Isotropic Proton Shifts for Co(salen)

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Abstract: The complete proton NMR spectrum of *N,N'*-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), is reported and discussed. Evidence is presented that the pattern of isotropic shifts obtained arises from a $(3d_{z^2})^1$ ground state electronic configuration. Comparison is made with previous NMR work from which a $(3d_{yz})^1$ ground state was postulated. Arguments are given against the former assignment and in favor of the $(3d_{z^2})^1$ assignment. In addition the temperature dependences of the isotropic shifts for each proton are presented. These suggest a possible spin equilibrium for Co(salen) at room temperature in solution.

The electronic structure of low spin cobalt(II) complexes has been studied widely by a number of techniques.[1-3] Of all the low spin cobalt(II) complexes, Co(salen) and its derivatives have been studied most extensively. However, there is still considerable question about the ground state electronic configuration of this complex. It is quite clear that in coordinating solvents which can occupy axial positions forming either 5- or 6-coordinate species, this complex possesses a ground state having the unpaired electron in the metal d_{z^2} orbital.[1f,l,m] However, there are differences of opinion about the ground state configuration for Co(salen) when it is four-coordinate, i.e., in "noncoordinating" solvents such as chloroform or in the diamagnetic host matrix Ni(salen). In this case configurations with the unpaired electron in $3d_{z^2}$[1l,m] and in $3d_{yz}$[1d,n,2] have been suggested. Recently Migita et al. have reported a partial NMR study of Co(salen) and certain ligand substituted derivatives in $CDCl_3$ solvent.[2] Although these workers were able to observe isotropic shifts for only three of the six types of protons in the complex,[3] they interpreted the pattern of observed shifts as arising from a $(3d_{yz})^1$ configuration on the cobalt. It is the purpose of this article to discuss the complete NMR spectrum of Co(salen) and to present evidence that the isotropic shifts reported by Migita et al. do not necessarily indicate a $(3d_{yz})^1$ ground state electronic configuration in $CDCl_3$ but that a $(3d_{z^2})^1$ ground state for Co(salen) *in solution* is more reasonable.

The temperature dependences for the isotropic shifts of those protons observed previously by Migita et al. showed apparent Curie law behavior.[2] However, the temperature dependences for the isotropic shifts of the protons which they did not observe show substantial non-Curie law behavior. It is possible, as discussed below, that there is a spin equilibrium at room temperature in solution for Co(salen).

Experimental Section

Preparations of Ligands and Complexes. The ligands bis(salicylaldehyde)ethylenediimine (salen), bis(5-deuteriosalicylaldehyde)ethylenediimine (5-d-salen), and bis(5,7-dideuteriosalicylaldehyde)ethylenediimine (5,7-di-d-salen) were prepared from the aldehyde and ethylenediamine by a modification of the method of Martell et al.[4] The complexes were prepared by a modification of a procedure reported by Bailes et al.[5] The details of the syntheses of the deuterated salicylaldehyde derivatives will be published elsewhere.[6]

Preparation of NMR Samples and Measurement of Spectra. The solvent used for spectral measurements was Me_2SO-d_6. The NMR samples were prepared by dissolving 10–20 mg of the solid complex in 0.3–0.5 ml of 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 before addition of solvent. The sample solution was then thoroughly flushed with argon before the NMR tube was sealed.

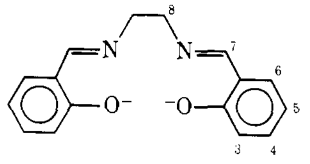
The NMR spectra were recorded on a Varian HA-100 spectrometer. Audio sidebands were used to calibrate peak positions, with Me_4Si serving as internal reference. The spectra of all complexes were run in the scan mode with external modulation of 25 kHz generated by a Hewlett-Packard 4204A oscillator.

For variable temperature work, 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 ethylene glycol. Estimated accuracy is ±2 °C. 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.

The NMR spectra of the diamagnetic ligands were obtained on the same instrument with an internal Me_4Si reference. All chemical shifts are reported in parts per million.

Results

Figure 1 shows the 100-MHz NMR spectra of Co(salen), Co(5-d-salen), and Co(5,7-di-d-salen) in Me_2SO-d_6 at 30 °C. I indicates the numbering scheme used for the ligand positions.



I

A comparison of these spectra with those reported by Migita et al.[2] indicates the presence of new peaks due to protons at positions 3, 7, and 8 not observed in their work. These resonances for Co(salen) occur at 8, 21, and 67 ppm downfield from Me_4Si, respectively. These peaks are obviously significantly broader than the other peaks in the spectrum which accounts for the failure of the authors of ref 2 to observe them. The observed isotropic shifts for Co(salen) are summarized in the first column of Table I. The assignments for all the peaks can be made unambiguously from the deuterium substitutions shown in Figure 1 and from methyl group substitutions reported in ref 2.

The temperature dependences of the isotropic shifts for Co(salen) are shown in Figure 2. Inspection of these data indicates that the isotropic shifts for protons at positions 3, 4, and 6 show apparent Curie law behavior. However the plots for the protons at positions 5 and 8 show substantial nonzero intercepts at $T^{-1} = 0$. The temperature dependence for the proton at position 7 shows a slope opposite in sign to that expected from the Curie law.

Discussion

The observed isotropic shifts arise in general from a contact contribution and a dipolar or pseudocontact contribution. The contact contribution to the isotropic shifts can be analyzed

Table I. Isotropic Shift Data for Co(salen)

Ligand position	Obsd isotropic shift[a]	Dipolar contribution[b]	Contact contribution	Contact contribution in $CDCl_3$ solvent[c]
3	−0.5	−4.3	+3.8	*d*
4	−8.6	−0.8	−7.8	−6.8
5	+22.4	−0.2	+22.6	+34.6
6	−4.0	−0.4	−3.6	−9.7
7	−12.7	−3.7	−9.0	*d*
8	−63.8	−9.6	−54.2	*d*

[a] Units are in ppm. The observed isotropic shift is referenced to the resonance position for that proton in the diamagnetic ligand. [b] The structural parameters necessary to calculate the geometric factors are available in ref 10. The *g* values for Co(salen) in Me_2SO have been reported by Ochiai.[9] [c] These contact shifts have been reported by Migita et al.[2] [d] Not observed in ref 2.

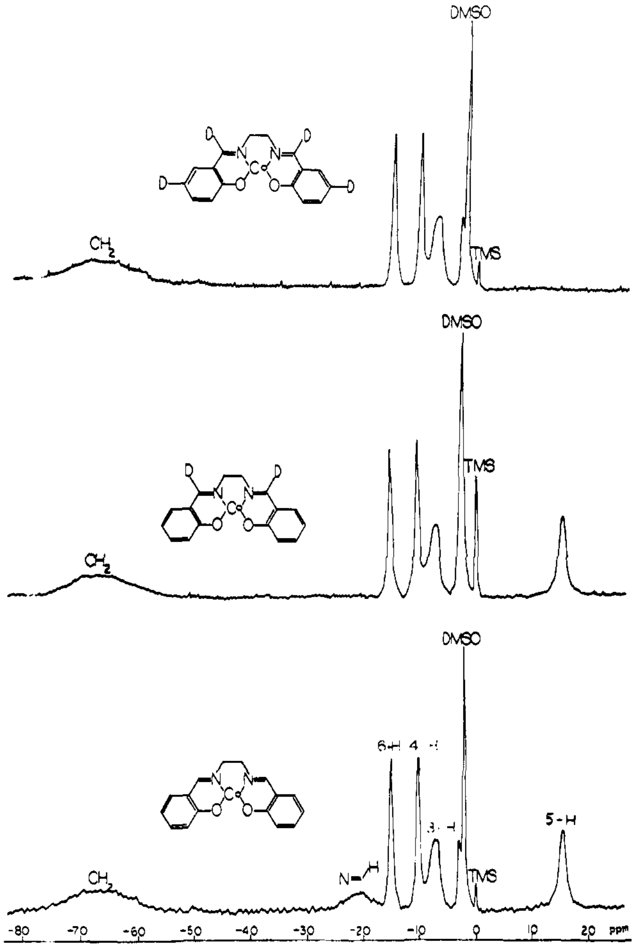


Figure 1. Proton NMR spectra for Co(salen) (bottom), Co(5-d-salen) (middle), and Co(5,7-di-d-salen) (top). All spectra were run in Me_2SO-d_6 and taken at 30 °C.

according to the equation[7,8]

$$\left(\frac{\Delta H}{H}\right)_{\text{contact}} = \frac{-\bar{g}\beta S(S+1)A_{\text{N}}}{(\gamma_{\text{N}}/2\pi)3kT} \qquad (1)$$

where A_N is the electronic-nuclear hyperfine coupling constant, $\bar{g} = \frac{1}{3}(g_x + g_y + g_z)$, and γ_N is the gyromagnetic ratio for the nucleus in question. The equation governing the dipolar contribution to the isotropic shift is[8]

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

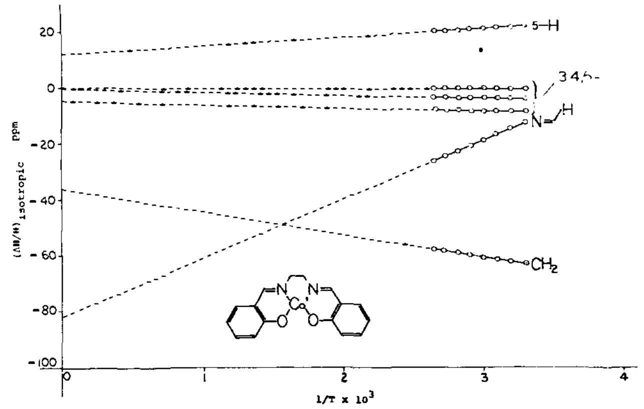


Figure 2. Plots of isotropic shifts vs. T^{-1} for all the protons in Co(salen).

where θ is the angle between the z axis and the metal proton 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 $(\sin^2\theta\cos 2\Omega)/r^3$ are referred to as the axial and rhombic geometric factors, respectively. In order to calculate the dipolar contribution to the observed isotropic shifts the *g* values and the geometry of the system must be known. For Co(salen) this information is available. The *g* values in Me_2SO have been reported by Ochiai to be $g_x = 2.50$, $g_y = 2.30$, and $g_z = 2.013$.[9] The geometric data for Co(salen) can be obtained from the x-ray crystal structure reported by Schaefer and Marsh.[10] The second column of Table I gives the calculated dipolar contribution according to eq 2.[11] The contact contributions to the observed isotropic shifts are given in the third column of Table I. By comparing the contact and dipolar contributions it is apparent that the observed isotropic shift is dominated by the contact contribution.

It is of interest to compare the data reported here to those given in ref 2. First of all it is important to emphasize that while the present data were obtained in Me_2SO-d_6 solvent, those reported by Migita et al. were obtained in the "noncoordinating" solvent $CDCl_3$. The third and fourth columns of Table I compare the contact shifts in Me_2SO-d_6 (this work) and in $CDCl_3$ (ref 2). Although only three peaks have been observed in $CDCl_3$, these results are, nevertheless, surprisingly similar. It is interesting and worthwhile to note that we have recently observed that the patterns of contact shifts in *N,N′*-ethylenebis(acetylacetonato)cobalt(III), Co(BAE), and in Co(F_3-BAE) are basically the same in $CDCl_3$ and Me_2SO-d_6.[12] In Me_2SO, Co(salen) would be expected to be axially coordinated and the *g* values which Ochiai has reported for Co(salen) in Me_2SO are consistent with a 5- or 6-coordinate species.[9]

The question as to the correct formulation of the electronic ground state configuration is rather interesting. Migita et al. have interpreted their results as indicating a $(3d_{yz})^1$ ground state configuration.[2] This conclusion was apparently based primarily on the fact that they concluded that ligand electron spin density was in an orbital of π symmetry. Because of the similarities in the pattern of contact shifts for protons at positions 4, 5, and 6 shown in the third and fourth columns of Table I, the same arguments which were used to argue for a $(3d_{yz})^1$ ground state in $CDCl_3$ could be given to suggest a $(3d_{yz})^1$ ground state in Me_2SO-d_6. However, a substantial amount of ESR work[1a-g] and theoretical considerations[1h,o] indicate that axially coordinated low spin cobalt(II) complexes always have a $(3d_{z^2})^1$ ground state electronic configuration. Since Co(salen) is, in fact, axially coordinated in Me_2SO, it is clear that the electronic ground state is most closely represented by the $(3d_{z^2})^1$ formulation and yet the same pattern of isotropic shifts is obtained as in $CDCl_3$. We would conclude, therefore, that the $(3d_{z^2})^1$ ground state is in fact correct for Co(salen) in both $CDCl_3$ and Me_2SO-d_6 solution.

It is true, as previously concluded,[2] that the delocalized spin in the ligand system of Co(salen) is in a π orbital, an orbital which is orthogonal to $3d_{z^2}$ (if the ligand system is planar). However, the mere presence of spin in a ligand π orbital is not sufficient evidence to conclude that $(3d_{z^2})^1$ cannot be the metal configuration. In the Co(BAE) system, which definitely has a $(3d_{z^2})^1$ ground state, the ligand spin density is also found largely in a π orbital.[12] The most likely cause of delocalization of spin from $3d_{z^2}$ into a ligand π orbital is, in our opinion, nonplanarity of the complex in solution. The types of geometrical distortions found in these complexes in solution have been discussed by Calligaris et al.[13] Either the "stepped" or "umbrella" conformations discussed in that article would allow direct overlap between the ligand π system and the $3d_{z^2}$ orbital. It has been argued that the small isotropic shifts, with negligible contact contribution, observed for cobalt(II) porphyrins are characteristic of the $(3d_{z^2})^1$ ground state.[14] However, the porphyrin ligand is rigidly planar ensuring strict orthogonality between $3d_{z^2}$ and the ligand π system which is not the case for Co(salen).

The temperature dependences of the isotropic shifts for Co(salen) as reported previously showed nearly Curie law behavior with relatively small nonzero intercepts.[2] However, when the temperature dependences for *all* the peaks in the Co(salen) spectrum are obtained, it becomes clear that there is drastic non-Curie law behavior (see Figure 2). The plots of isotropic shift vs. T^{-1} show substantial nonzero intercepts for the protons at positions 5 and 8. The very strange temperature dependence for the proton at position 7 (the methine proton), which shows a slope opposite in sign to that expected for the Curie law, is reminiscent of temperature dependent behavior found in certain systems exhibiting a spin equilibrium.[15] While Co(salen) in the solid state clearly does not show evidence of spin equilibrium, we are currently investigating the solution magnetic behavior of a number of Co(salen) derivatives to learn if this is a possible cause of the abnormal temperature dependence of the isotropic shifts. If there is a spin equilibrium in the system, the higher energy state is undoubtedly a ^4E state which is known to occur at fairly low energy in these complexes.[1o] It is also possible that abnormal temperature dependence could arise from a temperature dependent spin-orbit coupling to this state.

Co(salen) in Me_2SO definitely has a $(3d_{z^2})^1$ ground state.[9] The striking similarity in the observed pattern of isotropic shifts in Me_2SO-d_6 and $CDCl_3$ suggests strongly to us that the $(3d_{z^2})^1$ configuration is also the correct ground state for Co(salen) in $CDCl_3$ *at room temperature.* It is difficult to explain in detail why Co(salen) should have a $(3d_{z^2})^1$ ground state as it appears to have. The work of von Zelewsky and Fierz indicates that rigorously planar, four-coordinate Co(salen) has a $(3d_{yz})^1$ ground state at low temperature.[1d] However, that result was obtained for Co(salen) doped into a diamagnetic single crystal, an environment very much different from the solution environment. It is probably safe to call $CDCl_3$ a noncoordinating solvent, but it certainly is not an inert or noninteracting solvent. In fact, chloroform adducts of Co(salen) are quite stable. The strong interaction between $CDCl_3$ and Co(salen) plus the flexibility which the complex can have in solution apparently tend to stabilize the $(3d_{z^2})^1$ configuration to the point where it becomes the ground state.

Brief mention should be made of the spin delocalization mechanism in the Co(salen) system. We have attempted to calculate the pattern of contact shifts using a CNINDO calculation as has been reported previously for Co(BAE).[12] However, because of a number of accidental nearly degenerate ligand π orbitals the open shell calculations did not converge with the unpaired electron in the orbital(s) of interest. Therefore, we cannot quantitatively match the observed contact shift pattern. However, there is little doubt that the unpaired electron density is delocalized into the ligand HOMO as in the Co(BAE) system. The similar behavior of the protons in the ethylene bridge in both the Co(salen) and Co(BAE) systems supports the proposition that the same delocalization mechanism is operating in each.

NMR investigation of low spin cobalt(II) complexes appears to offer an important complimentary method to ESR for studying the electronic properties of these systems. However, there have been very few NMR studies of these complexes to date, although each has revealed interesting information.[2,12,14,16,17]

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