

Table IV. A Comparison of the Carbon-13 Chemical Shifts<sup>a</sup> and  $J_{\text{Pt-C}}$ <sup>b</sup> Values for Platinum(II) Chelates of Piperidine-Type Bidentate Ligands

Piperidine carbon	<i>trans</i> -[Pt(pip)Cl <sub>2</sub> ] <sup>-</sup>	<i>cis</i> -[Pt(pip)Cl <sub>2</sub> ] <sup>-</sup>	[Pt(bpy)-(pipen)] <sup>2+</sup> <sup>c</sup>
C-2	67.562 (25) <sup>b</sup>	64.57 (25)	63.64 (10)
C-3	29.21 (41)	28.70 (20)	26.54 (41) <sup>d</sup>
C-4	24.09 (5)	22.23 (<3)	18.88 (<3)
C-5	26.18 (48)	24.46 (26)	24.44 (30) <sup>d</sup>
C-6	53.63 (5)	50.36 (15)	48.64 (25)

<sup>a</sup> In ppm vs. Me<sub>4</sub>Si. <sup>b</sup> In Hz, found in parentheses behind chemical shifts. <sup>c</sup> Data taken from ref 8; bpy = 2,2'-bipyridine.

<sup>d</sup> This assignment may be reversed.

the appearance of these proline resonances more downfield from the similar resonances of the piperidine chelate are a manifestation of the differences in geometry imposed by the aliphatic rings in these two fused-ring compounds. For the C=O carbon, the proline shift (192.24 ppm) is close to that expected on the basis of shift parameters for methylglycines;<sup>2</sup> i.e.,  $\delta = \delta_0 + \delta(\text{C}-\text{CH}_3) + \delta(\text{N}-\text{CH}_3) = 190.28 + 1.32 - 1.65 = 190.01$  ppm plus a small contribution from C-4.

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**Registry No.** *cis*-K[Pt(pro)Cl<sub>2</sub>], 51139-35-6; [Pt(pro)(NH<sub>3</sub>)<sub>3</sub>]Cl, 66140-49-6; *trans*-K[Pt(pip)Cl<sub>2</sub>], 66085-34-5; *cis*-K[Pt(pip)Cl<sub>2</sub>], 66182-96-5; [Pt(pip)(NH<sub>3</sub>)<sub>3</sub>]Cl, 66085-35-6; [Pt(proH)(NH<sub>3</sub>)<sub>3</sub>]<sup>2+</sup>, 66140-50-9; *trans*-[Pt(pipH)Cl<sub>2</sub>]<sup>-</sup>, 66085-36-7; *trans*-[Pt(pipH)-(NH<sub>3</sub>)<sub>3</sub>]<sup>2+</sup>, 66085-37-8.

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## EPR Studies of Axial Ligation of a Low-Spin Cobalt(II) Macrocyclic Schiff Base Complex

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EPR studies demonstrate that 1:1 adducts of cobalt(II) 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaene with ligands containing phosphorus, nitrogen, sulfur, and oxygen donor atoms all have a  $(d_{xz}d_{yz}d_{z^2})^6d_{z^2}^1$  ground-state configuration and similar spin-density distributions. The primary difference between the adducts is the energy separation between the ground state and the  $(d_{xz}d_{yz}d_{z^2})^6d_{yz}^1$  state which decreases as the strength of the axial bond decreases, until in very weakly coordinating solvents such as neat toluene it is not possible to definitely say which is the ground state. All of the EPR spectra have rhombic symmetry which is due to a difference in the energies of the  $d_{yz}^1$  and  $d_{xz}^1$  states. This difference becomes larger as the strength of the axial bond increases. The EPR results are compared with results for analogous cobalt(II) porphyrin complexes. Solvent effects also occur and cause an orientation- and  $m_l$ -dependent broadening of the EPR lines in a manner consistent with the ground-state assignment.

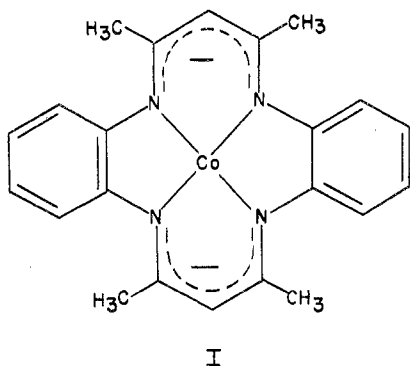
The use of EPR in studying the electronic structure of low-spin Co(II) compounds is well documented.<sup>1-14</sup> In particular this technique has been extensively applied to cobalt(II) porphyrins and related four-coordinate complexes. Since these compounds generally undergo axial ligation to form five- and six-coordinate structures which are also EPR active, the yield of electronic structural information obtained from EPR studies can be high. For example from the EPR parameters it is possible to determine the electronic configuration of the ground state as well as calculate the spin density which resides on the central Co(II) ion. Although this type of analysis has been performed for cobalt(II) porphyrin complexes, the dependence of these variables on the structural parameters associated with

the macrocyclic framework itself such as ring size, its charge, and degree of unsaturation has not been studied. Macrocyclic Schiff bases and their analogues exist in a diversity of structural types<sup>15</sup> and as such are useful vehicles for a systematic investigation of this kind of molecular-electronic structural relationship.

The Schiff base formed from *o*-phenylenediamine and acetylacetone, I, has a number of structural features in common with the porphyrins.<sup>16,17</sup> It is a highly conjugated although not aromatic (24π) tetraaza macrocyclic ligand. Analogous to the porphyrins, in the presence of transition-metal ions it readily deprotonates to give the dianionic form of the ligand. Its metallo derivatives are intensely colored and

give visible absorption as well as Raman spectra which are reminiscent of those observed for metalloporphyrins. Although the structural relationships between the Schiff base and the porphyrins are strong, some important differences should be noted. Extensive crystallographic investigation by Goedken and Day and their co-workers<sup>18-23</sup> have revealed that the ligand in its metal complexes is not flat but adopts a pronounced saddle shape. The deviations from planarity are greater than those found for a "ruffled" metalloporphyrin.<sup>24</sup> Moreover, the metal-nitrogen bond distances encountered for complexes of the Schiff base are generally shorter than those found for the analogous metalloporphyrins. The latter phenomenon appears to be a direct result of the fact that the inner ring of I is smaller than that of a porphyrin, 14 vs. 16 members.

In an effort to further explore the strengths and limitations of I and ligands of its class as useful porphyrin analogues, we have analyzed the EPR spectra of I and a series of its five-coordinate axial adducts. This paper reports the results of EPR studies of I and of the 1:1 adducts of I with phosphorus, nitrogen, sulfur, and oxygen donor ligands.



I

## Experimental Section

**Materials.** The cobalt(II) macrocyclic complex I was prepared as previously reported<sup>16</sup> and was recrystallized under an inert atmosphere as a violet solid, from acetonitrile.

Thiophene (Fisher), tetrahydrothiophene 1,1-dioxide (Aldrich), *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (Aldrich), triethyl phosphite (Matheson Coleman and Bell), triphenyl phosphite (MCB), and tris(*N,N*-dimethylamino)phosphine (Strem) were all reagent grade and were used without further purification. Imidazole (Aldrich) was dried under vacuum with P<sub>2</sub>O<sub>5</sub> for 24 h before use. Toluene (MCB), 2-methyltetrahydrofuran (Eastman Chemical Co.), and tetrahydrofuran (Eastman) 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<sub>2</sub>O<sub>5</sub> before use. Pyridine (Aldrich), 2,6-lutidine (Aldrich), 2-picoline (Eastman), 3-picoline (Eastman), and piperidine (Eastman) 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 at 280 K for 15 min in a magnetic field of 8000 G and then rapidly cooling to 90 K. Orienting the sample at 135 K as recommended by other workers<sup>25</sup> was less effective with all in-phase directions being observed in the EPR spectrum at an angle of 0°. <sup>25</sup>

**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 5 and 80 K were achieved by means of a helium transfer system (Air Products, Inc., Model LTD 3-110) and measured with the aid of a chromel-gold thermocouple located just below the sample. For

temperatures above 80 K a stream of dry nitrogen cooled by liquid nitrogen was used, and the temperature was measured by means of a calibrated copper-constantan thermocouple. The magnetic field was calibrated with powdered samples of ZnS containing Mn<sup>2+</sup> and with DPPH powder ( $g = 2.0036$ ).

**Calculations.** EPR spectra were simulated using the general EPR simulation program of Lefebvre and Maruani extended to include the effects of a large anisotropy in  $g$ , second-order calculations of the hyperfine structure, and a variable line width.<sup>26</sup> An orientation-dependent line width was incorporated by means of a line width tensor. The line width of each hyperfine component,  $m_I$ , could be varied independently. The transition probability was adjusted to agree with the result of Aasa and Vanngard<sup>27</sup> for field-swept spectra. The principal axes of the  $g$ , hyperfine, and line width tensors were assumed to be coincident. In the simulation of the spectrum of the pyridine adduct this restriction was relaxed but no improvement in the fit of simulated to experimental spectrum resulted. Computer simulations were performed using an IBM 370 Model 155 computer, the output from which was used to drive a Calcomp plotter.

Nuclear electric quadrupole terms in the Hamiltonian can cause shifts in the positions of the hyperfine lines. We therefore calculated the positions of the first-order hyperfine transitions including the quadrupole terms using an estimated value of  $|eqQ|$  of 150 MHz, which is similar to that found for other cobalt complexes.<sup>28,29</sup> However, no improvement in simulations was obtained by including quadrupole effects, which have therefore been neglected in this paper. This may be because the hyperfine lines most affected by the quadrupole moment are severely overlapped by hyperfine lines arising from other orientations. It is also possible that the quadrupole coupling constant of cobalt in our compounds is negligibly small, as found in the recent results of De Bolfo et al.<sup>30</sup> for cobalt(II) 4,4',4'',4''-tetrasulphthalocyanine.

EPR spectra of the adducts of I with axial ligands in which nitrogen or phosphorus atoms coordinate to the cobalt show a number of additional lines that can easily be confused with hyperfine lines. These lines arise from the angular dependence of the line positions and once identified as off-axis extrema are of assistance in determining the spectral parameters because they mark the end of a series of hyperfine lines, and their positions are quite sensitive to both  $g$  and cobalt hyperfine tensors.

## Results and Discussion

**EPR of 1:1 Adducts.** X-band EPR spectra were obtained of frozen glasses of I dissolved in toluene with small amounts added of a wide range of potential ligands. EPR parameters were calculated with the aid of computer simulations of experimental spectra and are listed in Table I. The EPR spectra of the adducts of I formed with each of 2-methyltetrahydrofuran (MTHF), thiophene, pyridine, and triethyl phosphite, are shown in Figures 1-4 together with spectra simulated using the parameters of Tables I and II. These spectra are typical for adducts with each of the four different types of donor atoms (O, S, N, and P) studied. 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.

No differences between spectra recorded at 9 and 90 K were observed. At higher temperatures, spectra became less resolved as expected when line broadening due to spin-lattice relaxation occurs. This broadening prevented liquid solution spectra from being observed except for the phosphorus adducts. Even when liquid solution spectra could be obtained the line width was so great that no resolved cobalt hyperfine structure was observed. Nevertheless computer simulation of isotropic spectra of the phosphorus adducts did enable the relative signs of the principal values of the cobalt nuclear hyperfine coupling constants to be determined.

The EPR tensors all have rhombic symmetry. The spectra show progressions of eight lines indicating an interaction of the unpaired electron with a single cobalt nucleus ( $I = 7/2$ ). In the presence of ligands expected to coordinate through a nitrogen-cobalt bond, an additional three-line splitting occurs on the high-field progression due to interaction of a single

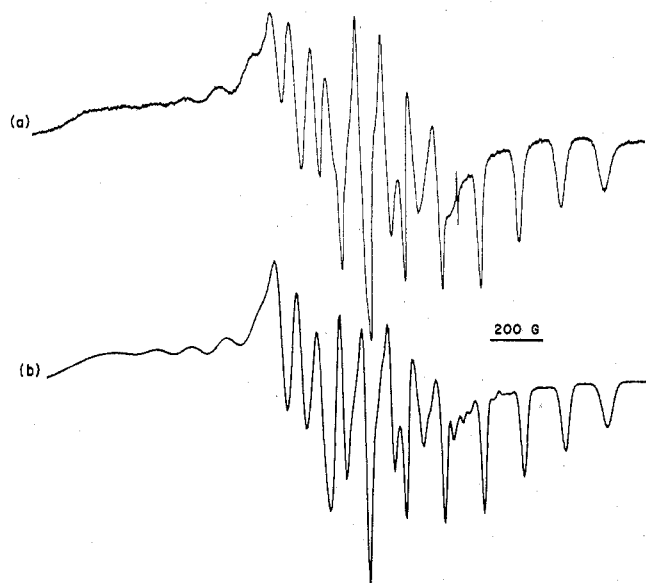


Figure 1. (a) EPR spectrum of I in toluene/MTHF at 90 K. (b) Computer simulation using the parameters of Tables I and II.

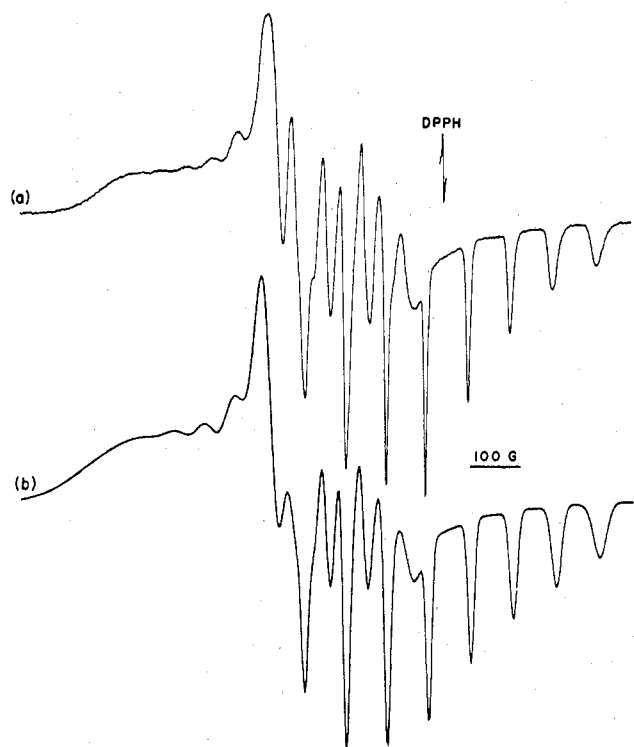


Figure 2. (a) EPR spectrum of I in toluene/thiophene at 90 K. (b) Computer simulation using the parameters of Tables I and II.

nitrogen nucleus ( $I = 1$ ). Phosphorus ligation to cobalt causes each cobalt hyperfine line to split into two equally intense lines, indicating interaction of a single phosphorus nucleus ( $I = 1/2$ ). No changes occurred upon addition of a large excess of ligand, in contrast to results obtained for cobalt tetraphenylporphyrin systems.<sup>4,6</sup> It therefore appears that the macrocyclic Schiff base complex only forms 1:1 adducts. Phosphorus and nitrogen ligand hyperfine coupling constants are found in Table I. Upon contact with air, the pyridine adduct of I reacted with oxygen with the formation of a dioxygen adduct. The EPR parameters were very similar to those reported for similar dioxygen adducts,<sup>1-12</sup> and therefore no detailed study was made of this six-coordinate species.

**EPR of I.** The EPR spectrum of I dissolved in toluene (Figure 5) is significantly different from the spectra obtained

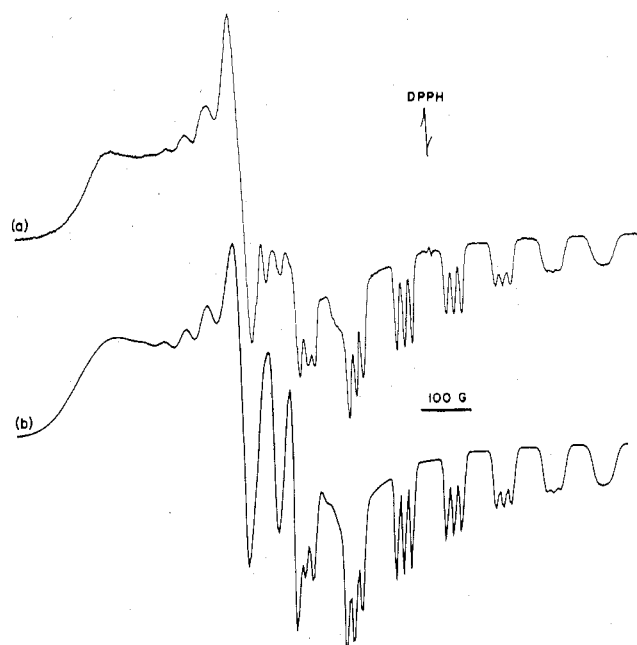


Figure 3. (a) EPR spectrum of I in toluene/pyridine at 90 K. (b) Computer simulation using the parameters of Tables I and II.

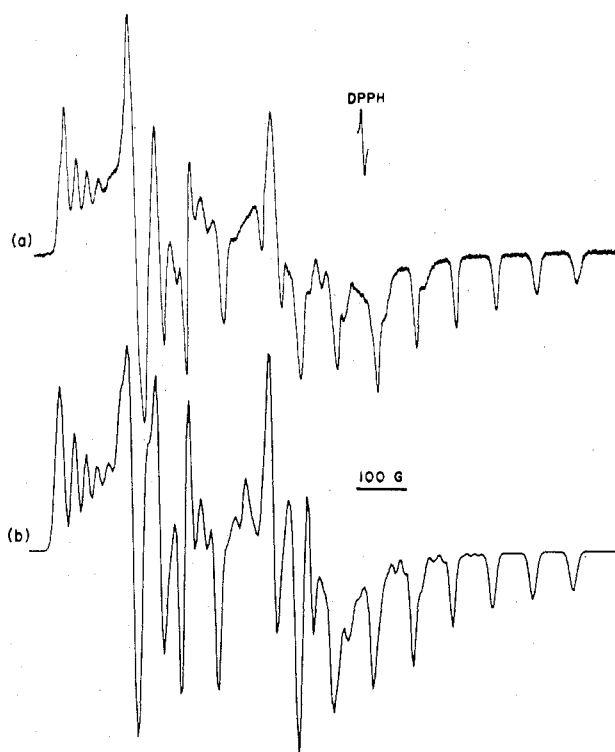


Figure 4. (a) EPR spectrum of I in toluene/triethyl phosphite. (b) Computer simulation using the parameters of Tables I and II.

for the 1:1 adducts in that it appears to have approximate axial symmetry and in that two of the principal  $g$  values are substantially less than 2.00 (Table I). Furthermore, the EPR parameters for I dissolved in hexamethylphosphoramide (HMPA), tetrahydrothiophene 1,1-dioxide, and the liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-butylaniline are very similar to those found for I dissolved in toluene. 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.

To help elucidate the nature of the species in toluene solutions we dissolved the complex I in the liquid crystal. The EPR spectrum in the rapidly frozen solvent was identical with

**Table I.** EPR Parameters for Complexes of I<sup>a</sup>

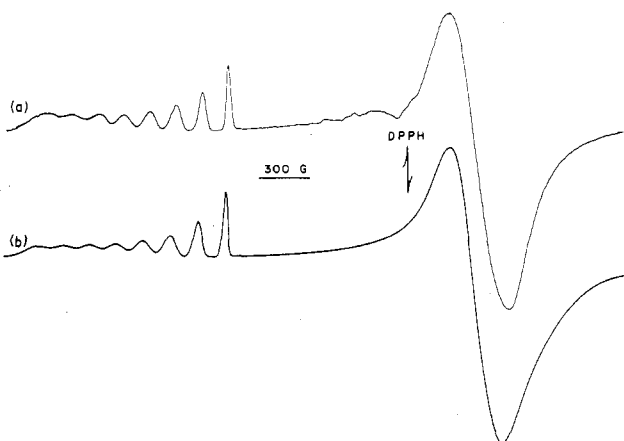
	$g_x$	$g_y$	$g_z$	$A_x, \text{cm}^{-1}$	$A_y, \text{cm}^{-1}$	$A_z, \text{cm}^{-1}$	$A_z(\text{N or P}), \text{cm}^{-1}$
Toluene	3.83	1.64	1.79	0.0274	-0.003	0.003	
HMPA	3.81	1.67	1.81	0.0267	-0.003	0.003	
THF	2.95	2.23	1.976	0.0172	0.0092	0.0137	
MTHF	2.88	2.24	1.978	0.0161	0.0091	0.0136	
Thiophene	2.58	2.19	1.987	0.0084	0.0052	0.0109	
Acetonitrile	2.52	2.16	1.995	0.0078	0.0046	0.0108	0.0013
2-Methylpyridine	2.49	2.16	2.001	0.0063		0.0101	0.0015
Imidazole	2.49	2.16	2.001	0.0063		0.0099	0.0014
3-Methylpyridine	2.47	2.16	2.001	0.0056		0.0098	0.0015 <sup>b</sup>
Tris( <i>N,N</i> -dimethylamino)phosphine	2.46	2.16	2.001	0.0056		0.0101	0.0014 <sup>c</sup>
Piperidine	2.46	2.16	2.001	0.0053		0.0101	0.0015
Pyridine	2.44	2.16	2.001	0.0041	0.0020	0.0099	0.0015
Triethyl phosphite <sup>f</sup>	2.25	2.12	2.004	-0.0024	0.0012	0.0073	0.0282 <sup>d</sup>
Triphenyl phosphite <sup>f</sup>	2.23	2.14	2.007	-0.0023	0.0016	0.0082	0.0270 <sup>e</sup>

<sup>a</sup> From computer simulation of spectra. <sup>b</sup>  $A_x(\text{N}) = 0.00125 \text{ cm}^{-1}$ . <sup>c</sup> The observation of nitrogen hyperfine structure in this case indicates that a cobalt-nitrogen bond is formed in preference to a cobalt-phosphorus bond. This is presumably a steric effect. <sup>d</sup>  $A_x(\text{P}) = 0.0258 \text{ cm}^{-1}$ ,  $A_y(\text{P}) = 0.0251 \text{ cm}^{-1}$ . <sup>e</sup>  $A_x(\text{P}) = 0.0264 \text{ cm}^{-1}$ ,  $A_y(\text{P}) = 0.0266 \text{ cm}^{-1}$ . <sup>f</sup> Relative signs of  $A$  were determined from computer simulation of isotropic spectra.

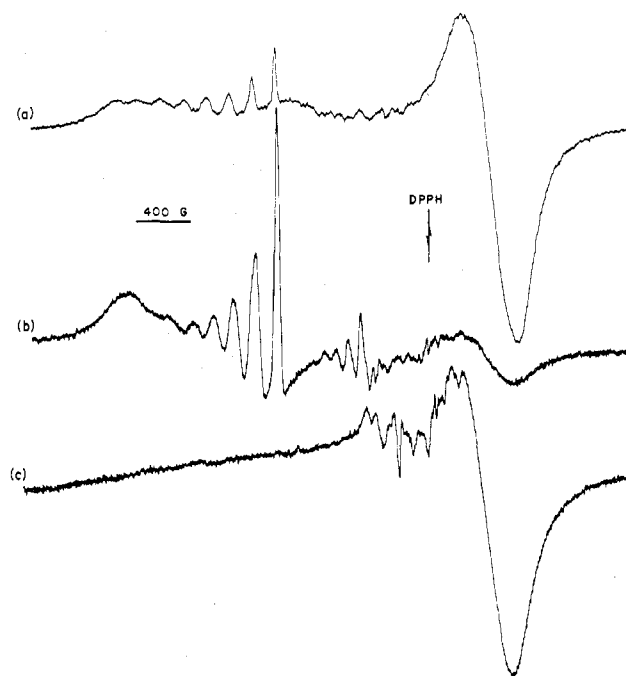
**Table II.** Hyperfine Component Peak-to-Peak Line Widths (G) for Complexes of I<sup>a</sup>

	$m_I$							
	$7/2$	$5/2$	$3/2$	$1/2$	$-1/2$	$-3/2$	$-5/2$	$-7/2$
x Direction								
MTHF	200	164	144	105	91	84	77	70
Thiophene	200	172	140	118	76	59	49	42
Acetonitrile	156	130	104	80	60	48	42	40
Pyridine	120	105	90	75	60	45	32	30
Triethyl phosphite <sup>b</sup>	17	16	13	14	17	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>
y Direction								
MTHF	41	32	29	19	19	20	29	54
Thiophene	49	42	33	23	22	22	29	47
Acetonitrile	39	36	33	30	30	33	35	36
Pyridine	30	26	22	20	20	22	26	30
Triethyl phosphite	About 10 <sup>c</sup>							
z Direction								
MTHF	26	20	17	17	18	22	28	39
Thiophene	19	18	16	15	17	21	26	37
Acetonitrile	17	14	11	9	10	13	14	17
Pyridine	14	11	9	8	9	11	14	18
Triethyl phosphite <sup>b</sup>	14	13	12	11	12	13	15	16

<sup>a</sup> From computer simulation of spectra. <sup>b</sup> Line widths are for the  $m_I(\text{P}) = +1/2$  component. <sup>c</sup> Inadequately resolved for reliable estimates.



**Figure 5.** (a) EPR spectrum of I in toluene at 90 K. (b) Computer simulation using the parameters of Tables I and II. The small peaks near  $g \sim 2.2$  are due to the presence of small amounts of acetonitrile which forms a 1:1 adduct with I.



**Figure 6.** EPR spectrum of I in liquid crystal: (a) before orientation at 90 K; (b) after orientation at 0°; (c) after orientation at 90°.

the spectrum of the complex in frozen toluene solutions. However, spectra obtained of the nematic phase (see Experimental Section) showed an orientation dependence. At 0°, the lines at  $g = 3.83$  are greatly enhanced compared to the line at  $g \sim 1.7$ , whereas at 90° only the line at  $g \sim 1.7$  is obtained (Figure 6). The  $g = 3.83$  absorption seen at 0° most likely corresponds to the long axis of the complex which is an in-plane direction. We arbitrarily designate this as the  $x$  axis without wishing to imply at this point that the direction necessarily corresponds to the principal axis labeled  $g_x$  for the 1:1 adducts in Table I. The Cu(II) analogue of I, oriented in the same liquid crystal, also showed enhancement of one of the in-plane orientations at 0°, and indeed was found to orient rather more readily than the cobalt complex.

The best simulation of the four-coordinate complex was obtained by assuming a slight rhombicity in the EPR parameters, although the line width was too great to allow an accurate determination of the parameters along the  $y$  and  $z$  axes. The values of these parameters (Table I) are therefore less accurate for toluene and HMPA than for the other complexes.

**Interpretation of EPR Parameters of 1:1 Adducts.** Except for the case of I dissolved in toluene or HMPA, which will be discussed separately, the EPR parameters of I in the various solvents appear to be related. The entries in Table I have been arranged to emphasize this relationship. As the two largest principal values of the *g* tensor decrease, the principal values of the cobalt hyperfine coupling constant,  $|A|$ , decrease while the smallest principal value of *g* increases. Furthermore in all cases  $|A_2| < |A_1|$ ,  $|A_3|$  where  $g_1 > g_2 > g_3$ . These trends indicate that the adducts have a common ground-state configuration. The presence of a hyperfine interaction with nitrogen and phosphorus atoms, which must coordinate along the axial or *z* direction of I, is strong evidence that the unpaired electron is in an orbital with a large component in this direction ( $d_{xz}$ ,  $d_{yz}$ , or  $d_{z^2}$ ).

McGarvey<sup>31</sup> has extended the theory for the spin Hamiltonian parameters of low-spin Co(II) complexes<sup>32,33</sup> to third order, including the effect of admixture of excited quartet states with the ground doublet state. We have utilized this theory to determine the ground state of the 1:1 adducts of I. Because EPR of glasses does not relate the principal axes of the tensors to the geometric axes, all possible assignments of the unique *z* axis must be considered. No assignment of axes nor any combination of signs of the principal values of the cobalt hyperfine coupling tensor gave a good fit of the EPR parameters to the theoretical expressions with physically meaningful values of the molecular orbital parameters for a  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{yz}^1$  or  $(d_{x^2-y^2}d_{yz}d_{z^2})^6d_{xz}^1$  ground state.<sup>34</sup> A good fit was, however, obtained for a  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$  ground state. No assumptions were made about the sign of the cobalt hyperfine coupling constants but the only reasonable fit of the experimental data to the theoretical expressions for the thiophene, THF, MTHF, and nitrogen adducts was obtained with all of the principal values of the hyperfine coupling constant being positive. For the phosphorus adducts, the relative signs of the principal values of the cobalt nuclear hyperfine coupling constants were determined by computer simulation of the isotropic spectra. A reasonable fit of the experimental data to the theoretical expressions was obtained only with  $A_z > 0$ .

For a  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$  ground state the value of  $g_z$  is predicted to be close to 2<sup>31</sup> and therefore we identify the *z* direction with the principal axis having *g* closest to 2. We are not able to determine the geometrical orientations of the other principal axes. The assignment of a  $d_{z^2}$  ground state is consistent with the ground states found for a large number of adducts of other low-spin Co(II) macrocyclic complexes.<sup>3,4,6-9</sup> Furthermore the magnitudes of the nitrogen and phosphorus hyperfine splittings for adducts of I are very similar to those observed for adducts of these complexes.<sup>3,4,6-9</sup>

Because the symmetry of the 1:1 adducts of I is no higher than  $C_{2v}$ ,<sup>18,23</sup> admixture of  $d_{x^2-y^2}$  to the  $d_{z^2}$  state is symmetry allowed. Including this mixing, McGarvey<sup>31</sup> obtains

$$g_z = g_e + \frac{2}{3}(c_3^2 + c_4^2 + c_3c_4) + (3a^2 - b^2)c_1c_2 - [(3a)^{1/2} + b]^2c_2^2 - [(3a)^{1/2} - b]^2c_1^2 - 8b^2c_6$$

where  $c_1 = \xi/\Delta(^2B_1)$ ,  $c_2 = \xi/\Delta(^2B_2)$ ,  $c_3 = \xi/\Delta(^4B_1)$ ,  $c_4 = \xi/\Delta(^4B_2)$ ,  $c_6 = \xi/\Delta(^2A_2)$ , and the half-filled orbital in the ground state is  $(ad_{z^2} + bd_{x^2-y^2})$ . The doublet excited states  $^2B_1$ ,  $^2B_2$ , and  $^2A_2$  correspond to the  $(d_{x^2-y^2}d_{yz}d_{z^2})^6d_{xz}^1$ ,  $(d_{x^2-y^2}d_{xz}d_{z^2})^6d_{yz}^1$ , and  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{xy}^1$  configurations, respectively. The quartet states  $^4B_1$  and  $^4B_2$  correspond to the  $(d_{x^2-y^2}d_{xz})^4d_{yz}^1d_{z^2}^1d_{xy}^1$  and  $(d_{x^2-y^2}d_{yz})^4d_{xz}^1d_{z^2}^1d_{xy}^1$  configurations,  $\Delta$  is the energy difference between the designated state and the  $^2A_1$  ground state, and  $\xi$  is the spin-orbit coupling constant of Co(II).

If the terms  $c_3$  and  $c_4$  which involve quartet states are both zero,  $g_z$  is found to be less than  $g_e$  for any value of *b*. Since

Table III. Orbital Coefficients for Complexes of I<sup>a</sup>

	$c_1$	$c_2$	$P, \text{cm}^{-1}$	$K, \text{cm}^{-1}$	$\rho_{3d}^b$	$\rho_{4s}^c$
Toluene <sup>d</sup>		0.32	0.014	0.010	0.55	0.12
Toluene <sup>e</sup>		-0.32	0.024	-0.0067	1.06	0.01
THF	0.056	0.164	0.0134	0.0080	0.53	0.10
MTHF	0.055	0.152	0.0130	0.0081	0.52	0.10
Thiophene	0.037	0.099	0.0095	0.0055	0.37	0.07
Acetonitrile	0.031	0.087	0.0100	0.0053	0.39	0.07
Pyridine	0.032	0.071	0.0137	0.0025	0.54	0.06
Triethyl phosphite	0.028	0.034	0.0140	0.0003	0.55	0.04

<sup>a</sup> Coefficients  $c_i (i \geq 3)$  are assumed to be zero as explained in the text; *b* is zero except for the adducts of pyridine ( $b = 0.05$ ) and triethyl phosphite ( $b = 0.2$ ). <sup>b</sup> Calculated using  $\rho_{3d} = P/0.0254$ . <sup>c</sup> Calculated using  $\rho_{4s} = (K + 0.0084\rho_{3d})/0.1232$ . <sup>d</sup> Assuming a  $d_{z^2}$  ground state. <sup>e</sup> Assuming a  $d_{yz}$  ground state.

we observe values of  $g_z$  greater than  $g_e$  for the phosphorus adducts (Table I), we conclude that  $c_3$  and  $c_4$  are not both zero, at least for these adducts. Thus the effects of low-lying quartet states are not negligible.

The influence of such states on the EPR parameters has been neglected in past studies of similar complexes even though  $g_z > g_e$ .<sup>7-9,14</sup> Lin<sup>35,36</sup> suggests that  $^4B_1$ ,  $^4B_2$ , and  $^4A_2$  states may all lie fairly close to the ground state in such 1:1 adducts (the  $^4A_2$  term enters the other equations but does not affect  $g_z$ ), and McGarvey<sup>31</sup> has reached a similar conclusion at least for adducts with axially symmetric EPR tensors. The unusual temperature dependence of the magnetic susceptibility of the pyridine adduct of *N,N'*-ethylenebis(salicylaldiminato)cobalt(II) has also been attributed to the mixing of excited quartet states into the ground doublet state.<sup>37,38</sup>

Application of McGarvey's equations for a  $d_{z^2}$  ground state does not result in a unique solution because there are 12 molecular orbital parameters and only six experimental parameters. Contributions from the doublet states which are associated with quartet states  $^4B_1$ ,  $^4B_2$ , and  $^4A_2$  will be much smaller than the quartet state contributions<sup>31</sup> and have therefore been neglected. The calculated EPR parameters are insensitive both to  $c_6$  and to these doublet contributions and therefore  $c_6$  has also been neglected. In order to find the values of the remaining eight molecular orbital parameters, the coefficients  $c_3$ - $c_6$  were varied systematically and  $c_1$ ,  $c_2$ , *b*, *P* (i.e.,  $gg_N\beta\beta_N(r^{-3})$ ), and *K*, the Fermi contact term, were calculated from five of McGarvey's equations, 19-24, and the experimental data. The remaining equation was used to calculate  $A_z$  which was then compared with the experimental values to determine whether suitable agreement was reached.

Even with these constraints a large number of possible solutions can be obtained. Nevertheless some limitations can be placed upon the magnitudes of the molecular orbital coefficients. For each of the adducts, suitable agreement between theory and experiment could be obtained only if  $c_3 < 0.3$ ,  $c_4 < 0.1$ ,  $c_5 < 0.3$ . In the case of the oxygen, sulfur, and acetonitrile adducts of I, *b* is found to be very close to zero. However, for the pyridine and phosphorus adducts a best fit between theory and experiment was obtained with nonzero values of *b*. Nevertheless, for all adducts  $b < 0.25$ . Thus the ground state has a maximum of 6%  $d_{x^2-y^2}$  character and in most cases has considerably less.

For convenience of tabulation the values of  $c_1$ ,  $c_2$ , *P*, and *K* listed in Table III have been calculated from McGarvey's equations with the further approximation that the  $c_i (i \geq 3)$  are all zero. This is the approximation used by Maki et al.<sup>32</sup> and most other workers<sup>2,7-10,13,14</sup> except that terms in  $c_1c_2$  and  $c_2^2$  have been retained. We find  $c_4$  to be small and therefore equating it to zero has little effect upon the values of the other molecular orbital coefficients. However, because  $c_3$  and/or  $c_5$  may deviate significantly from zero, the values for the

molecular orbital coefficients listed in Table III are only an approximation. We find that as  $c_3$  and  $c_5$  are varied between 0 and 0.3,  $P$  and  $K$  fluctuate within  $\pm 0.001 \text{ cm}^{-1}$  of the values in Table III. The values of  $c_1$  and  $c_2$  are little affected by variations in  $c_3$  but both decrease substantially as  $c_5^2$  increases. For example, if  $c_5 = 0.2$ , the values of  $c_1$  and  $c_2$  required to obtain the best fit of data to the model are both about 0.02 smaller than if  $c_5 = 0$ . The magnitude of this effect on  $c_1$  and  $c_2$  is very similar for all of the 1:1 adducts of I that we have investigated. The most important conclusion of our analysis is that the trends which can be observed in Table III are not affected by the assumptions made about the  $c_i$  ( $i \geq 3$ ). Discussion of these trends will be deferred until a later section.

**Interpretation of EPR Parameters of the Four-Coordinate Complex.** The EPR parameters of I in toluene are very similar to those found by von Zelewsky and Fierz<sup>39</sup> for  $N,N'$ -ethylenebis(salicylaldiminato)cobalt(II) doped in single crystals of the corresponding nickel(II) complex.

Because the line width in the high-field region of the spectrum (Figure 5) is very large, it is not possible to deduce very accurate values for all of the principal values of  $g$  and  $A$ , thus complicating the assignment of a ground state to this complex. The observation that one of the in-plane principal values of  $g$ ,  $g_x$ , is very large can be explained if the ground state is either  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{yz}^1$  or  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$ . In both cases the large value of  $g_x$  occurs because the expression for  $g_x$  is dominated by the term involving the separation between these two states regardless of which is the ground state (McGarvey's equations 19 and 41).<sup>31</sup> The large value of  $|A_x|$  is similarly explained. Even though we are not able to assign a definite ground state, our calculations show that the energy difference between the  $d_{yz}$  and  $d_{z^2}$  states is about  $3\xi$  which corresponds to about  $1500 \text{ cm}^{-1}$  if the Co(II) free-ion value of  $\xi = -515 \text{ cm}^{-1}$  is used.<sup>40</sup> The calculated energy separation probably represents an upper limit since  $\xi$  is often reduced from the free ion value by covalent effects.<sup>32</sup>

In order to determine the ground state it is necessary to know the principal values of  $g$  and  $|A|$  in the  $y$  and  $z$  directions. The EPR parameters we obtain from computer simulations are consistent with McGarvey's equations for a  $d_{yz}$  ground state, although only if  $g_z$  is assigned to be greater than  $g_y$ , and if  $A_y < 0$ . Under these conditions a fit is obtained with  $P = 0.024 \text{ cm}^{-1}$ ,  $K = -0.0067 \text{ cm}^{-1}$ , and  $\eta_3 \sim 0.32$ , where  $\eta_3 = \xi/\Delta(^2A_1)$ , and  $\Delta(^2A_1)$  is the separation between the ground state and the  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$  state. The remaining molecular orbital parameters are either less than 0.1 or have negligible effect upon the fit. On the other hand the EPR parameters of Table I do not fit the model for a  $d_{z^2}$  ground state very well for any choice of signs of  $A_x$ ,  $A_y$ , or  $A_z$ , even if the assignment of the  $y$  and  $z$  directions is reversed, quartet terms are included, or a significant amount of  $d_{x^2-y^2}$  character is introduced into the ground state. Nevertheless, because there is difficulty in accurately simulating EPR spectra which are poorly resolved and because McGarvey's equations ignore some excited quartet terms arising from double excitations which Lin<sup>36</sup> has found to be important in the case of uncoordinated cobalt porphyrins, we are reluctant to assign a  $d_{yz}$  ground state in preference to a  $d_{z^2}$  ground state for the four-coordinate complex. We therefore list in Table III the molecular orbital parameters which best fit the observed EPR parameters for both ground states even though the fit to the model for a  $d_{z^2}$  ground state was worse.

**Unpaired-Spin Densities.** From the nuclear hyperfine coupling constants it is possible to deduce the unpaired-spin densities on the cobalt and coordinating atoms. Cobalt 3d spin densities ( $\rho_{3d}$ ) are determined from a comparison of the calculated value of  $P$  with the theoretical value of  $P_0 = 0.0254 \text{ cm}^{-1}$  for a cobalt 3d electron.<sup>41</sup> Cobalt 4s spin densities ( $\rho_{4s}$ )

are estimated from the relationship  $K = 0.1232\rho_{4s} - 0.0084\rho_{3d}$ . The results for the various complexes are given in Table III.

The ligand hyperfine coupling constants obtained for nitrogen and phosphorus ligands can be treated in a similar manner to obtain the spin density on the coordinating axial atom. The isotropic hyperfine coupling constants for <sup>31</sup>P or <sup>14</sup>N yield the 3s or 2s spin densities<sup>43</sup>  $\rho_{3s} = a_{\text{iso}}^{\text{P}}/0.3396$  or  $\rho_{2s} = a_{\text{iso}}^{\text{N}}/0.0514$ . The anisotropic couplings give the 3p or 2p spin densities;  $\rho_{3p} = (A_{zz}^{\text{P}} - a_{\text{iso}}^{\text{P}})/0.01922$  or  $\rho_{2p} = (A_{zz}^{\text{N}} - a_{\text{iso}}^{\text{N}})/0.00319$ . The 3s spin density on the phosphorus atom is 0.08 for the triethyl phosphite and triphenyl phosphite adducts while the 3p spin densities are 0.09 and 0.03, respectively. For the nitrogen adducts the nitrogen hyperfine coupling constant in the  $z$  direction ranges from 0.0013 to  $0.0015 \text{ cm}^{-1}$ . Although nitrogen hyperfine structure was usually not resolved in the other orientations, partially oriented frozen solutions of I in 3-methylpyridine were obtained in which the nitrogen hyperfine coupling constant along the  $x$  direction was observable and found to be  $0.00125 \text{ cm}^{-1}$ . Thus the nitrogen hyperfine coupling is approximately isotropic and the 2s spin density on the nitrogen is about 0.025.

Except possibly in the case of toluene where the ground state is uncertain, the Fermi contact term,  $K$ , is positive which indicates strong admixture of the 4s orbital with the  $3d_{z^2}$  orbital. This contribution is reduced as the strength of the crystal field due to the axial ligand increases, from oxygen to phosphorus coordination. The same result has been observed for similar systems<sup>31,44</sup> although the 4s spin density is somewhat larger for our system. We find for our series of complexes that the amount of 4s character increases as the strength of the crystal field along the  $z$  axis decreases for a  $d_{z^2}$  ground state; thus we would expect a four-coordinate complex with a  $d_{z^2}$  ground state to have more 4s character in the ground state than any of the adducts. This has been observed for several four-coordinate porphyrin and phthalocyanine complexes.<sup>31,35,36</sup> On the other hand, a four-coordinate complex with a  $d_{yz}$  ground state will have little 4s character in the ground state because such mixture is symmetry forbidden except in the  $C_i$  point group.

Structurally similar complexes are expected to have similar  $P$  values, as indeed we observe for the 1:1 adducts of I. The values of  $P$  given in Table III are sensitive to some of the other parameters so the cobalt spin densities are subject to fairly large errors. Even so, the values of  $P$  we calculate for the series of adducts are remarkably small when compared with those of most other workers<sup>7-9,31,44</sup> although a few cases have been noted where  $P$  is unusually small.<sup>13,45-47</sup> Since the magnitudes of the hyperfine coupling constants of the atoms coordinating in the axial position are similar to those observed for other complexes<sup>4,6-10,44</sup> a large proportion of the spin density is unaccounted for.

No resolved nitrogen hyperfine structure due to the in-plane nitrogen atoms was observed, in contrast to the case of the copper analogue of I dissolved in toluene, where a splitting of  $0.00115 \text{ cm}^{-1}$  is observed in the parallel direction and of  $0.00129 \text{ cm}^{-1}$  in the perpendicular direction for each of the four nitrogen atoms. Thus for the copper analogue of I, about 22% of the spin density is on the nitrogen atoms with most of the remainder on the copper atom, predominantly in the  $d_{xy}$  orbital which lies in the plane of ligand. There is only a small spin density on the carbon atoms of the macrocycle, which is expected if the primary means of spin delocalization is via the  $\sigma$  bonds. In the cobalt complex I, there is a much smaller spin density on the nitrogen atoms of the ligand as shown by the lack of hyperfine structure. Since the unpaired electron lies mainly in the  $d_{z^2}$  orbital of the cobalt, the primary means of spin delocalization is by way of  $\pi$  bonding. The macrocyclic ligand has extensive  $\pi$  bonding and therefore the

unpaired spin density on the ligand is expected to be localized throughout the  $\pi$  system of the ligand and not concentrated on the nitrogen atoms. We suggest that the low spin density on the cobalt atom may be due to extensive spin-delocalization throughout the macrocyclic ligand. The spin density on our ligand is greater than is found on the macrocycle in tetraphenylporphyrin complexes. This effect is most likely due to both the distortion from planarity and shorter metal-nitrogen bond lengths in I than in tetraphenylporphyrin compounds.<sup>18,19</sup> A shorter metal-nitrogen bond distance should lead to better overlap and significantly enhance delocalization of the unpaired electron through the  $\pi$  system.

A second possible explanation of the unusually low  $P$  values lies in the fact that McGarvey's equations<sup>31</sup> neglect mixing of 4p character into the ground state. Such mixing is allowed in low symmetry and could lead to a reduction in the cobalt hyperfine coupling without changing the total spin density on the cobalt. Thus values of  $P$  calculated from McGarvey's equations may be in error. Such an explanation provides a rationalization of the normal values for the nitrogen and phosphorus hyperfine coupling constants of the axial ligands.

**Structural Characteristics.** For a Co(II) macrocyclic complex with a  $d_{z^2}$  ground state as the strength of the ligand field along the  $z$  axis increases, the energy of the  $d_{z^2}$  orbital is expected to rise substantially relative to the energies of the  $d_{xz}$  and  $d_{yz}$  orbitals. These orbitals are in turn expected to rise somewhat in energy relative to the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals, which have no component along the  $z$  axis. Thus as the ligand field strength along the  $z$  axis increases,  $c_2$  and  $c_1$  should decrease. On this basis the strength of the ligand field increases in the order  $O < S < N < P$  for the adducts of I.

A large difference in energy between the  $d_{yz}^1$  and  $d_{xz}^1$  states exists even when the axial bond is either very weak or non-existent as in toluene solutions, although we are not able to determine  $c_1$  with any accuracy in this case. This lifting of degeneracy is probably due to the difference between the NCoN angles at the metal center that crystallographic studies<sup>18,19</sup> have shown to exist.

The destabilization of the  $d_{yz}$  orbital relative to that of the  $d_{xz}$  orbital can be attributed to an antibonding interaction of the  $d_{yz}$  orbital with a linear combination of the  $\pi$  orbitals of the macrocycle and a bonding interaction of the  $d_{xz}$  orbital with a different linear combination. Dedieu et al.<sup>48</sup> have performed ab initio LCAO-MO-SCF calculations for several cobalt(II) (acacen) complexes and find an analogous interaction of the  $d_{xz}$  and  $d_{yz}$  orbital with  $\pi$  orbitals of the ligand. Deviations from planarity would emphasize the effect.

The Co(II) macrocycle I is unusual in that it forms 1:1 adducts with ligands that have oxygen and sulfur donor atoms. To our knowledge no 1:1 cobalt macrocyclic adducts with oxygen and sulfur donors have been studied by EPR and it seems likely that in many cases they do not form.<sup>49</sup> However, many adducts with nitrogen and phosphorus donors have been studied by EPR. Compared with the results of other workers<sup>48</sup> for nitrogen and phosphorus adducts of Co(II) macrocyclic compounds, the EPR parameters for the adducts of I show greater sensitivity to the nature of the axial ligand. Because most work has been performed on adducts which have axially symmetric EPR parameters, we compare our values for  $(g_x + g_y)/2$  with published values of  $g_{\perp}$ . For our adducts,  $g_{\perp} = (g_x + g_y)/2$  is rather less than typically observed for phosphorus adducts of Co(II) macrocycles,<sup>7-9</sup> and while  $g_{\perp}$  for the pyridine adduct of I is fairly typical of values observed for nitrogen adducts,<sup>4</sup> the value for the acetonitrile adduct of I is larger than previous results would have led us to expect. Thus the EPR parameters for the adducts of I are more sensitive to the nature of the axial ligand than is the case for most analogous adducts of Co(II) macrocycle complexes.

Because the EPR parameters of the various methyl-substituted pyridine adducts of I are almost identical, we conclude that the size of the axial ligand has little effect upon the EPR parameters. The nonplanarity of I is probably responsible for the sensitivity of the EPR parameters to the nature of the axial ligand. Even in the four-coordinate complex I, the cobalt lies out of the plane of the four nitrogen atoms.<sup>16</sup> As the strength of the bond between cobalt and the ligating atom increases, the cobalt is likely to move further out of the plane, emphasizing the electronic or bonding effects.

The trends observed for the EPR and molecular orbital parameters of the 1:1 adducts of I are consistent with the results found for toluene solutions of I. The energy separation between the  $d_{z^2}$  and  $d_{yz}$  states steadily decreases as the ligand field decreases from phosphorus to oxygen coordination and this trend is expected to continue. Thus the similar energies of the  $d_{yz}$  and  $d_{z^2}$  states in the four-coordinate complex and the ambiguity in ground state is not surprising. While it is not possible to determine by experiment which axis of the molecule corresponds to the largest  $g$  value in the 1:1 adducts, on the basis of these trends it seems likely that the axis of the largest  $g$  value for the 1:1 adducts is the same as that for the four-coordinate complex. The liquid crystal results show that the long axis (the  $x$  axis) of the molecule may be identified with the largest  $g$  value in the four-coordinate complex and we believe this to be also the case for the 1:1 adducts.

When the EPR results of the low-spin Co(II) adducts of I are compared with those found for cobalt(II) porphyrins<sup>5-9,31</sup> several differences between the two systems become apparent. Unlike most cobalt(II) porphyrin compounds which display axial symmetry, the adducts of I exhibit rhombic symmetry. This difference is due to the presence of alternating five- and six-membered chelate rings in the Schiff base. Goedken and co-workers<sup>18-23</sup> have shown that the N-M-N bond angles for the five- and six-membered rings are significantly different. Thus the in-plane  $x$  and  $y$  directions are nonequivalent and rhombic symmetry is imparted to the system. The 16-membered porphyrin structure on the other hand has four symmetrically placed six-membered chelate rings. In the absence of unsymmetrically placed peripheral substituents these compounds exhibit axially symmetric EPR parameters.

Spin density calculations show that the Schiff base is more effective than a porphyrin at removing electron density from the cobalt ion. This effect appears to be a direct result of the different macrocyclic "hole" sizes provided by the Schiff base and porphyrins. Crystallographic investigations<sup>18-23</sup> have demonstrated that the M-N bond distance for complexes of this Schiff base are slightly shorter (by about 0.1 Å) than those found in a metalloporphyrin. Since a decreased metal-nitrogen bond distance should give rise to increased  $\pi$  back-bonding, the Co(II) spin density for I should be lower than that found for a cobalt(II) porphyrin. This is observed to be the case.

All attempts to form six-coordinate adducts of I analogous to those formed with some cobalt(II) porphyrins<sup>4,6,9</sup> have failed. Solutions of I in neat pyridine and various liquid phosphines gave only the EPR spectrum characteristic of the five-coordinate adduct. The reasons for this difference are not entirely clear but three possible contributing factors can be cited. First the macrocyclic Schiff base is not flat but is saddle shaped. In those cases where 2:1 adducts of low-spin Co(II) complexes have been observed<sup>4,6,9</sup> the ligand has been planar. Structural analyses<sup>18-23</sup> have shown that the deviations from planarity are significant and in all cases greater than those observed for "ruffled" porphyrins. Thus steric interaction between the axial ligand and the cyclic framework may prevent the binding of a second base. A second possible factor is related to the size of the macrocyclic "hole", which crystallographic studies<sup>18-23</sup> have shown to be smaller in I than in cobalt(II) porphyrins.

For this reason the metal ion is displaced farther from the plane of the four nitrogen atoms of the macrocycle than is the case in metalloporphyrin complexes. The greater the extent of this displacement, the less favorable are the steric conditions for coordination of a second base.

In spite of these differences between the adducts of I and the cobalt(II) porphyrins there are some similarities. The spin density on the nitrogen and phosphorus atoms of the axial ligand is similar in both cases.<sup>7-9</sup> Furthermore, the pyridine adducts of I and the cobalt(II) porphyrins both form dioxygen adducts which have very similar EPR parameters.<sup>10-12</sup> We attribute the ability of the pyridine adduct of I to add oxygen but not a second pyridine molecule to the fact that the dioxygen adduct has a  $\text{Co}^{\text{III}}\text{O}_2^-$  configuration.<sup>10-12</sup> Cobalt(III) is smaller than cobalt(II) and is likely to be displaced less from the center of the four nitrogen atoms of the macrocycle. Thus on the basis of this observation it seems likely that the size of the macrocyclic "hole" is the most important factor preventing the formation of six-coordinate complexes of I. Studies of a planar analogue of I currently in progress<sup>49</sup> are expected to elucidate the relative importance of the various factors.

**EPR Line Width.** All spectra of the 1:1 adducts in glasses could be simulated quite well with Gaussian line shape provided that the line width was allowed to vary with both orientation and  $m_I$ . Because the hyperfine lines were not resolved in the  $y$  and  $z$  directions for the four-coordinate complex, the line widths could not be determined as accurately and will therefore not be considered further. The first-derivative peak-to-peak line widths at a given orientation,  $\Delta H(m_I, \theta)$ , obtained from computer simulation of spectra, are given in Table II. In the  $x$  direction the line width of the cobalt hyperfine lines increased to lower field while in the  $y$  and  $z$  directions the hyperfine lines had larger widths at the ends of the series than in the center. Furthermore, the line width in the  $x$  direction increased as the value of  $g_x$  increased, and the line width varied in the order  $\Delta H_x(m_I) > \Delta H_y(m_I) > \Delta H_z(m_I)$  in all cases.

Since the line widths are independent of the concentration of I and also of temperature below 90 K, they are not due to spin-lattice or cobalt-cobalt interactions. The solvent does have an effect in some cases. For example, overall resolution is less in piperidine than in a toluene/piperidine mixture. This effect does not, however, appear to be orientation or  $m_I$  dependent.

An  $m_I$ -dependent line width has been observed for some other low-spin cobalt(II) complexes. Tsay et al.<sup>50</sup> and Rollmann and Chan<sup>29</sup> attribute the variation in line width to a distribution of cobalt hyperfine coupling constants caused by differing solvent effects from molecule to molecule. Such a variation predicts a dependence on  $|m_I|$  such that the lines at the ends of a series ( $m_I = \pm 7/2$ ) should be broader than the lines at the center ( $m_I = \pm 1/2$ ). Although we observe such a trend for the lines in the  $y$  and  $z$  directions for our adducts, this explanation is insufficient to explain the observed line width variation in  $x$  direction. If, however, both  $g$  and  $A$  vary from molecule to molecule, then a line width variation such as we observe can be explained.

From our data (Table I) and discussions above, we find that an increase in the ligand field strength along the  $z$  axis causes a substantial decrease in both  $g_x$  and  $A_x$ , little change in  $g_y$  and  $g_z$ , fairly large decrease in  $A_y$  and  $A_z$ . Thus, if the line broadening is due to a distribution of crystal field strength over all molecules, the changes in  $g$  and  $A$  will be such that along the  $x$  axis the lines will be broadest at low field while along the  $y$  and  $z$  axes the lines will be dominated by the hyperfine coupling contribution to the line width and will be broadest at the ends of the series. This is indeed the observed trend. We therefore attribute the  $m_I$ - and orientation-dependent line

width to variations in the crystal field about the cobalt atom from molecule to molecule, probably as a result of solvent interactions.

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**Registry No.** I, 60193-64-8; I-HMPA, 66303-95-5; I-THF, 66324-12-7; I-MTHF, 66303-94-4; I-thiophene, 66303-93-3; I-acetonitrile, 66303-92-2; I-2-methylpyridine, 66303-91-1; I-imidazole, 66303-90-0; I-3-methylpyridine, 66303-89-7; I-tris(*N,N*-dimethylamino)phosphine, 66303-88-6; I-piperidine, 66324-11-6; I-pyridine, 66303-87-5; I-triethyl phosphite, 66324-42-3; I-triphenyl phosphite, 66303-86-4.

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## Photodecomposition of *cis*-Azidoamminebis(2,4-pentanedionato)cobalt(III)

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Irradiation of methanolic solutions of  $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$  with 350-nm radiation yields azide radicals and  $\text{Co}(\text{acac})_2$ . The quantum yield for cobalt(II) formation was  $0.019 \pm 0.001$  and evidence suggests that secondary recombination is ineffective under the conditions used. The second-order rate constant for secondary recombination is estimated to be  $7.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . There is no evidence for nitrene or coordinated nitrene formation at this wavelength. The results suggest that although several states are populated by the 350-nm exciting radiation, only the charge transfer to metal state(s) involving the azido group results in photodecomposition.

### Introduction

The photodecomposition of coordinated azides is of special interest because of the varied modes of photodecomposition which have been observed involving this ligand.<sup>1–8</sup> In addition, the work of Zink<sup>9</sup> suggests that such complexes illustrate the relationship between the numerous excited states available to such complexes and their observed photoreactions. Nonetheless, relatively few detailed studies have been carried out on azido complexes, and further study will be necessary if an understanding of their photochemistry is to be realized.

Investigations of the azidopentaammines of the cobalt triad suggest that the metal will have a major influence on which modes of photodecomposition will be observed.<sup>2,7,8</sup> Furthermore, replacing the amines of the azidopentaamminecobalt(III) ion with cyano groups also changes the mode of decomposition.<sup>1</sup> The *cis*-azidoamminebis(2,4-pentanedionato)cobalt(III) complex,  $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ , has been chosen for investigation in order to judiciously exploit the  $\beta$ -diketonate ligand and its derivatives in hope of probing various features of the photochemistry of coordinated azides. The photodecomposition of a number of tris( $\beta$ -diketonates) of cobalt(III) have been studied, and their spectra and photochemistry are now reasonably well understood.<sup>11,12</sup> The reactive state is believed to be a singlet ligand to metal charge transfer state, CTTM, and the reactions involve reduction of the metal center and a one-electron oxidation of the  $\beta$ -diketonate ligand.<sup>10</sup> The photochemical behavior of azido complexes, on the other hand, is more varied and less well understood. To date, three modes of photodecomposition involving the azido group have been observed. Photosubstitution involves the loss of the azido group as azide ion,<sup>13</sup> photo oxidation–reduction involves its loss as azide radical and reduction of the metal center,<sup>2–5</sup> and coordinated nitrene formation involves cleavage of nitrogen–nitrogen bond of the azido group to form molecular nitrogen and coordinated nitrene.<sup>6–9</sup>

Furthermore, whereas the electronic state(s) responsible for  $\text{Co}(\text{acac})_3$  photochemistry has been identified<sup>11–13</sup> and in azide ion, hydrazoic acid, and organic azides internal azide electronic

transitions have been identified,<sup>14,15</sup> no such transitions have been identified in azido complexes.<sup>8,16,17</sup> In  $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$  the charge-transfer states involving the 2,4-pentanedione and azide are similar in energy and one might expect either or both pentanedione or azide radicals to result from charge-transfer excitation. Furthermore, charge-transfer excitations have yielded both nitrene formation and substitution reactions. The 350-nm region has been characterized as the charge-transfer region of  $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$ <sup>11–13</sup> whereas, by analogy to  $\text{Co}(\text{acac})_3$ , one might expect to observe 2,4-pentanedionate radical formation; by analogy to  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  one would expect azide radicals. The behavior of  $\text{Rh}(\text{NH}_3)_3\text{N}_3^{2+}$  suggests the possibility of coordinated nitrene intermediacy, and that of  $\text{Co}(\text{CN})_5\text{N}_3^{3-}$  suggests azide ion formation. The compound under study has at least one feature in common with each of these compounds, and a study of its photochemistry will help to unravel the features important to the photochemistry of coordinated azides.

### Experimental Section

**Materials.**  $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$  was prepared by the method of Ellan and Ragsdale.<sup>18</sup> The product was recrystallized several times from ethanol and dried in air. Prior to use in photolyses or in the preparation of calibration curves, it was dried under vacuum at 55 °C for 6 h to yield  $\text{Co}(\text{acac})_2$ .

*cis*- $\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3$  was prepared by a modification of the method of Boucher and Herrington.<sup>17</sup> A solution was prepared by dissolving 2.0 g (7.8 mmol) of  $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$  in 125 mL of methanol and 5 mL of triethyl orthoformate. Similarly, solutions were prepared by dissolving 2 mL of concentrated ammonia in 10 mL of methanol and 2 mL of triethyl orthoformate and dissolving 3 mL of 30% hydrogen peroxide in 10 mL of methanol and 3 mL of triethyl orthoformate. All three solutions were boiled for 5 min and cooled to room temperatures. Then, 0.75 g (17.8 mmol) of  $\text{NaN}_3$  was added to the  $\text{Co}(\text{acac})_2$  solution, followed by the ammonia solution. The hydrogen peroxide solution was then added dropwise with stirring over a period of several hours. The solvent was allowed to evaporate and the moist residue extracted with chloroform. The extracts were combined, filtered, and dried over sodium bicarbonate. Two volumes of mixed hexanes were added and the product collected by filtration. The product was purified by chromatography on silica gel. The column was developed with 5% (v/v) methanol in chloroform. The product