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Electron Paramagnetic Resonance of Low-Spin Cobalt(II) Complexes: Effect of Axial Ligation upon the Ground State

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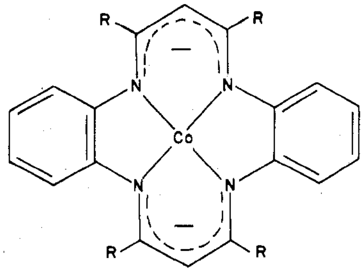
EPR studies of frozen solutions of cobalt(II) dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenate reveal that the ground state changes upon coordination of an axial ligand. In the presence of weak ligands such as sulfur and oxygen donors, the cobalt remains four-coordinate and the ground state is $(d_{xz}d_{x^2-y^2}d_{z^2})^6d_{yz}^1$. Ligands containing nitrogen and phosphorus donor atoms form 1:1 adducts which have $(d_{xz}d_{x^2-y^2}d_{yz})^6d_{z^2}^1$ ground state. The results are compared with those reported for a nonplanar analogue and for Co(II) porphyrins. The effects of ring size and deviations from planarity upon the ground state are also discussed.

In recent years extensive use has been made of EPR to study the electronic structure of low-spin Co(II) compounds.[1-22] In particular, studies of Co(II) porphyrins and related four-coordinate complexes have aroused much interest because there was some controversy over the nature of the ground state and also because they readily undergo axial ligation to form five- and six-coordinate structures. For all such five- and six-coordinate complexes studied to date, the ground state is $(d_{x^2-y^2}d_{yz}d_{yz})^6d_{z^2}^1$.[1-7] Much greater uncertainty accompanies the assignment of the ground state of the four-coordinate complexes. Examples of $(d_{x^2-y^2}d_{xz}d_{z^2})^6d_{yz}^1$,[8-12] $(d_{xz}d_{yz}d_{z^2})^6d_{x^2-y^2}^1$,[13] and $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$ [13-20] ground states have been reported although recently many of the initial assignments have been modified as more advanced theoretical treatments of low-spin d^7 systems have become available.[20-22]

We recently reported the results of an EPR investigation of axial ligation of the macrocyclic Co(II) Schiff base complex, I.[17] Although this complex possesses a number of structural features in common with porphyrins, it differs structurally from the naturally occurring macrocyclic compounds in two important respects. The inner ring of I has only 14 members compared to the 16 interior members of a porphyrin ring. Furthermore, extensive crystallographic investigations[23-28] have shown that the Schiff base is saddle shaped and that the *o*-phenylene and diiminate moieties are displaced on opposite sides of the plane defined by the four nitrogen donor atoms, whereas the porphyrins are planar.[26-31]

The EPR results for 1:1 adducts of I were found to differ in several important respects from the analogous adducts of Co(II) porphyrins. Although all adducts have a $d_{z^2}^1$ ground state, the EPR parameters for the adducts of I do not have axial symmetry, and 2:1 adducts are not formed. Furthermore a significantly higher spin density resides on the Schiff base than on the porphyrin ligand. These differences between the two systems appear to be related to the structural differences in ring size and planarity.



I, R= CH_3
II, R= H

In order to separate the effects that ring size and deviations from planarity have upon the electronic structure and the EPR parameters for this type of macrocyclic complex, we examined the EPR parameters of the Schiff base complex II and its axial adducts. Although II has a 14-membered inner ring, crystallographic studies[32] reveal that the molecule is planar, in contrast to I. This paper reports EPR studies of axial ligation of the planar macrocycle II and compares the results with those

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Table I. EPR Parameters for Complexes of II[a]

	g_x	g_y	g_z	A_x, cm^{-1}	A_y, cm^{-1}	A_z, cm^{-1}	A_z(N or P), cm^{-1}
toluene	3.55	1.79	1.89	0.0196	−0.0025	0.0026	
thiazole	2.42	2.17	2.00	0.0059	0.0015	0.0107	0.00159
pyridine	2.38	2.17	2.00	0.0045	0.0009	0.0103	0.00178
pyrazine	2.39	2.17	2.00	0.0046	0.0018	0.0105	0.00179
quinoline	2.38	2.17	2.00	0.0046	0.0009	0.0103	0.00178
3-picoline	2.38	2.17	2.00	0.0045	0.0009	0.0103	0.00174
triethyl phosphite[f]	2.22	2.13	2.01	−0.0012	−0.0028	0.0080	0.0306[b]
triethylphosphine[f]	2.21	2.11	2.008	−0.0012	−0.0030	0.0076	0.0232[c]
trimethylphosphine[f]	2.21	2.10	2.008	−0.0008	−0.0035	0.0076	0.0251[d]
tri-*n*-butylphosphine[f]	2.21	2.11	2.008	−0.0012	−0.0029	0.0077	0.0236[e]

[a] From computer simulation of spectra. [b] A_x(P) = 0.0258 cm^{-1}, A_y(P) = 0.0268 cm^{-1}. [c] A_x(P) = 0.0167 cm^{-1}, A_y(P) = 0.0168 cm^{-1}. [d] A_x(P) = 0.0199 cm^{-1}, A_y(P) = 0.0180 cm^{-1}. [e] A_x(P) = 0.0170 cm^{-1}, A_y(P) = 0.0170 cm^{-1}. [f] Relative signs of A were determined from computer simulation of isotropic spectra.

found for I and other low-spin Co(II) complexes.

Experimental Section

Materials. The Co(II) macrocyclic complex II was prepared under an inert atmosphere according to the following method.[33] To 250 mL of water were added 60 mmol of nickel(II) acetate tetrahydrate and 130 mmol of *o*-phenylenediamine. After the addition of 130 mmol of malonaldehyde tetramethyl acetal the solution was refluxed for 4 h. During this time a dark red solid precipitated from the reaction mixture. The solution was allowed to cool to room temperature. The precipitate was recovered under nitrogen by filtration and washed with water and acetonitrile. The sample was recrystallized from hot toluene; $\mu_{\mathrm{eff}} = 2.44\ \mu_{\mathrm{B}}$ ($S = {}^1/_2$). Anal. Calcd for $C_{18}H_{14}N_4CO$: C, 64.44; H, 4.38; N, 15.21. Found: C, 64.49; H, 4.59; N, 15.30.

Thiazole, thiophene (Fisher), triethyl phosphate, triethyl thiophosphate, *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (Aldrich), triethyl phosphite, triethylphosphine, trimethylphosphine, and tri-*n*-butylphosphine (Matheson Coleman and Bell) were all reagent grade and were used without further purification. Toluene (MCB), 2-methyltetrahydrofuran, and tetrahydrofuran (Eastman Chemical Co.) were reagent grade and were dried by distillation from lithium aluminum hydride under a nitrogen atmosphere. Reagent grade acetonitrile (Eastman) was further distilled from P_2O_5 before use. Pyrazine, pyridine, quinoline (Aldrich), and 3-picoline (MCB) were reagent quality and were distilled from potassium hydroxide pellets. All solvents were deaerated with a stream of nitrogen gas at room temperature for 15 min before use.

Sample Preparation. Preparation of EPR samples was carried out under a dry atmosphere of nitrogen. The solid cobalt compound (sufficient to yield ca. 0.01 M solution) was dissolved in toluene, and varying amounts of ligand were added. About 0.25 mL of the solution was transferred to a quartz EPR tube, and the samples were degassed on a vacuum line using the usual freeze–pump–thaw method before the tube was sealed.

Oriented nematic-phase samples were obtained by keeping a solution of I in the liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-butylaniline in the nematic range[34] for 15 min in a magnetic field of 8000 G and then rapidly cooling to 90 K.

Physical Measurements. EPR spectra were recorded using a Varian E-9 spectrometer equipped with a dual cavity and operating at 9.3 GHz with 100-kHz modulation. Sample temperatures between 80 and 300 K were achieved by means of a stream of dry nitrogen cooled by liquid nitrogen and were measured with the aid of a calibrated copper–constantan thermocouple located just below the sample. The magnetic field was calibrated with powdered samples of ZnS containing Mn^{2+} and with DPPH powder ($g = 2.0036$).

Calculations. EPR spectra were simulated using the computer program previously described.[17] The principal axes of the **g**, hyperfine, and line width tensors were assumed to be coincident. Quadrupole effects were neglected. The line width was found to vary with orientation and m_I in a manner similar to that previously reported for I.[17]

Results

EPR of 1:1 Adducts. X-Band EPR spectra were obtained of frozen glasses of II dissolved in toluene with small amounts added of a wide range of potential ligands. The presence of toluene facilitated the formation of good glasses and did not affect the EPR spectra except that in some cases it resulted in smaller line widths than were obtained in the absence of toluene. EPR parameters were calculated with the aid of computer simulation of experimental spectra and are listed in Table I. Representative EPR spectra for complexes of II

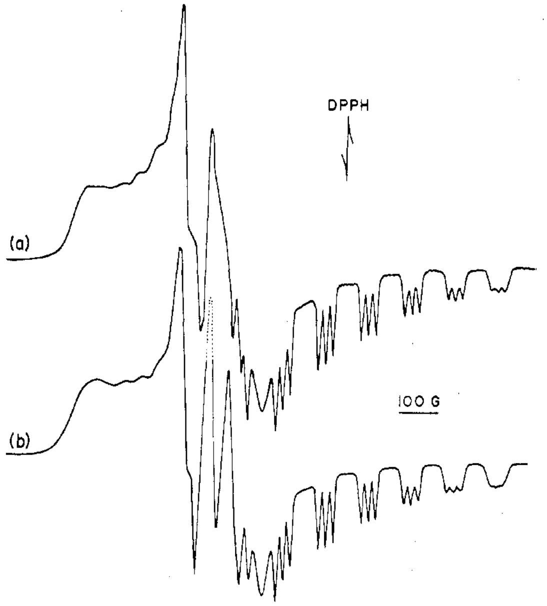

Figure 1. (a) EPR spectrum of II in toluene/pyridine at 90 K. (b) Computer simulation using the parameters of Table I.

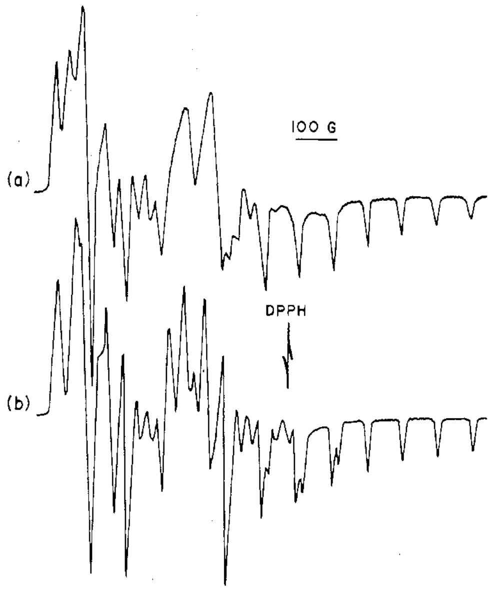

Figure 2. (a) EPR spectrum of II in toluene/triethyl phosphite at 90 K. (b) Computer simulation using the parameters of Table I.

Table II. Orbital Coefficients for Complexes of II[a]

	c_1	c_2	c_3	P, cm^{-1}	K, cm^{-1}	ρ_{3d}[b]	ρ_{4s}[c]	ρ_L[d]
toluene[e]		−0.274		0.024	−0.0067	0.94	0.01	
thiazole	0.031	0.069	0.14	0.0171	0.0029	0.68	0.07	0.10
pyridine	0.030	0.063	0.10	0.0167	0.0022	0.66	0.06	0.14
triethyl phosphite	0.023	0.037	0.10	0.0158	−0.0007	0.63	0.04	0.23
triethylphosphine	0.019	0.034	0.12	0.0154	−0.0005	0.61	0.04	0.28

[a] Coefficients $c_i (i \geqslant 3)$ are assumed to be zero as explained in the text. [b] Calculated using $\rho_{3d} = P/0.0254$. [c] Calculated using $\rho_{4s} = (K + 0.0084\rho_{3d})/0.1232$. [d] ρ_L is the spin density on the ligand donor atom (P or N). [e] Calculated for a d_{yz} ground state.

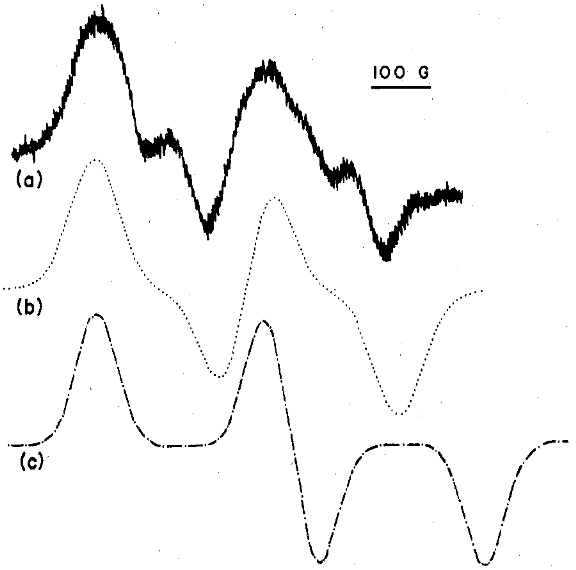

Figure 3. (a) EPR spectrum of II in toluene/triethyl phosphite at 300 K. Computer simulation using the isotropic cobalt hyperfine coupling constant calculated from the parameters of Table I with (b) A_x, $A_y < 0$ and $A_z > 0$ (···) and with (c) A_x, A_y, $A_z > 0$ (–·–).

with trivalent phosphorus and nitrogen ligands are shown in Figures 1 and 2, together with spectra simulated using the parameters of Table I.

The nuclear hyperfine splitting due to the nitrogen and phosphorus atoms, which is observed on the high-field progression of hyperfine lines arising from the cobalt, clearly indicates that 1:1 adducts are formed. No evidence for the formation of 2:1 adducts was found even in neat amine or phosphine solutions. In neat pyridine an orientation-dependent spectrum was obtained, indicating partial ordering of the adduct molecules. In this case, the superhyperfine interaction with one nitrogen atom was observed on all cobalt hyperfine lines. However, in all cases where good glasses were obtained, the nitrogen superhyperfine splitting was unresolved except along the high-field progression of lines. The phosphorus splitting was always resolved along all three principal axes.

At room temperature, lines were broadened to the extent that only spectra of the phosphorus adducts could be obtained, and even then no resolved cobalt hyperfine structure was observed. Nevertheless computer simulation of the isotropic spectra (Figure 3) did enable the isotropic cobalt hyperfine coupling constant to be estimated and thus enable the relative signs of the principal values of the hyperfine coupling tensor for cobalt to be determined.

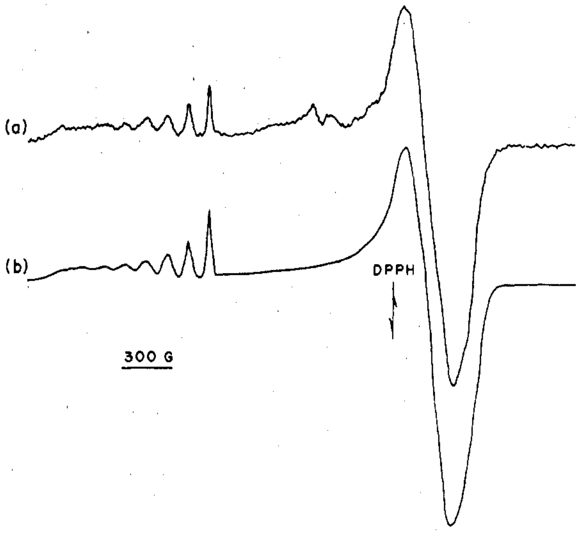

Figure 4. (a) EPR spectrum of II in toluene at 90 K. (b) Computer simulation using the parameters of Table I.

EPR of Four-Coordinate II. The EPR spectrum of II dissolved in toluene (Figure 4) was almost identical with the spectra obtained in neat thiophene, MTHF, THF, acetonitrile, triethyl phosphate, triethyl thiophosphate, and the liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-butylaniline. Such a small effect of large structural changes in the potential fifth ligand indicates that the cobalt is essentially four-coordinate and only interacting very weakly with the solvent. The EPR spectrum of II dissolved in the liquid crystal and oriented in the magnetic field showed enhancement of the lines near $g = 3.5$ at an orientation of 0° which indicates that the principal axis associated with $g = 3.55$ is the long axis of the molecule.[34]

Interpretation of EPR Parameters of the Five-Coordinate Complexes. The theory for the spin Hamiltonian parameters of low-spin Co(II) complexes has been extended to third order by McGarvey.[20] We have utilized this theory to calculate molecular orbital parameters from the EPR parameters of the adducts of II (Table II). In general, the EPR parameters of the axial adducts of II were found to be similar to those for the corresponding five-coordinate complexes of I.[17] Nitrogen and phosphorus donor ligands form 1:1 adducts with II which have a $(d_{xz}d_{x^2-y^2}d_{yz})^6 d_{z^2}{}^1$ ground state.

Because McGarvey's equations for a $d_{z^2}{}^1$ ground state involve twelve molecular orbital parameters[20] and there are only six experimental parameters, the same approximations which were applied to the complexes of I[17] were also used for the adducts of II. We did, however, check the validity of our approximations by varying all 12 parameters. The results in Table II were obtained with the approximation that all parameters except c_1, c_2, c_3, b, P, and K were zero, where $c_1 = \xi/\Delta(^2B_1)$, $c_2 = \xi/\Delta(^2B_2)$, $c_3 = \xi/\Delta(^4B_1)$, $P = gg_n\beta\beta_n\langle r^{-3}\rangle$, and K is the Fermi contact term. The half-filled orbital in the $^2A_1$ ground state is $(ad_{z^2} + bd_{x^2-y^2})$, Δ is the energy difference between the designated state and the ground state, and ξ is the spin–orbit coupling constant of Co(II). The effect of varying the remaining parameters was found to be similar for each of the adducts studied. Therefore the trends that can be observed in Table II are not affected by the assumptions made about these parameters.

Although no assumptions were made regarding the assignment of principal axis or the signs of the cobalt hyperfine coupling constants, the EPR parameters for the 1:1 adducts are consistent only with a $d_{z^2}{}^1$ ground state and only with the signs given in Table I. In all cases $b < 0.25$ which corresponds to a maximum of 6% $d_{x^2-y^2}$ character in the ground state. The observation of superhyperfine coupling to the axial nitrogen and phosphorus atoms is also consistent with a $d_{z^2}{}^1$ ground state. This ground state is common to a large number of five-coordinate Co(II) macrocyclic complexes.[1-7] The nuclear hyperfine coupling constants observed for the axial adducts of II can be used to deduce the unpaired-spin densities on the cobalt ion and the various coordinating atoms. The cobalt 3d spin densities, ρ_{3d}, for these complexes were determined from a comparison of the calculated value of P with the theoretical value of $P_0 = 0.0254$ cm^{-1} for a cobalt 3d electron.[35] Cobalt 4s spin densities (ρ_{4s}) were estimated from the relationship[36] $K = 0.1232\rho_{4s} - \rho_{3d}$. The results are given in Table II.

Interpretation of EPR Parameters of the Four-Coordinate Complex. The ground state of the unligated four-coordinate complex II was found to be $(d_{xz}d_{x^2-y^2}d_z)^6d_{yz}{}^1$. By use of the expressions developed by McGarvey,[20] a satisfactory fit of the experimental parameters to the theoretical expressions could be obtained only if $g_z > g_y$ and if $A_y > 0$. Under these conditions a fit was obtained with $P = 0.024$ cm^{-1}, and $\eta_3 = \xi/\Delta(^2A_1) \approx 0.27$ (Table II), where $\Delta(^2A_1)$ is the energy separation between the $^2A_1$ state and the $^2B_2$ ground state. Thus η_3 and c_2 measure the same quantity and differ only in sign ($c_2 = -\eta_3$). The remaining molecular orbital parameters either were less than 0.1 or had negligible effect upon the fit. No fit of the experimental parameters to the theoretical expressions could be obtained with the assumption of a $d_{z^2}{}^1$ ground state. The large line width observed along the x and y principal axes leads to fairly large uncertainties in the EPR parameters for these axes. For the four-coordinate macrocyclic complex, I, we were not able to definitely say which was the ground state.[17] However, for the planar complex II, the smaller values of g_x and $|A_x|$ make the assignment more certain.

Discussion

Structural Considerations. In order to adequately compare the electronic, structural, and ligating properties of I, II, and a typical Co(II) porphyrin, the relevant structural features of each of these macrocyclic systems will be discussed.

Similar to Co(II) porphyrins, the cyclic Schiff base complexes I and II contain tetraaza ligands which are dinegatively charged. However, each of the synthetic analogues has an aromatic 14-membered interior ring as opposed to a 16-membered inner ring which is present in the porphyrin framework. In addition, X-ray structural analyses have consistently shown that the metal–nitrogen bond distances for the Schiff base complexes are shorter than the corresponding distances in metalloporphyrins.[23-28] For metal complexes having a metal ion displaced from the donor plane, i.e., five-coordinate complexes, the displacements found are greater for the Schiff bases than they are for the porphyrins. The shortened metal–nitrogen bond distances and the large out-of-plane displacements appear to be a direct result of the smaller macrocyclic hole provided by the Schiff base relative to that of a porphyrin.

The two Schiff bases I and II together with metalloporphyrins span a diversity of possible ring deformations. While the Ni(II) analogue of II is a planar, relatively flat molecule as are certain metalloporphyrins, the tetramethyl analogue, I, is a distorted structure. Due to steric interactions between the methyl groups and the benzene moieties, all known complexes with this macrocyclic Schiff base have a pronounced saddle shape. Moreover, this distortion is greater than that found for a ruffled porphyrin and could potentially affect the ability of its complexes to undergo axial ligation.

The Ground State and Axial Ligation. The most striking feature of II when it is compared to the tetramethyl analogue I or a Co(II) porphyrin is its inability to form axial adducts with S or O donor ligands. Dissolution of II in 2-methyltetrahydrofuran (MTHF) or thiophene gave only the spectrum characteristic of the four-coordinate complex. In contrast, both cobalt(II) tetraphenylporphyrin[37] and I[17] gave unique spectra with MTHF and thiophene indicating the formation of 1:1 adducts.

Since II is relatively flat, like cobalt(II) tetraphenylporphyrin, this difference in axial ligation does not appear to be due to steric effects. More probably, the origin of the difference lies in a difference in electronic factors between I, II, and cobalt(II) tetraphenylporphyrin. Specifically, the energy separation between the $d_{yz}{}^1$ and $d_{z^2}{}^1$ states appears to be important in axial ligation. We report a $d_{yz}{}^1$ ground state for both I and II in the absence of axial ligands, for example, in toluene solutions. However, for complex II the value of g_x, which is inversely proportional to the energy separations between the $d_{yz}{}^1$ and $d_{z^2}{}^1$ states, is smaller than for complex I. Thus the energy separation between the two states is larger for II than for I.

When the unmethylated analogue is subjected to a weak axial field, e.g., MTHF or thiophene, the ground state remains $d_{yz}{}^1$ and axial binding does not take place. However, in the presence of strong axial ligands, e.g., pyridine and phosphines, the energy of the $d_{z^2}{}^1$ state is raised above the energy of the $d_{yz}{}^1$ state resulting in a $d_{z^2}{}^1$ ground state and axial ligation. In contrast, the energy separation for the tetramethyl analogue, I, is small and even the small ligand field strength of MTHF or thiophene is sufficient to invert the ground state from $d_{yz}{}^1$ to $d_{z^2}{}^1$ and produce a stable five-coordinate structure. The results show that in order for a strong axial bond to form it is necessary to have a $d_{z^2}{}^1$ rather than a $d_{yz}{}^1$ ground state. A half-filled d_{z^2} orbital overlaps sufficiently with the ligand donor orbital to form a stable bond whereas a half-filled d_{yz} orbital apparently does not. This result is expected on the basis of symmetry considerations. Interaction of a donor σ lone pair of the axial ligand with a half-filled d_{z^2} orbital leads to formation of a stable σ bond whereas a half-filled d_{yz} orbital does not have the correct symmetry to interact; and a filled d_{z^2} orbital will not form a bond with the orbital containing the donor lone pair.

A typical Co(II) porphyrin already has a $d_{z^2}{}^1$ ground state and therefore a change in ground state is not a prerequisite to axial ligation. Therefore Co(II) porphyrins readily bind N, P, S, and O donor ligands and even form axial adducts with weak π donors such as pyrene and toluene.[3] Other four-coordinate Co(II) complexes have been reported to have a $d_{yz}{}^1$ ground state[8-12] but their properties in the presence of weak donor ligands have not yet been adequately explored. von Zelewsky and Fierz[9] found a $d_{yz}{}^1$ ground state for four-coordinate Co^{II}(salen) and Wayland[5] found its 1:1 adducts with nitrogen and phosphorus donors to have a $d_{z^2}{}^1$ ground state, but the binding of weak ligands has not been investigated. Molecular orbital calculations by Hitchman[38] for Co^{II}(salen) confirm that a change in ground state should occur upon coordination of an axial ligand or upon formation of a dimer where an axial bond is formed with the oxygen atom of a neighboring molecule.

We are not able to explain why the energy separation between the $d_{yz}{}^1$ and $d_{z^2}{}^1$ states is larger for the planar species than for the nonplanar one. Any differences in the in-plane crystal field affect both states as both d_{yz} and d_{z^2} orbitals have an in-plane component. Thus although the expected Co–N bond distance for II is less than for I, the effect upon the energies of the two states is not obvious.

The values calculated for the spin density on the cobalt ion for the axial adducts of II (Table II) are consistently larger than those found for the five-coordinate tetramethyl analogues.[17] Furthermore, the amount of spin residing on the axial ligand is also slightly greater for the adducts of II so that the total spin density observable by EPR is significantly greater for II than for I. For example, the sum of the spin density on cobalt and on the axial ligand is about 0.9 for the nitrogen and phosphorus adducts of II but varies within the range 0.5–0.8 for the tetramethyl analogues. The remaining spin density must be delocalized onto the macrocycle.

Calligaris et al. have reviewed the structural information available on Co(salen) and related ligand systems.[39] It is apparent that the cobalt chelates have a tendency to distort from planarity in solution. This distortion which occurs in the five-coordinate complexes removes the orthogonality between the metal d_{z^2} orbital, which has σ symmetry, and the macrocyclic ligand π system and thus allows an interaction between the d_{z^2} orbital and the π orbitals of the macrocyclic framework. Such an interaction is likely to be somewhat greater in the case of the saddle-shaped macrocycle I since the ligand is nonplanar. This would have the effect of reducing the spin density on the cobalt ion to a greater extent for the saddle-shaped complex I than for II in which the macrocycle is planar. This is in fact observed to be the case.

Neither of the Schiff base complexes form 2:1 adducts, although 2:1 adducts are formed with Co(II) porphyrins.[2,5,6] Since II is planar, steric hindrance to addition of a second axial ligand is not expected to be different from that experienced by the first axial ligand. Furthermore, the observation that the spin density on the cobalt in II is similar to that found for the five-coordinate adducts of porphyrins indicates that the low spin density on cobalt in the tetramethyl analogue[17] is not a sufficient reason to explain why I does not form 2:1 adducts. Although it is generally found that strong bases such as pyridine display a greater tendency to form 2:1 adducts with Co(II) macrocyclic complexes than do weak bases such as quinoline,[2] the basicity of the donor alone is not sufficient to account for the lack of formation of 2:1 adducts since in some cases strong bases form only 1:1 adducts[2,5,17] while in others weaker bases form 2:1 adducts.[2]

We propose that an additional factor governing the formation of 2:1 adducts is the hole size of the macrocyclic ring. In the 1:1 adducts, the cobalt ion is displaced from the plane of the four nitrogen atoms of the macrocycle. The small hole size of the 14-membered ring provides a strong resistance to diminishing the out-of-plane distance in forming a six-coordinate species. Only upon oxidation of Co(II) to the smaller Co(III), as in the six-coordinate dioxygen adducts, is the metal able to approach close enough to the macrocyclic plane to add a sixth ligand. Porphyrins which have a 16-membered ring and a larger hole are thus more likely to form six-coordinate complexes than macrocycles such as I or II which have a smaller ring size. X-ray structural analyses of Co(salen)(py) reveal a cobalt–nitrogen bond length of 1.90 Å,[40] similar to that found for I and considerably less than that found for porphyrins.[26] Thus although Co(salen) does not have a closed-ring structure, it has a hole size similar to that of a 14-membered ring and indeed forms only 1:1 adducts even with strong donor bases.[5]

This study has shown that the hole size is one of the important factors preventing the formation of 2:1 adducts with axial ligands and that deviations from planarity in the macrocycle are not the reason 2:1 adducts do not form with I. The strength of the metal ion–donor atom interaction, which is related to the base strength and the π-bonding properties of the axial ligand, is an additional factor that appears to be important.[2] The shape of the molecules does, however, affect the energies of the ground and excited states of the complex. In the nonplanar complex I, the $d_{z^2}{}^1$ state is at a higher energy relative to the $d_{yz}{}^1$ state than is the case in the planar complex, II. Because of the greater accessibility of a half-filled d_{z^2} orbital, I can form 1:1 adducts with weaker ligands than can its planar analogue.

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Registry No. II, 41283-94-7; II·thiazole, 67761-74-4; II·pyridine, 67761-75-5; II·pyrazine, 67761-76-6; II·quinoline, 67761-77-7; II·3-picoline, 67761-78-8; II·triethyl phosphite, 67761-79-9; II·triethylphosphine, 67761-80-2; II·trimethylphosphine, 67761-81-3; II·tri-*n*-butylphosphine, 67761-82-4; *o*-phenylenediamine, 95-54-5; malonaldehyde tetramethyl acetal, 102-52-3.

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