

backbone in the out-of-plane linkage in exchange and upon coordination.

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Registry No. (+)₅₄₆-[Co(EDPA)]⁻, 56816-58-1; (-)₅₄₆-[Co(EDPA)]⁻, 56816-59-2; (+)₅₈₉-EDPA⁴⁺, 56845-77-3; (-)₅₈₉-EDPA⁴⁺, 56845-78-4; (+)₅₈₉-EDTA-d₂, 56783-74-5; (-)₅₈₉-EDTA-d₂, 56783-75-6.

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Isotropic Shifts in Two Low-Spin Cobalt(II) Complexes

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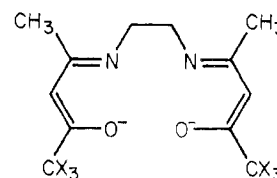
The proton magnetic resonance spectra of Co(BAE) and Co(F₃BAE) have been obtained and interpreted. These low-spin d⁷ complexes show spectra strikingly different from those of the other low-spin cobalt(II) systems for which NMR spectra have been reported. In the complexes discussed here there is a substantial contact contribution to the isotropic shifts. The pattern of contact shifts was interpreted with the help of CNINDO molecular orbital calculations. It was concluded that α -spin density is delocalized into the ligand HOMO. The pattern and magnitude of the contact shifts are surprisingly insensitive to the presence or absence of axial bases. However the line widths and therefore the electron relaxation time is quite dependent on axial ligation and on the nature of the solvent. In addition the temperature dependence of the isotropic shifts is discussed. Finally, the NMR behavior of the Co(BAE) and Co(F₃BAE) systems is contrasted to that of other low-spin d⁷ systems.

Introduction

The electronic properties of low-spin cobalt(II) complexes have received substantial attention in recent years.¹⁻¹¹ This is due in part to the fact that many of these complexes bind oxygen reversibly. In addition certain members of this class of complexes have been suggested as model systems for vitamin B_{12r}. One group of low-spin cobalt(II) systems which have received a great deal of recent attention is the cobalt(II) porphyrins.^{2,12,13} Interest in cobalt(II) porphyrins has been heightened by the discovery that cobalt-substituted hemoglobin, "coboglobin", binds oxygen in a cooperative fashion.^{14,15} Thus, there are several lines of current research to which the properties of low-spin cobalt(II) complexes are relevant.

La Mar and Walker have reported the NMR spectra of several cobalt(II) porphyrins.¹³ This work showed quite clearly that the observed isotropic shifts were due primarily to the dipolar or pseudocontact interaction. Besides this work on cobalt(II) porphyrins the NMR spectra of other low-spin cobalt(II) systems have revealed rather small contact contributions to the isotropic shifts.^{16,17} Thus, all of the previous low spin cobalt(II) systems have qualitatively exhibited the same behavior when examined by NMR spectroscopy.

Bis(acetylacetonate)ethylenediiminecobalt(II), Co(BAE), is one of the low-spin cobalt(II) complexes which has been studied in great detail. The ligand system is



where X = H for BAE and X = F for F₃BAE.

The magnetic properties and ESR spectra of the complexes are quite representative of the low-spin d⁷ electronic configuration and thus are formally similar to cobalt(II) porphyrins and vitamin B_{12r}.⁴ However, we have found that the NMR spectrum of this particular cobalt(II) complex is substantially different from the other low-spin cobalt(II) complexes which have been investigated.

In this system there is a substantial contact contribution to the observed isotropic shift. We report here a study of the NMR spectra of bis(acetylacetonate)ethylenediiminecobalt(II) and the related bis(trifluoroacetylacetonate)ethylenediiminecobalt(II). It will be shown that the isotropic shifts are largely contact in origin. In addition the reasons for the striking dissimilarity between this system and other low-spin cobalt(II) systems such as the cobalt(II) porphyrins will be discussed.

Experimental Section

Preparation of Ligands and Complexes. The ligands bis(acetylacetonate)ethylenediimine (BAE) and bis(3-trifluoroacetylacetonate)-

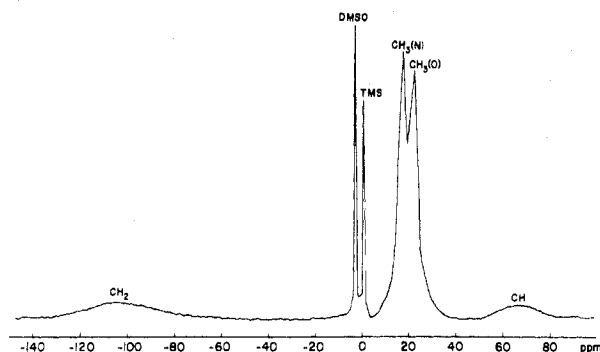


Figure 1. Proton magnetic resonance spectrum of Co(BAE) (100 MHz) in DMSO- d_6 at 30°C.

ethylenediimine (F₃BAE) were prepared by the method of Martell et al.¹⁸ The cobalt(II) complex of BAE was prepared by the method of Everett and Holm¹⁹ and the complex of F₃BAE was prepared by the method of West.²⁰ Due to the oxygen sensitivity of these complexes, air was rigorously excluded during synthesis, purification, and storage.

Preparation of NMR Samples and Measurement of Spectra. The solvents used in all cases were CDCl₃ (obtained from Thompson-Packard, Inc.) or DMSO- d_6 (Aldrich Chemical Co.). Choice of solvents was dictated by low solubility of the complexes in other common organic solvents. The NMR samples were prepared by dissolving 10–20 mg of the solid complex in 0.3–0.5 ml of the appropriate deuterated solvent. Strict precaution was taken in preparing NMR samples to prevent contact with air. The solvents were vigorously deoxygenated prior to use and the samples were kept under a blanket of argon prior to addition of solvent. The sample solution was then thoroughly flushed with argon before the NMR tube was sealed. At no time was the complex allowed exposure to air.

The NMR spectra were recorded on a Varian HA-100 spectrometer. Audio side bands were used to calibrate peak positions, with TMS serving as internal reference. The spectra of all complexes were run in the scan mode with external modulation of 25 kHz generated by a Hewlett-Packard 4204A oscillator.

For variable-temperature studies, the probe temperature was monitored with a Varian V-4341/V-6057 variable-temperature accessory with a V-6040 controller. The system was precalibrated with methanol for the low-temperature range and ethylene glycol for the high-temperature range. The estimated accuracy is $\pm 2^\circ\text{C}$. The low solubility of the complexes and the large line widths prevented resolution of peaks below 280 K.

For a given sample the spectra were recorded from low to high temperature. After the highest temperature spectrum was obtained, the probe temperature was returned to the original low-temperature setting and the spectrum rerecorded at that temperature. This confirmed that the higher temperatures caused no decomposition and that the sample tube admitted no air during the period of operation which usually lasted 3–4 hr.

The NMR spectra of the diamagnetic ligands were obtained on the same instrument with an internal TMS reference. All chemical shifts are reported in ppm.

Molecular Orbital Calculations. CNDO and INDO molecular orbital calculations were carried out on a ligand fragment using the CNINDO program obtained through the Quantum Chemistry Program Exchange. The calculations were performed on the University of Hawaii IBM 360-65 computer system.

Results

The NMR spectra of Co(BAE) and Co(F₃BAE) are shown in Figures 1 and 2, respectively. The peak positions are affected very little by changes in solvent, but there is a substantial effect on the line widths.²¹ Assignments of the NMR spectra were made primarily on the basis of relative peak intensities and in certain instances by chemical substitution. The observed isotropic shifts ($\nu_{\text{iso}} = \nu_{\text{complex}} - \nu_{\text{free ligand}}$) at 30°C are summarized in the first column of Table I.

Figures 3 and 4 show the temperature dependence of the observed isotropic shifts for Co(BAE) and Co(F₃BAE), respectively. The plots of isotropic shift vs. $1/T$ are linear as

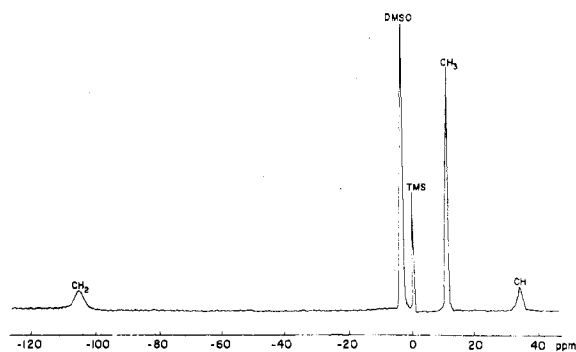


Figure 2. Proton magnetic resonance spectrum of Co(F₃BAE) (100 MHz) in DMSO- d_6 at 30°C.

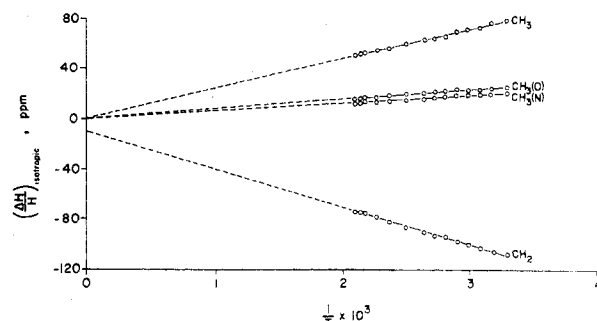


Figure 3. Plot of isotropic shifts for protons in Co(BAE) vs. $1/T$.

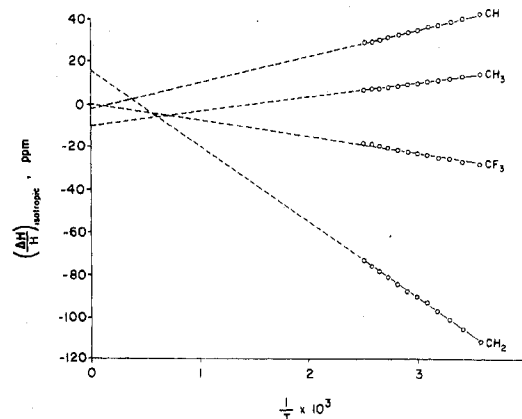


Figure 4. Plot of isotropic shifts for protons and fluorine in Co(F₃BAE) vs. $1/T$.

Table I. Dipolar and Contact Contributions to the Isotropic Shifts for Co(BAE) and Co(F₃BAE)^a

Compd	Nucleus	Contribution, ppm		
		Isotropic ^b	Dipolar	Contact
Co(BAE)	CH ₂	-108.4 (32)	-8.7	-99.7
	CH ₃ (N)	20.9 (7)	-1.6	22.5
	CH ₃ (O)	26.3 (10)	-2.1	28.4
	CH	78.7 (14)	0.2	78.5
Co(F ₃ BAE)	CH ₂	-101.6 (3.3)	-10.2	-91.4
	CH ₃	12.1 (0.6)	-2.2	14.3
	CH	38.9 (1.0)	-0.4	39.3

^a Spectra obtained in DMSO- d_6 at 30°C. ^b The numbers in parentheses are the line widths in ppm.

expected from the Curie law. However, these plots do not all extrapolate to a zero intercept, the methylene protons showing the greatest deviation from zero intercept. This behavior is not uncommon in paramagnetic systems and has been discussed in several articles.^{13,22–24}

The observed isotropic shifts arise in general from a contact contribution and a dipolar or pseudocontact contribution. The

Table II. Geometric Factors, g Values,^a and Calculated Dipolar Shifts for Co(BAE) and Co(F₃BAE)^{b,c}

	g_x	g_y	g_z	$10^{-22}(3 \cos^2 \theta - 1)/r^3, \text{cm}^{-3}$	$10^{-22}(\sin^2 \theta \cos 2\Omega)/r^3, \text{cm}^{-3}$	$(\Delta H/H)_{\text{dipolar}}, \text{ppm}$
Co(BAE)	2.435	2.225	2.012	-1.82	-2.58	-8.7
CH ₂				-1.27	2.90	0.2
CH				0.98	0.15	-2.1
CH ₃ (O)				0.91	0.32	-1.6
CH ₃ (N)						
Co(F ₃ BAE)	2.52	2.30	2.01			
CH ₂				-1.82	-2.58	-10.2
CH				-1.27	1.90	-0.4
CH ₃ (N)				-0.91	0.32	-2.2

^a The g values for Co(BAE) were taken from ref 8 and those for Co(F₃BAE) were taken from ref 27. ^b The molecular geometry was obtained from ref 26. ^c The symbols are defined in the text.

equation governing the contact interaction between the electron and nucleus is^{24,25}

$$\left(\frac{\Delta H}{H}\right)_{\text{contact}} = \frac{-\bar{g}\beta S(S+1)A_N}{(\gamma_N/2\pi)3kT} \quad (1)$$

where A_N is the electronic-nuclear hyperfine coupling constant, $\bar{g} = 1/3(g_x + g_y + g_z)$, and γ_N is the gyromagnetic ratio for the nucleus in question. The equation describing the dipolar interaction between the electron and nucleus is²⁵

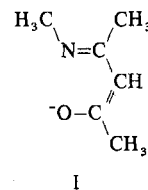
$$\left(\frac{\Delta H}{H}\right)_{\text{dipolar}} = \frac{-\beta^2 S(S+1)}{9kT} \left\{ g_z^2 - \frac{1}{2}(g_x^2 + g_y^2) \left[\frac{3 \cos^2 \theta - 1}{r^3} - \frac{3}{2}(g_y^2 - g_x^2) \frac{\sin^2 \theta \cos 2\Omega}{r^3} \right] \right\} \quad (2)$$

where θ is the angle between the z axis and the metal-proton vector, r the length of the proton-metal vector, and Ω the angle between the projection of this vector on the xy plane and the x axis. The terms $(3 \cos^2 \theta - 1)/r^3$ and $(\sin^2 \theta \cos 2\Omega)/r^3$ in eq 2 are referred to as the axial geometric factor and rhombic geometric factor, respectively. From the rather large magnitude of the observed shifts, it is very likely that the contact contribution to the isotropic shift is dominant. This will be shown to be true subsequently. It is possible in this system to separate the contact and dipolar contributions. From eq 2 it can be seen that a knowledge of the geometry for a complex and the electronic g values allows the dipolar shift to be calculated. For Co(BAE) this information is known. The g values have been reported by Hoffman⁴ and Ochiai.⁸ The geometric parameters can be calculated from the X-ray crystal structure reported by Bruckner et al.²⁶ The g values for Co(F₃BAE) have also been reported.²⁷ The geometric factors for the protons in Co(F₃BAE) can be assumed to be the same as for the corresponding protons in Co(BAE). With this information available, the dipolar contribution to the isotropic shift can be calculated. Table II summarizes the g values, geometric factors, and dipolar shifts at 30°C for Co(BAE) and Co(F₃BAE).

The observed isotropic shift for each proton is a sum of the contact and dipolar shifts. Thus, the contact shift is obtained by subtracting the dipolar contribution from the observed shift. The contact shifts for each proton in both complexes are summarized in Table I. The electronic-nuclear hyperfine coupling constant, A_N , can be calculated for each proton from the contact shift according to eq 1. Because of the nonzero intercepts shown in Figures 3 and 4, the coupling constants were determined from the slope of plots of contact shift vs. $1/T$. To do this, over the range of temperatures shown in Figures 3 and 4, each observed shift was adjusted by sub-

tracting the dipolar contribution for that temperature.

Molecular Orbital Calculations. It has been demonstrated very clearly that the results of appropriate molecular orbital calculations are an extremely useful aid in the interpretation of NMR contact shifts.²⁸⁻³¹ At the present time the CNDO/INDO method of calculation^{32,33} appears to be the most reliable for this purpose.³⁰ For this reason, CNDO/INDO calculations have been performed on the "ligand fragment" (I) which represents half of the BAE ligand system.



The geometry for this fragment was chosen to be identical with that of the BAE system in Co(BAE). Three types of open shell, INDO, calculation were performed, each designed to learn the effect of placing unpaired spin density in a particular orbital(s). Removal of one electron from I, leaves unpaired spin in the highest occupied π orbital (HOMO) while addition of one electron leaves unpaired spin in the lowest unoccupied π molecular orbital (LUMO). It was also of interest to determine the effect of placing unpaired spin density in the σ system of the ligand. The most suitable method for doing this proved to be the use of a hydrogen atom as a "spin probe".^{30,34} This procedure has been used to successfully account for the spin density distribution in a Ni(II) complex of pyridine¹⁹ and a Ni(II) complex of 2,2-iminobis(acetamidoxime).³⁴

Briefly, in the calculation a hydrogen atom is located at a position such that the hydrogen 1s orbital overlaps with the ligand σ orbitals. The resulting unpaired electron density distribution in the σ system can be used to predict the patterns of contact shifts. From the results of the INDO calculations, the theoretical electronic-nuclear hyperfine coupling constants, A_N , were calculated. This procedure was included in the INDO program which was used. Thus, from the three types of INDO calculations, the theoretical coupling constants for unpaired spin density in the LUMO, HOMO, and σ system were calculated for ligand system I. These results are summarized in Table III.

Discussion

Analysis of Isotropic Shifts. The information in Table I clearly indicates that the observed shifts are predominantly contact in origin. Determination of the contact contribution to the isotropic shift requires calculation of the dipolar contribution as outlined in the Results. This calculation depends upon the choice of geometry and electronic g values. The g values which were used for calculation of the Co(BAE) dipolar shifts were obtained on a species with an axially coordinated pyridine.⁸ In DMSO the complex has an axially

Table III. Calculated and Experimental Coupling Constants^a

Calcd	$A_{CH_3(O)}$	A_{CH}	$A_{CH_3(N)}$	A_{CH_2}	$A_{CH_3(O)}/A_{CH_2}$	A_{CH}/A_{CH_2}	$A_{CH_3(N)}/A_{CH_2}$
σ^b	0.7	2.3	-0.8	4.9	0.14	0.47	-0.16
LUMO ^b	11.7	4.5	18.2	9.0	1.30	0.50	2.04
HOMO ^b	-10.8	-11.7	-10.0	18.3	-0.59	-0.64	-0.55
			Exptl				
Co(BAE)	-0.4	-0.9	-0.3	1.1	-0.38	-0.89	-0.31
Co(F ₃ BAE)		-0.5	-0.3	1.3		-0.38	-0.22

^a Coupling constants in gauss. ^b One unpaired electron in σ system, LUMO or HOMO, respectively.

coordinated solvent and one would expect at least a similar pattern of g values. It is true that the g values in solution may be somewhat different from those used in calculating the dipolar shifts; however, repeating this calculation for a reasonable range of g values causes only modest changes in the dipolar shifts.⁴⁵ Thus the conclusion that the observed shifts are largely contact in origin can still be made.

The predominant contact contribution to the isotropic shift is quite different behavior from that previously observed in other low-spin cobalt(II) complexes.^{13,16,17} Reasons for this difference will be discussed below. The pattern of measured hyperfine coupling constants, when compared to the theoretical coupling constants, gives a reasonably clear picture of the spin delocalization mechanism in these complexes. Table III gives values for the theoretical coupling constants, with various possibilities for the ligand orbital containing unpaired spin. While the absolute magnitudes for the theoretical and experimental coupling constants cannot be compared directly, the theoretical and experimental ratios of coupling constants for different protons can be compared meaningfully. The ratios of coupling constants for the two methyl groups and the vinyl proton to the methylene coupling constant are included in the last three columns of Table III. The values of coupling constant ratios in the row labeled HOMO are the values expected when α -spin density is delocalized into the highest occupied MO. Likewise the ratios listed in the other two rows are the coupling constant ratios predicted for a spin delocalization into the LUMO and σ system, respectively. Inspection of this table reveals that all of the experimental coupling constant ratios are negative. The INDO calculations show that placing α -spin density in the HOMO qualitatively reproduces the pattern of observed shifts. That is, α -spin density in the HOMO results in an upfield shift of the two methyl groups, a larger upfield shift for the vinyl proton, and a downfield shift for the methylene protons. The calculated and experimental coupling constant ratios are not in excellent quantitative agreement. This may be due to small contributions from placing unpaired spin density into other ligand orbitals or to differences in solution geometry used in the CNINDO calculations (see below). Nevertheless, the primary conclusion that α spin is delocalized into the HOMO is well substantiated by the INDO results.

The conclusions that the isotropic shifts are dominated by a large contact term and that α spin is delocalized into the HOMO are surprising and interesting in view of the other low-spin cobalt(II) systems studied by NMR.^{13,16} In the other complexes which have been investigated, the unpaired electron is clearly in the $3d_{z^2}$ orbital which is orthogonal to the ligand π system. Thus the small contact contributions observed are quite reasonable. The question may be raised as to whether the $(d_{z^2})^1$ configuration is the ground state for the Co(BAE) system. McGarvey has discussed the theory of the spin-Hamiltonian parameters for low-spin cobalt(II) systems.¹¹ He has concluded that for lower symmetry systems such as Co(BAE) it is difficult to deduce the correct ground state especially without single-crystal ESR results. There are several possibilities for the electronic ground state in this system. These include (a) the common 2A_1 ground state in which the

unpaired electron is in the $3d_{z^2}$ orbital, (b) a 2B_2 ground state in which the unpaired electron is in the $3d_{yz}$ orbital, and (c) a ground state in which the unpaired electron is in a mixed configuration of the form $(d_{z^2} + a d_{x^2-y^2})$. It is also possible that coupling can occur between d_{z^2} and low-lying quartet states.¹¹

Most low-spin cobalt(II) systems fall into category (a) or (a) plus (c) in that a $(3d_{z^2})^1$ configuration is the ground state. A few of the complexes which have been studied show the 2B_2 ground state with a $(3d_{yz})^1$ configuration. Among these systems is Co(salen), a complex very similar to Co(BAE). Von Zelewsky and Fierz have concluded that the d_{z^2} and d_{yz} orbitals in Co(salen) differ very slightly in energy with the d_{yz} orbital containing the unpaired electron.⁹ This configuration holds in a single crystal where the cobalt is clearly four-coordinate. However, in solution it is possible for solvation to occur at an axial coordination site. It is generally agreed to be true that the five- or six-coordinate low-spin cobalt(II) species have the $(3d_{z^2})^1$ ground state. McGarvey's analysis shows that when the axial position(s) is (are) occupied, the $3d_{z^2}$ orbital is raised in energy resulting in a $^2A_1[(3d_{z^2})^1]$ ground state even for those complexes which could have a 2B_2 ground state as the four-coordinate species. For example, Wayland found that Co(salen) adducts have a $(3d_{z^2})^1$ ground-state configuration.¹⁰ This makes it quite certain that, in DMSO solution, the ground state is primarily $(3d_{z^2})^1$. It is quite interesting that the isotropic shifts in $CDCl_3$ are virtually identical with those in DMSO.²¹ Thus, even though chloroform is not at all likely to solvate the complex in the same manner as DMSO, the ground-state electronic configuration must be the same in the two solvents. Addition of pyridine causes some changes in the shifts, but the pattern remains the same with the contact contribution still clearly dominant. Therefore it does not appear that the differences in NMR behavior between the Co(BAE) system and the others previously studied are due to a totally different electronic ground state; i.e., the 2B_2 state is not the ground state in solution in this system.

The conclusion that unpaired spin is delocalized into the HOMO is somewhat uncomfortable because the HOMO is an orbital with π symmetry. As mentioned above, it appears, based on discussions in the literature,^{10,11} that the unpaired electron in Co(BAE) (in solution) is in $3d_{z^2}$, an orbital with σ symmetry. These two orbitals should therefore be orthogonal. This is true only if the complex maintains the planarity in solution which it shows in the solid state. The observation that α -spin density is, indeed, delocalized into the HOMO may be evidence for nonplanarity of the Co(BAE) complex in solution. Calligaris et al. have reviewed the structural information available on some metal BAE and related ligand systems.³⁵ It is apparent that the cobalt chelates have a tendency to distort from planarity to either a "stepped" or "umbrella" configuration. Either type of distortion would remove the orthogonality between the metal d_{z^2} orbital and the ligand π system and thus allow direct transfer of unpaired spin from the metal to the ligand π system.

The patterns of contact shifts and the spin delocalization mechanism in Co(BAE) and Co(F₃BAE) are somewhat similar to the situation in Ni(acac)₂(py)₂ and in nickel β -keto

amines.³⁶ Several workers have studied the Ni(acac)₂(py)₂^{31,37-39} system. In this system the vinyl proton is shifted upfield and the methyl groups are shifted slightly downfield. The primary spin delocalization mechanism has been shown to be delocalization of α spin into the HOMO. This is the case despite the expected orthogonality between the nickel orbitals containing unpaired spin and the ligand π system. In this case, as in the Co(BAE) system, it appears that a geometrical distortion in the complex removes the orthogonality between the ligand π orbitals and metal σ orbitals.^{31,40} The pattern of contact shifts in a variety of β -keto amine complexes has been reported by Everett and Holm.³⁶ They observed upfield contact shifts for the methyl protons and larger upfield shifts for the vinyl protons. This is very similar to those reported here for the BAE ligand system. Everett and Holm concluded that α spin was delocalized into the HOMO just as found here for Co(BAE).

In addition to the argument based on geometrical distortions in solution, there is another possibility which could be used to explain spin delocalization into a ligand π orbital. There are a number of quartet excited states which can mix with the ground state through the spin-orbit interaction.¹¹ This spin-orbit mixing becomes relatively more important when base molecules are complexed along the z axis. Such mixing would place unpaired electron density in metal orbitals which could overlap directly with ligand π orbitals and thus show spin delocalization into the π system.

Since the molecular orbital containing the unpaired electron undoubtedly has a large contribution from $3d_{z^2}$, it might be expected that the contact shifts should be dependent on the presence or absence of axial ligands. However, the observed isotropic shifts for Co(BAE) are virtually identical in CDCl₃ and DMSO-*d*₆.²¹ Furthermore, when a fivefold excess of pyridine is added to a CDCl₃ solution of Co(BAE), there are modest changes in the peak positions but the overall pattern of shifts remains the same. Thus, even though the presence of axial bases affects some properties of the complexes (i.e., the tendency to undergo reversible oxygenation), this does not appreciably affect the spin delocalization pattern.

The presence of axial bases does, however, greatly affect the line widths which are observed in this system. As mentioned above, the spectrum of Co(BAE) has been obtained in CDCl₃ and in DMSO-*d*₆. The former solvent is expected to be relatively inert while DMSO undoubtedly coordinates at an axial position. The observed line widths in DMSO are considerably greater than in chloroform. For example, at 30°C the methylene line width for Co(BAE) is approximately 23 ppm in CDCl₃ and 32 ppm in DMSO-*d*₆. Furthermore, addition of pyridine to a chloroform solution of Co(BAE) causes broadening of the NMR peaks. La Mar and Walker have discussed the line widths in cobalt(II) porphyrins.¹³ In that system, the energy difference between the e_g orbitals (d_{xz} and d_{yz}) and d_{z^2} is related to the electron relaxation time and, therefore, to the NMR line widths. If the energy difference between these orbitals is small, electron relaxation is efficient and the NMR lines are relatively narrow. The wider the energy separation becomes, the less efficient is the electron relaxation process and broader lines result.⁴¹ If the same electron relaxation processes operate in Co(BAE), the addition of an axial ligand should cause broadening of the NMR lines.⁴⁴ An axial ligand will cause the energy separation between d_{xz} or d_{yz} and d_{z^2} to increase. This will diminish the effectiveness of the electron spin relaxation process and thus increase the NMR line width. The analysis of La Mar and Walker¹³ for cobalt(II) porphyrin is consistent with the line broadening which we observe in the presence of DMSO or pyridine.

It is also quite interesting that the line widths in cobalt(II) porphyrins are very much sharper than those in Co(BAE).

While the differences in relaxation cannot be solely responsible for such large differences in the NMR lines, this must be a contributing factor. The very sharp lines in cobalt(II) porphyrins suggest efficient electron relaxation which, in turn, would be due to a small separation in energy between the e_g (d_{xz} , d_{yz}) orbitals and d_{z^2} . Ochiai has indeed observed a much smaller energy gap between these orbitals in cobalt(II) porphyrin than in any other low-spin cobalt(II) system which he has studied.⁸

Temperature Dependence of Isotropic Shifts. The plots of isotropic shift vs. $1/T$ shown in Figures 3 and 4 exhibit nonzero intercepts for some of the nuclei, especially the methylene protons. This behavior, which is not expected from either eq 1 or 2, has nevertheless been observed in a wide variety of systems. Several suggestions have been offered for causes of nonzero intercepts in such plots. Perry and Drago, for example, have discussed the effect of subtle chemical changes with temperature as a factor contributing to nonzero intercepts.²³ The plots shown in Figures 3 and 4 are for DMSO-*d*₆ as solvent. The temperature dependences of the isotropic shifts for Co(BAE) have also been determined in CDCl₃. In this solvent the intercepts are somewhat larger than in DMSO-*d*₆. It has been shown previously that CHCl₃, because of its hydrogen-bonding properties, contributes to the nonzero intercept. The explanation proposed for this is that the chloroform interacts with the ligand in a temperature-dependent manner. It is surprising that the relatively strong interaction between the complex and DMSO through axial solvation does not result in larger nonzero intercepts. The methylene protons show the largest nonzero intercepts because of the fact that they receive the most spin density and also because conformational changes in the ligand system most drastically affect the orientation of these protons.³⁵ The nature of the conformational changes in the ligand system is discussed below. Obtaining a hyperfine coupling constant, \mathcal{A}_N , according to eq 1 is complicated by the presence of nonzero intercepts. Measurement of \mathcal{A}_N from the contact shift at a single temperature will give a value different from \mathcal{A}_N calculated from the slope of a plot of contact shift vs. $1/T$. The coupling constants reported in Table III were obtained from the slope of such plots. Only for the methylene protons do the two methods for calculating \mathcal{A}_N result in significantly different values.

The factors which have been discussed previously with respect to the electronic state could also cause nonzero intercepts in this system. Mixing of d_{z^2} and $d_{x^2-y^2}$ occurs in the ground state of these complexes.¹¹ If the mixing of these orbitals is temperature dependent, non-Curie temperature dependence would result. In a similar manner temperature-dependent spin-orbit mixing of quartet excited states would give non-Curie behavior.

Comparison with Other Low Spin Cobalt(II) Systems. The low-spin cobalt(II) systems for which NMR results have been reported previously show behavior quite different from that exhibited by Co(BAE). The results of La Mar and Walker shown quite clearly that the contact contribution to the isotropic shifts in cobalt(II) porphyrins is very small.¹³ It was estimated that the largest contact shift in the cobalt(II) porphyrin studied amounts to approximately 4 ppm. The contact shifts in bis(dithioacetylacetonato)cobalt(II) are quite small, on the order of a few ppm.¹⁶ A σ -spin delocalization mechanism was suggested in this species. However this is incompatible with the results found in systems discussed here and in other related systems. The B_{12r} form of vitamin B₁₂ is a low-spin cobalt(II) species for which qualitative NMR results have been reported. Brodie and Poe have obtained the NMR spectra of four cobalt(II) corrinoids.¹⁷ For all of the derivatives on which they obtained spectra, no large contact

shifts were observable. It is possible that there are some significantly contact-shifted peaks in this system but that they are broadened to such an extent as to be undetectable with the experimental conditions which were employed. We would expect the vinyl proton at carbon C-10 of the corrin ring to be contact-shifted significantly upfield. In addition, the methyl groups attached to C-5 and C-15 of the corrin ring might be expected to be contact-shifted measurably.

The striking difference in NMR behavior between cobalt(II) porphyrins and Co(BAE) deserves comment. In cobalt(II) porphyrin, the ligand system is rigid and, in the absence of additional strong ligands, the cobalt atom lies in the plane of the pyrrole nitrogens. In this system, therefore, the d_{2^2} orbital containing the unpaired electron is strictly orthogonal to the porphyrin π system and no direct transfer of spin density into the π system will occur. Assuming that spin-orbit mixing of quartet states with the 2A_1 ground state is not important, the only mechanisms for transfer of spin into the porphyrin are direct delocalization into the porphyrin σ system or an indirect transfer of β spin into the π system after spin polarization on the metal. Neither of these schemes should be expected to result in significant amounts of spin density at ligand protons. Thus, the observed small contact shifts are expected. In Co(BAE) and Co(F₃BAE) the unpaired electron is apparently also largely in the $3d_{2^2}$ metal orbital. However, the ligand system is not rigid as is the porphyrin ligand. The nature of distortion from planarity in this ligand system has been thoroughly discussed by Calligaris et al.³⁵ There are two types of distortion from planarity, a "stepped" conformation and an "umbrella" conformation. Either of these geometries allows nonzero overlap between the cobalt $3d_{2^2}$ orbital and the BAE π orbitals. Therefore, direct delocalization of α spin into the HOMO is possible and sizable contact shifts are consistent with the known properties of this complex. It is also possible, as discussed above, that differences in the electronic ground state could account for, or contribute to, the different NMR behavior. If this were the case, it would be necessary to assume, for instance, that spin-orbit mixing of quartet state is important in the Co(BAE) system but not in the others studied by NMR.

The assumption of ligand planarity in the calculation of dipolar shifts and the geometry chosen for molecular orbital calculations deserve comment in light of the fact that in solution the BAE ligand appears to deviate somewhat from planarity. The geometric factors reported in Table II are not very sensitive to small deviations from planarity with the possible exception of the methylene protons. However, the dipolar contribution to the observed isotropic shift is relatively minor for all protons and the errors introduced from this contribution should be rather small. The molecular orbital calculations assumed a planar ligand fragment I. Either the "stepped" or "umbrella" deformation maintains near planarity for the O-C-C-C-N portion of the molecule while the methylene bridge buckles. We expect, therefore, that the molecular orbitals and calculated hyperfine coupling constants are very good for the methyl and vinyl protons. Some error may be introduced in the calculated methylene coupling constant. We conclude that these factors contribute to the lack of quantitative agreement between theoretical and measured coupling constant ratios (Table III). However, the major conclusions which can be drawn from the data are not affected.

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- (45) The g values chosen for calculation of the dipolar shifts were thought to apply most reasonably to the complexes in solution. However, due to uncertainty about these parameters in solution, the dipolar shift was recalculated for a suitable range of g values.^{8,11} For any choice of g values corresponding to an axially coordinated species, the dipolar shifts are minor compared to the total isotropic shift.