Delta E(\text{quartet–doublet}) = \epsilon(x^2 - y^2) - \epsilon(yz) - 4(B - C)$$

where the ϵ's are the energies of the one-electron levels.

The last term of the above expression, i.e. $4(B + C)$, is not influenced by small structural changes, and inversion of the ground state can be observed upon stabilization of $(x^2 - y^2)$ and destabilization of (yz). In addition we notice that the energy of the (z^2) orbital does not appear in the above expression. This means that addition of an axial ligand influences the quartet–doublet energy separation essentially through the simultaneous radial expansion of the macrocyclic ring. Thus increase of the in-plane bond lengths and strengthening of the axial perturbation favor the quartet ground state.

Structural data, available for the two hosts H_2hp and Zn-(hp)·H_2O, are in agreement with the above reasoning. The free ligand shows Ct–N distances of 1.927 (isoindole) and 2.246 (pyridine) Å.[21] The corresponding values for Zn(hp)·H_2O are 1.969 and 2.250 Å, whereas the axial water oxygen is at 2.111 Å.[15]

The other two excited states are the doublets $(x^2 - y^2)^2(yz)$ and $(x^2 - y^2)^2(xz)$ respectively located at several hundred and a few thousand wavenumbers from the ground state. The energy separation between these two states is a direct measure of the orthorhombic splitting. The origin of this splitting is depicted in Figure 4. It is apparent that (xz) and (yz) interact with two ligand π orbitals of similar energies. Therefore, the extent of the orthorhombic splitting is mainly due to the strong geometrical inequivalence of the ligand nitrogens. In fact, the largely different

(18) With use of the coordinates of Figure 1 the magnetic tensor matrix elements, $M_{\mu\nu}$, of Co(hp) are of the form

$$\begin{pmatrix} M_{xx} & M_{yx} & 0 \\ M_{xy} & M_{yy} & 0 \\ 0 & 0 & M_{zz} \end{pmatrix}$$

with $M_{xy} \neq M_{yx}$.

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Table IV. Configuration Interaction Matrix (Ligand Field + Interelectronic Repulsion + Spin–Orbit Coupling)[a]

	Φ_1+		Φ_2+	Φ_2-	Φ_3+	Φ_3-	Φ_4+	Φ_4-	Φ_5+	Φ_5-
Φ_1+	0									
Φ_1-	0	0								
Φ_2+	$-0.781 - 0.053i$	0	Δ_1/ξ							
Φ_2-	0	$-0.781 + 0.053i$	0	Δ_1/ξ						
Φ_3+	$0.873 - 0.212i$	0	0.500	0	Δ_2/ξ					
Φ_3-	0	$0.873 + 0.212i$	0	0.500	0	Δ_2/ξ				
Φ_4+	$0.321 + 0.025i$	0	$0.314i$	0	0	0	Δ_3/ξ			
Φ_4-	0	$0.321 - 0.025i$	0	$-0.314i$	0	0	0	Δ_3/ξ		
Φ_5+	$0.556 - 0.043i$	0	0	0	0	0	0	0	Δ_3/ξ	
Φ_5-	0	$0.556 + 0.043$	0	0	0	0	0	0	0	Δ_3/ξ

[a] Δ_1 is the energy of the doublet $(75)^2(78)$, Δ_2 is the energy of the doublet $(75)^2(79)$, Δ_3 is the energy of the quartet $(75)(76)(78)$, and ξ is the spin–orbit coupling constant ($\xi < 0$).
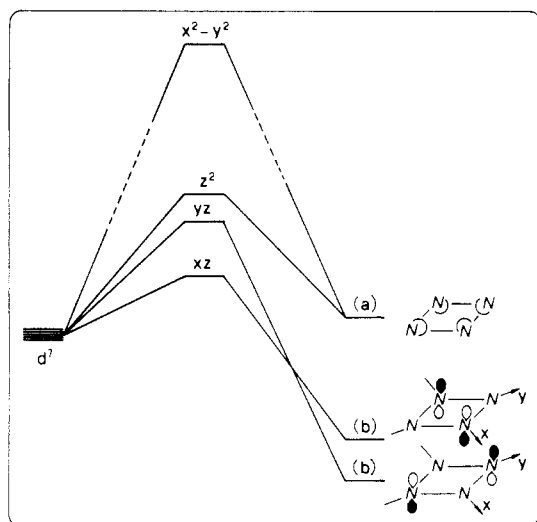
Figure 4. MO diagram of Co(hp). Only orbitals with preponderant metal 3d character are shown.

Figure 5. Ground-state diagram of Co(hp) and related complexes. Regions 1, 2, and 3 have been derived by making use of the first-order energy expressions of Table III. The coordinates of the "triple point" are indicated.

bonding distances imply that the overlap between metal and ligand orbitals is much more efficient along the y than along the x axis.

Another important outcome of Figure 4 is the strong interaction between (z^2) and the "highest" occupied σ orbitals of the ligand. In the case of Schiff base complexes these two orbitals belong to different irreducible representations of the C_{2v} point group and do not interact with each other.[1] It is this interaction that destabilizes the (z^2) orbital and explains the ground state present in Co/Ni(hp), or in higher symmetry compounds, as opposed to Schiff base complexes, where (yz) is usually the highest occupied molecular orbital.

The remaining fitting parameters, i.e. the orbital reduction factor k and the radial and Fermi contributions in eq 6, P and K, are in good agreement with the results of a recent MS-Xα calculation performed on planar Co(II) complexes[4] and do not require further comment.

Conclusions

Figure 5 summarizes the various ground states possible for a Co(II) complex as a function of the in-plane and axial ligand field strengths.

The abscissa is the difference between the energies of the (z^2) and (yz) one-electron levels and can be interpreted as an increasing axial σ interaction. The ordinate is the difference between the energies of the $(x^2 - y^2)$ and (yz) orbitals and can be interpreted as an increasing in-plane σ interaction. Typical representatives of region 1 are, among others, the title compound, Co(II) porphyrins and phthalocyanines, and Co(II) Schiff base complexes with axial ligands. All 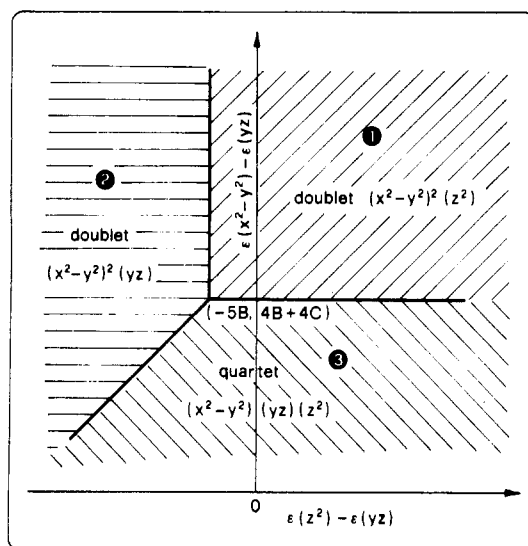the planar Co(II) Schiff base complexes belong to region 2. The quartets considered in the previous section and other compounds such as Co(3-MeOsalen)·H$_2$O[22] fall into region 3.

In the case of Co/Ni(hp) both the doublet $(x^2 - y^2)^2(yz)$ and the quartet $(x^2 - y^2)(yz)(z^2)$ are low-lying excited states and the compound lies very close to the "triple point" of Figure 5.

As shown before, the energy of the quartet depends essentially on the strength of the in-plane ligand field and Co(hp) can easily undergo a spin crossover by simply using different host lattices. As opposed to this, the relative energy of the two doublets is related to the overall symmetry of the systems. In the case of Co(hp), quasi-D_{2h}, or other high-symmetry compounds, the key point is the strong σ interaction between the (z^2) orbital and a ligand orbital of matching energy. Apparently ground-state inversion between the two doublets requires lower symmetries which prevent such interaction. In this case the energies of the (z^2) orbital is considerably lowered and (yz) becomes the highest occupied molecular orbital.

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