

and co-workers did not observe the bands detected in the present studies, however, most of which are bands due to the NH_3 entity in the complex. Their studies were conducted either in glassy NH_3 matrices, or in highly concentrated Ar/NH_3 samples, at 3–20% NH_3 . In their experiments, the regions near the NH_3 fundamentals probably blacked out, making detection of bands in the 3100–3400- and 1100- cm^{-1} regions very difficult. Instead, these workers monitored the intensity and splitting of the nitrate or chlorate anion bands as a measure of the interaction. While their experiments and the present experiments were quite different, overall there seems to be good qualitative agreement with the results of Devlin on the nature of the interaction.

Conclusions

The spectra of the reaction products of NH_3 and alkali halide salts have been recorded in dilute argon matrices. These spectra and the available isotopic data point to a 1:1 complex in which the species maintains a C_{3v} geometry, and in which the metal cation is bound to the lone pair on the nitrogen. Using the transition metal ammine complexes as a model, all of the observed product bands can be assigned to anticipated normal vibrations, with the band locations appropriate for a weaker

interaction between NH_3 and the alkali metal cations than between NH_3 and transition metal cations.

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Isotropic Shifts in a Series of Cobalt Bis(salicylaldehyde)ethylenediimine Derivatives

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Abstract: The isotropic shifts in Me_2SO for a number of ligand substituted Co(salen) complexes have been determined. The isotropic shifts in the series as a whole exhibit two interesting and unusual aspects. Substitutions at the periphery of the ligand cause dramatic changes (as large as 400 ppm) in the resonance positions of certain protons in the ligand. In addition non-Curie-law temperature-dependent behavior is observed for some of the complexes. Both the drastic changes in resonance positions throughout the series and the unusual temperature dependence can be explained with a simple model which allows for two electronic states to contribute significantly to the observed isotropic shifts. It appears as if there are at least one doublet and one quartet state contributing to the isotropic shifts in this series. In view of the fact that both a doublet and quartet state contribute to the observed shifts it is unlikely that a detailed analysis of the spin delocalization mechanism(s) can be made.

The properties of low-spin cobalt(II) complexes have received considerable attention in the past several years. This is due to a variety of factors including the ability of certain of these systems to bind oxygen¹ as well as the fact that vitamin B_{12} is a low-spin cobalt(II) system.² Of particular interest has been the electronic structures of these complexes. A detailed understanding of the electronic structures of these low-spin d^7 systems should lead to better insight into the ability of some of the complexes to undergo reversible oxygen binding.

An impressive arsenal of experimental and theoretical techniques has been employed to study the electronic properties of low-spin cobalt(II) complexes. Experimental methods which have been used include magnetic measurements,³ ESR spectroscopy,⁴ electronic absorption spectroscopy,^{4a,5,8c} photoelectron spectroscopy,⁶ and NMR spectroscopy.⁷ A number of theoretical calculations,⁸ notably the recent article by Hitchman,^{8c} have addressed the nature of the electronic structures in these low-spin cobalt(II) systems. It is clear that in five-coordinate adducts of low-spin cobalt(II), a ground state with the unpaired electron in d_{z^2} (2A_1 in C_{2v} symmetry of $^1A_{1g}$

in D_{4h} symmetry) is most common and perhaps universal. The question of the electronic state in the four-coordinate configuration has, however, been a point of debate. Several lines of work have been interpreted as indicating the unpaired electron to be in d_{z^2} . Other work has been interpreted as indicating that the unpaired electron resides in d_{yz} (2A_2 in C_{2v} symmetry; see Figure 1 for definition of axes). Hitchman's recent analysis of the electronic structure of Co(salen) in the four-coordinate configuration shows the 2A_2 (d_{yz}) state to be about 1100 cm^{-1} lower in energy than the 2A_1 (d_{z^2}) state.^{8c}

It is noteworthy, however, that virtually all of the interesting chemistry of low-spin cobalt(II) systems has been carried out in solution.² The attempts to study electronic properties of these complexes in solution have in general been more qualitative and have not led to unambiguous interpretation.

Of the experimental work which has been carried out in solution on these complexes, NMR spectroscopy has been used to a rather limited extent but has provided interesting information.⁷ In this article we wish to report an NMR study of a substantial series of Co(salen) complexes in Me_2SO solution.

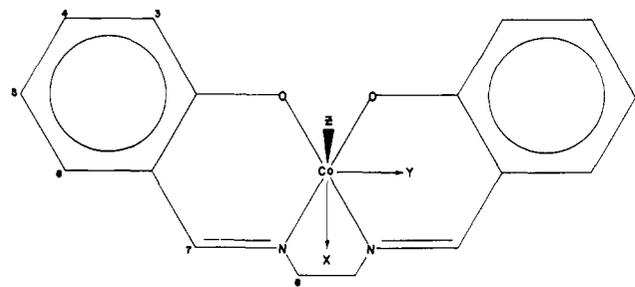


Figure 1. Ligand numbering system for Co(salen). The coordinate system used in this work is also shown.

This work reveals a more complex electronic situation for this class of complexes in solution than has been normally appreciated. NMR studies on low-spin cobalt(II) complexes have been limited to Co(thioacac)₂,^{7a} cobalt(II) porphyrins,^{7b} Co(BAE) and Co(F₃BAE),^{7d} and Co(salen).^{7c,e,f} In our work with Co(salen) we previously encountered some difficulty in completely assigning the contact shifted proton spectrum of Co(salen).^{7e} This resulted in an attempt to synthesize and study a number of ligand substituted derivatives of this system. To our initial surprise, relatively subtle substitutions at the periphery of the salen ligand caused dramatic changes in the ¹H NMR spectrum of the respective cobalt complex. Furthermore, the Co(salen) complex itself demonstrates confusing temperature dependence of the isotropic shifts. This anomalous temperature dependence is also manifested in several of the complexes of the substituted ligands. In this paper we report a rather extensive NMR study of the Co(salen) system and provide a semiquantitative model which explains the unusual NMR behavior. It is clear from this work that at least two electronic states are important in determining the solution NMR behavior in Me₂SO solution for this system.

Experimental Section

The parent salen ligand and all the derivatives¹⁵ of this ligand were prepared by a modification of the procedure reported by Martell et al.⁹ as follows (for salen). To a solution of salicylaldehyde (24.4 g, 0.2 mol) in 95% ethanol (200 mL) was added dropwise a solution of ethylenediamine (6.0 g, 0.1 mol) in ethanol (50 mL). The solution was refluxed for 30 min and allowed to cool. The crystals thus obtained were filtered and a further small crop of crystals was obtained by dilution of the filtrate with an equal volume of water and allowing the resulting solution to stand for 1 day. The combined batch of crystals was further recrystallized from 95% ethanol with only slight loss. All of the ligands prepared in this fashion were characterized by melting point, elemental analysis, mass spectrum, and NMR. The yields of pure ligand ranged from 74 to 95%.

Preparation of the cobalt(II) complexes of these ligands was accomplished by a modification of the procedure reported by Bailes.¹⁰ This procedure is given here for Co(salen) but was successfully applied for all the complexes studied. To a hot solution of salen (2.7 g, 0.01 mol) in 95% ethanol (40 mL) was added in a dropwise fashion under nitrogen a solution of cobalt(II) acetate tetrahydrate (2.5 g, 0.0 mol) in warm water (10 mL, ca. 60 °C). In some cases the ligand was not soluble in the amount of ethanol used above. Under these circumstances, 2 equiv of potassium hydroxide was added to generate the more soluble ligand dianion. The mixture was heated under reflux for 1 h after which time the solid produced was filtered under nitrogen, washed with 95% ethanol, and dried under vacuum. All complexes were characterized by elemental analyses, mass spectra (where possible), and melting points.

The deuterated ligands were prepared from the appropriate deuterated salicylaldehydes. Salicylaldehyde-*α-d* and 5-Cl-salicylaldehyde-*α-d* were prepared by methods previously employed for deuteration of aldehydes.¹¹ For the ligands deuterated at the ring positions several known methods proved unfeasible. Finally this was successfully accomplished by a method previously reported for the preparation of benzene-*1-d*.¹² A complete description of the deuteration reactions will be reported elsewhere.¹³

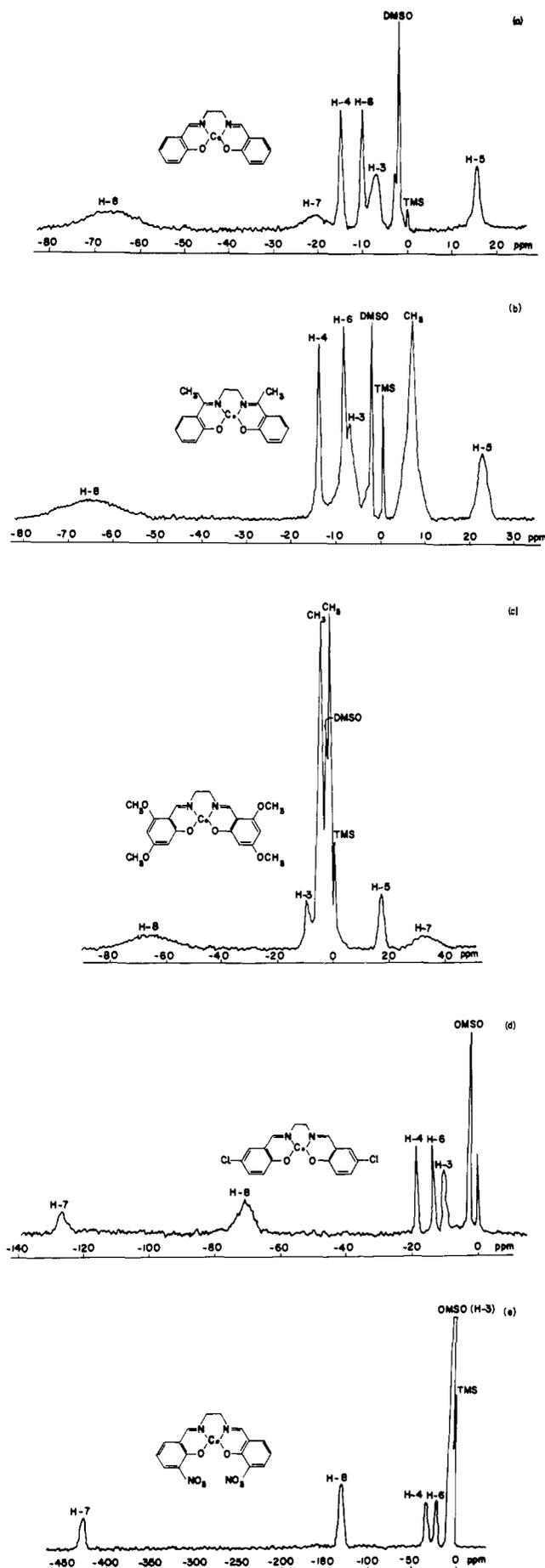


Figure 2. 100-MHz spectra of (a) Co(salen), (b) Co(7-CH₃-salen), (c) Co(4,6-di-CH₃O-salen), (d) Co(5-Cl-salen), and (e) Co(3-NO₂-salen). Spectra were obtained in Me₂SO-*d*₆ at 30 °C.

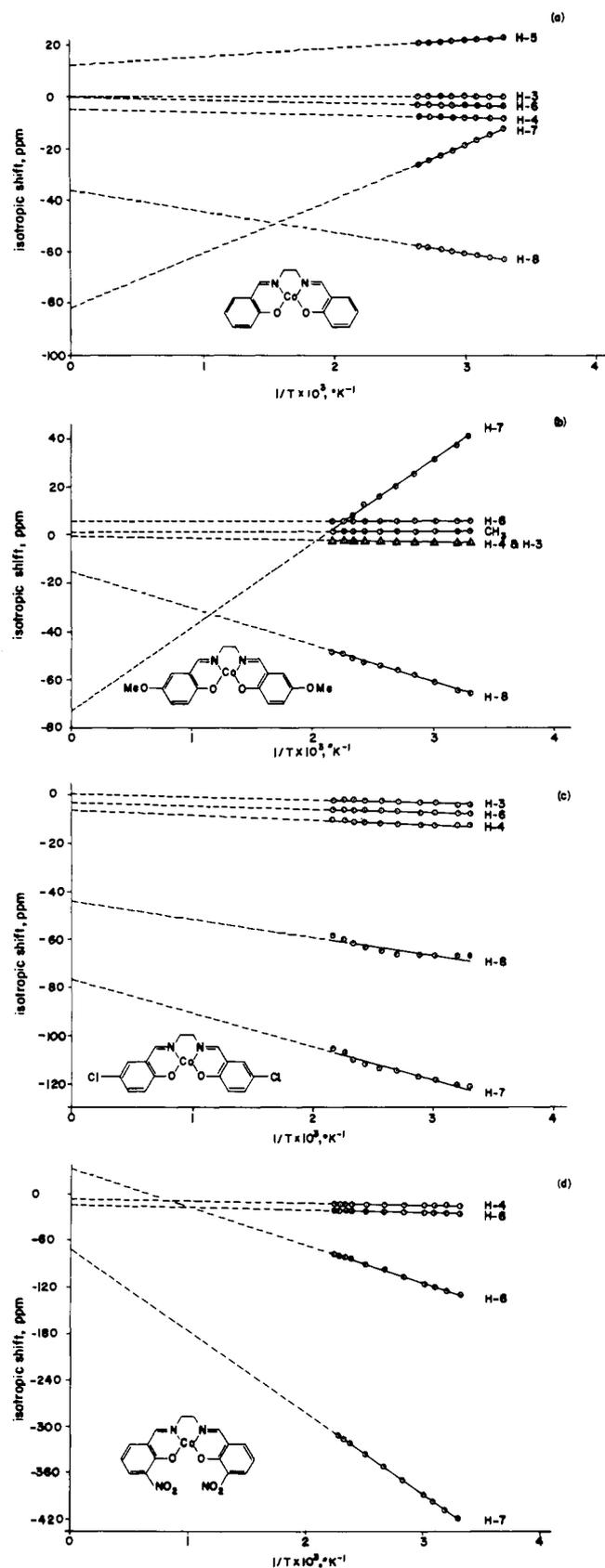


Figure 3. Plots of isotropic shift vs. $1/T$ in $\text{Me}_2\text{SO}-d_6$ for (a) $\text{Co}(\text{salen})$, (b) $\text{Co}(5\text{-OCH}_3\text{-salen})$, (c) $\text{Co}(5\text{-Cl-salen})$, and (d) $\text{Co}(3\text{-NO}_2\text{-salen})$.

The NMR samples were prepared by dissolving 10–20 mg of complex in 0.3–0.5 mL of $\text{Me}_2\text{SO}-d_6$ (Aldrich Chemical Co.). Spectra were recorded on a Varian HA-100 spectrometer. Audio sidebands were used to calibrate peak positions with Me_4Si serving as an 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-4347/V-6057 variable temperature accessory with a V-6040 controller. The system was pre-calibrated with methanol for the low-temperature range and ethylene glycol for the high-temperature range. 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 re-recorded at that temperature to confirm that no decomposition had occurred. Temperatures are estimated to be accurate to $\pm 2^\circ\text{C}$. The low solubilities of complexes and poor resolution due to broad lines caused the lower limit to be 280 K for variable temperature studies.

Results

Figure 1 shows the ligand numbering system and coordinate system used for discussion in this article. Figure 2 shows the 100-MHz spectra of several $\text{Co}(\text{salen})$ derivatives. All these spectra were obtained in $\text{Me}_2\text{SO}-d_6$. Figure 3 shows plots of isotropic shifts vs. $1/T$ for five $\text{Co}(\text{salen})$ derivatives. The data illustrated in these figures are for only a fraction of the complexes investigated. Table I gives the isotropic shifts for each proton for all the complexes investigated. These data are for the shifts at ambient temperatures, $30 \pm 2^\circ\text{C}$. Assignment of peaks in the spectra involves comparison with deuterated and methylated ligand derivatives as will be discussed below. Because of space limitations figures for the temperature dependences of all the complexes studied cannot be reproduced. Therefore the temperature dependences of the isotropic shifts for protons at positions 5, 7, and 8 for all the complexes are summarized in Table II in the following fashion. For each proton the slope and intercept at $1/T = 0$ of a plot of isotropic shift vs. $1/T$ is reported.

The solution magnetic susceptibilities of $\text{Co}(\text{salen})$, $\text{Co}(3\text{-C}_2\text{H}_5\text{O-salen})$, and $\text{Co}(3\text{-NO}_2\text{-salen})$ were measured in Me_2SO by the Evans method. At 30°C the solution magnetic moments were determined as follows: $\text{Co}(\text{salen})$, $2.7 \mu_{\text{B}}$; $\text{Co}(3\text{-C}_2\text{H}_5\text{O-salen})$, $2.5 \mu_{\text{B}}$; and $\text{Co}(3\text{-NO}_2\text{-salen})$, $4.7 \mu_{\text{B}}$.

Discussion

For all the complexes studied in this work, the isotropic shifts arise predominantly from the contact contribution. This behavior contrasts with that found in cobalt(II) porphyrins^{7b} but is the same as that reported previously for $\text{Co}(\text{BAE})$ ^{7d} and $\text{Co}(\text{salen})$ ^{7e} itself. The separation of contact and dipolar terms was accomplished using appropriate equations described elsewhere.^{7e} The calculations of the dipolar contributions were approximate for most of the derivatives because of the fact that the values for the g tensor components are not known separately for each derivative. The g values for $\text{Co}(\text{salen})$ in Me_2SO were used for calculation of all the dipolar shifts, thus causing some to be rather approximate. However, calculation of the dipolar shifts for a reasonable range of g values (see ref 8c) revealed that the dipolar shifts are indeed small compared to the contact contributions. The structural parameters for calculation of the dipolar shift were taken from the work of Shaefer.¹⁴

Assignment of Proton Spectra. As discussed previously, our original reason for preparing the derivatives reported here was to aid in proper assignment of the $\text{Co}(\text{salen})$ spectrum. However, this proved to be of little use in assignment of peaks because in many instances a single substitution in the aromatic ring caused dramatic changes in several of the peak positions. (Compare, for example, the spectra of $\text{Co}(\text{salen})$ and $\text{Co}(5\text{-Cl-salen})$ in Figure 2.) Because of this, a number of deuterated derivatives of the salen ligand system were prepared in order to make unambiguous spectral assignments. Therefore, comparison of the spectra of $\text{Co}(\text{salen})$, $\text{Co}(5\text{-}d\text{-salen})$, and $\text{Co}(7\text{-}d\text{-salen})$ provided unambiguous assignments of the 5 and

Table I. Observed Isotropic Shifts for Co(salen) Derivatives^a

complex	3 ^b	4	5	6	7	8
Co(salen)	-0.5	-8.6	+22.4	-4.0	-12.7	-62
Co(7- <i>d</i> -salen)	-0.5	-8.6	+22.4	-4.0		-62
Co(5,7-di- <i>d</i> -salen)	-0.5	-8.6		-4.0		-62
Co(4-CH ₃ O-salen)	+3.2	(-2.0) ^c	+27.0	-3.0	-4.0	-70
Co(5-CH ₃ O-salen)	-3.6	-3.6	(+1.2) ^c	+5.6	+41	-66
Co(3-C ₂ H ₅ O-salen)		-12.6	+27	-7.4	-28	-78
Co(4,6-di-CH ₃ O-salen)	-3		+25		+41	-66
Co(7-CH ₃ -salen)	-0.6	-7.7	+29	-1.9	(+8.9) ^c	-60
Co(5-Cl-salen)	-3.8	-12.2		-7.1	-120	-68
Co(5-Cl,7- <i>d</i> -salen)	-3.8	-12.2		-7.1		-68
Co(5-Br-salen)	-3.9	-12.5		-7.2	-126	-68
Co(5-Br,7- <i>d</i> -salen)	-3.9	-12.5		-7.2		-68
Co(3-NO ₂ -salen)		-24.1	+5.0	-14.3	-421	-104
Co(5-NO ₂ -salen)	-12.0	-18.0		-12.5	-299	-96
Co(3-CH ₃ -salen) ^d	(-36.1) ^c	-7.3	<i>e</i>	-1.3	<i>e</i>	<i>e</i>
Co(4-CH ₃ -salen) ^d	<i>e</i>	(+12.0) ^c	-1.9	<i>e</i>	<i>e</i>	<i>e</i>
Co(5-CH ₃ -salen) ^d	<i>e</i>	-6.3	(-22.8) ^c	-1.3	<i>e</i>	<i>e</i>

^a Units are in parts per million. The observed isotropic shifts are referenced to the resonance position for that proton in the diamagnetic ligand. These shifts are for ambient temperatures (30 °C). The solvent was Me₂SO-*d*₆. ^b Ligand position; see Figure 1. ^c Shifts reported in parentheses are for the protons of the substituent (CH₃O- or CH₃-). ^d The data for these complexes are from ref 7c. These data were obtained in CDCl₃. ^e These peaks were not observed in ref 7c.

Table II. Summary of Plots of Isotropic Shifts vs. 1/*T* in Me₂SO-*d*₆

complex	5 ^a	7	8
Co(salen)			
slope ^b	3.7 × 10 ³	21.1 × 10 ³	-8.6 × 10 ³
intercept ^c	10	-83	-36
Co(4-CH ₃ O-salen)			
slope	6.6 × 10 ³	20.8 × 10 ³	-13.1 × 10 ³
intercept	6	-73	-27
Co(5-CH ₃ O-salen)			
slope		34.7 × 10 ³	-15.4 × 10 ³
intercept		-73	-15
Co(3-C ₂ H ₅ O-salen)			
slope	4.9 × 10 ³	-3.7 × 10 ³	-14.3 × 10 ³
intercept	11	-16	-31
Co(4,6-di-CH ₃ O-salen)			
slope	5.9 × 10 ³	17.3 × 10 ³	-13.5 × 10 ³
intercept	6	-16	-21
Co(7-CH ₃ -salen)			
slope	8.2 × 10 ³		-10.4 × 10 ³
intercept	3		-26
Co(5-Cl-salen)			
slope		-13.0 × 10 ³	-7.3 × 10 ³
intercept		-77	-44
Co(5-Br-salen)			
slope		-3.9 × 10 ³	-4.3 × 10 ³
intercept		-113	-54
Co(3-NO ₂ -salen)			
slope	<i>d</i>	-106 × 10 ³	-42 × 10 ³
intercept	<i>d</i>	-72	33
Co(3-NO ₂ -salen)			
slope		-30 × 10 ³	-25.8 × 10 ³
intercept		-200	-96

^a Ligand position. ^b This is the slope of a plot of isotropic shift vs. 1/*T*. The units are ppm/K. ^c This is the intercept of the isotropic shift vs. 1/*T* plot extrapolated to 1/*T* = 0. The units are ppm. ^d The peak for the 5 proton overlapped with the solvent preventing analysis of the temperature dependence.

7 positions. Because of the tremendous variations in peak positions upon substitutions in the aromatic rings, deuterated derivatives of some of the substituted salen ligands were prepared. This was especially important for the proton at position 7, which was very sensitive to substitution of the aromatic ring (compare spectra in Figure 2). Thus, for the proton at position 7, care was taken to provide an unambiguous assignment for

several derivatives. The proton at positions 3 and 4 can be unambiguously assigned from the 3-Me salen and 4-Me salen complexes reported in ref 7c. In addition, the proton at position 3 is found consistently to give a considerably broader NMR peak than the other ring protons. This can be used, therefore, to assign the 3 proton. The protons at position 8 (-CH₂-) can be easily assigned by integration of the spectra. In general the following observations can be made about the spectra of the series of complexes as a whole. The methylene protons are always found shifted considerably downfield (-50 to -100 ppm) as they are in the analogous Co(BAE) complex. The ring proton at position 5 is shifted considerably upfield +10 to +20 ppm. The proton at position 4 generally occurs a few parts per million downfield from the proton at position 6. These two peaks have virtually identical line widths. The behavior of the proton at position 7 is most interesting. Its position in the various spectra shifts dramatically as the ring positions are substituted. For example, this proton is shifted downfield by over 400 ppm in Co(3-NO₂-salen), occurs at ~120 ppm in Co(5-Cl-salen) and -12.7 ppm in Co(salen), and is shifted upfield approximately 60 ppm in Co(4,6-diOCH₃-salen). In addition, the isotropic shifts for this proton show anomalous temperature dependences in several of the compounds.

Changes in Isotropic Shift Patterns upon Ligand Substitution. Upon substitution of the aromatic ring of the ligand system, dramatic changes are observed in the pattern of isotropic shifts. The shift for the proton at position 7 is particularly sensitive to variations in the ligand. As noted above, the resonance position at room temperature for this proton (at ambient temperature) occurs at -420 ppm in Co(3-NO₂-salen) while it occurs at +60 ppm in Co(4,6-di-CH₃O-salen). In all the other complexes, the resonance position for this proton occurs between these two extremes. The methylene protons (position 8) always are found shifted substantially downfield. However, once again substantial variation is observed. The shift at room temperature is -104 ppm in Co(3-NO₂-salen) but is -61 ppm in Co(7-Me-salen). In the other complexes, the room temperature shifts for the methylene protons lie between these extremes. For the other protons the variations in isotropic shifts upon ligand substitution are not as dramatic because the shifts are not as large. Nevertheless, significant variations are observed for every proton. We believe that the reason for this behavior is the fact that at least two electronic states contribute to the observed shifts for most of the derivatives. This will be

discussed at length below. However, it is pertinent to discuss the temperature dependence for the isotropic shifts before developing a model which explains both the wide variation in observed shifts and the unusual temperature dependence.

Temperature Dependences of Isotropic Shifts. The anomalous temperature dependences of the isotropic shifts is one of the most interesting questions to be addressed in these compounds. Figure 3 gives plots of isotropic shifts vs. $1/T$ for each of the protons in several compounds. A complete description of temperature dependences for all the compounds is summarized in Table II. Inspection of the temperature dependence data reveals that the shifts for the proton at position 7 show by far the most anomalous behavior. For example, in Co(5-NO₂-salen) the plot of isotropic shift vs. $1/T$ gives an intercept of -20 ppm at $1/T = 0$. In other derivatives such as Co(5-Cl-salen) and Co(5-Br-salen) the plot of isotropic shift vs. $1/T$ is almost flat, resulting in a large negative intercept. For other derivatives such as Co(salen) and Co(4-OCH₃-salen) the negative isotropic shift for the proton at position 7 becomes *more negative* at high temperatures. This is qualitatively opposite behavior from the expected Curie law behavior for the isotropic shifts. The methylene protons in most of the complexes also show large negative intercepts in the plots of isotropic shift vs. $1/T$. For the other protons, the nonzero intercepts are not as large because the magnitudes of the shifts are substantially smaller but, nevertheless, significant nonzero intercepts are indeed observed.

A Model for the Isotropic Shift Behavior in the Co(salen) System. The purpose of this section is to provide a model which explains in a semiquantitative fashion both the variation in the isotropic shifts throughout the series of substituted complexes as well as the anomalous temperature dependences. Before doing this the following observations should be made. (1) If one reviews the contact shifts for the proton at position 7, two extreme types of behavior are observed. In Co(3-NO₂-salen) we see a very large negative contact shift while in Co(4,6-di-OCH₃-salen) we see a positive contact shift. We do not observe extreme anomalous temperature-dependent behavior in either case. (2) Those ligands with the most electron-withdrawing substituents on the aromatic ring show large negative shifts for the proton at the 7 position while the complex with the most electron-releasing substituents (two methoxy groups) shows a relatively large positive contact shift for this proton. (3) The complexes exhibiting the most anomalous temperature dependence are those with substituents intermediate between 3-NO₂- and 4,6-di-OCH₃- in electron-withdrawing or releasing ability.

We propose that in this series of complexes there are two electronic states each of which contributes to the observed isotropic shifts, especially for complexes of intermediate behavior. One state is a quartet spin state (see below). The behavior exhibited for Co(3-NO₂-salen) is an example of a nearly "pure" quartet state. The most obvious characteristic of this electronic configuration is the extremely large negative shift for the proton at position 7. The other electronic state is a doublet spin state. A complex in which this is the only important electronic state exhibits (we propose) a positive contact shift for the proton at position 7. We suggest that Co(4,6-di-OMe-salen) exhibits this behavior. A complex in either "pure" state should show relatively normal Curie law behavior.

Let us assume that in all of the complexes studied, only these two electronic states contribute to the observed isotropic shifts. The variation in the isotropic shifts of the complexes is due primarily to the energy differences between the two electronic states and hence to the relative populations between the two states. For the following analysis the quartet state will be labeled (q) while the doublet state will be labeled (d). For the proton at position 7, state (d) will show a plot of $(\Delta H/H)_{\text{iso}}$ vs. $1/T$ which obeys Curie law behavior and shows a positive

(upfield) shift. Using the data for Co(4,6-di-OMe-salen) as a guide we propose that at 25 °C a complex in a pure (d) state has an isotropic shift of +64 ppm. Thus,

$$\left(\frac{\Delta H}{H}\right)_{\text{iso}} = \frac{1.91 \times 10^4}{T} \text{ for state (d)}$$

In a like manner, state (q) shows a plot of $(\Delta H/H)_{\text{iso}}$ vs. $1/T$ which exhibits Curie law behavior with a negative isotropic shift. We will assume that the shift at 25 °C is -436 ppm (from Co(3-NO₂-salen)). Thus,

$$\left(\frac{\Delta H}{H}\right)_{\text{iso}} = \frac{-1.30 \times 10^5}{T} \text{ for state (q)}$$

If for a given complex the observed shift is due to a contribution from each state, then

$$\left(\frac{\Delta H}{H}\right)_{\text{iso}} [\text{obsd}] = P_{(d)} \frac{1.91 \times 10^4}{T} + P_{(q)} \frac{(-1.30 \times 10^5)}{T} \quad (1)$$

where $P_{(d)}$ and $P_{(q)}$ are the mole fractions of complex in state (d) and (q), respectively (this assumes fast exchange between state (d) and state (q)). Recognizing that $P_{(q)} = 1 - P_{(d)}$ and assuming that the relative populations of the two states are determined by the Boltzmann distribution, $P_{(q)}/P_{(d)} = (1 - P_{(d)})/P_{(d)} = e^{-\Delta E/RT}$, we can see that $P_{(d)} = 1/(1 + e^{-\Delta E/RT})$. Here ΔE is the difference in energy between the two electronic states $\Delta E = E_{(q)} - E_{(d)}$. By substitution into eq 1

$$\left(\frac{\Delta H}{H}\right)_{\text{iso}} [\text{obsd}] = \left(\frac{1}{1 + e^{-\Delta E/RT}} \times \frac{1.49 \times 10^5}{T}\right) - \frac{1.30 \times 10^5}{T} \quad (2)$$

This equation gives the temperature dependence of the isotropic shift for the proton at position 7 as a function of the energy separation between the two electronic states. This equation can be used to calculate an expected isotropic shift at any temperature for a given value of ΔE . Thus not only the observed shift but also its temperature dependence can be predicted. Figure 4 shows the calculated plots of $(\Delta H/H)_{\text{iso}}$ vs. $1/T$ for three values of ΔE : 514, 354, and 113 cm⁻¹. These values were chosen because these predicted plots of $(\Delta H/H)_{\text{iso}}$ vs. $1/T$ qualitatively reflect the behavior observed in three of the complexes studied. Line (b) of Figure 4 reflects the behavior which we find for Co(5-OCH₃-salen). Line (c) of Figure 4 reflects the behavior found for Co(salen) and Co(4-OMe-salen), that is, a small negative isotropic shift with inverse Curie law dependence. Line (d) in Figure 4 reflects the behavior found for Co(5-Cl-salen) and Co(5-Br-salen), that is, a relatively large negative isotropic shift with a large negative intercept in the Curie law plot. Thus it appears that most of the unusual behavior previously noted for the proton at position 7 can be at least qualitatively accounted for with the simple model which has been suggested. A similar analysis could be applied to other protons in the system, notably the methylene protons at position 8.

This model for the isotropic shift behavior in the Co(salen) system is obviously oversimplified. For example, neither pure electronic state is likely to give perfect Curie law behavior as is assumed. Nevertheless, a reasonable reflection of the observed temperature dependence for the isotropic shifts in a number of the Co(salen) derivatives can be obtained. Refinements in the simple model could give quantitative fits to observed behavior.

The values for the energy separation between the doublet and quartet states is rather small in view of the recent work by Hitchman on solid Co(salen).^{8c} The very simple model proposed here would not be expected to provide quantitative information of this type. Nevertheless, the qualitative trends do

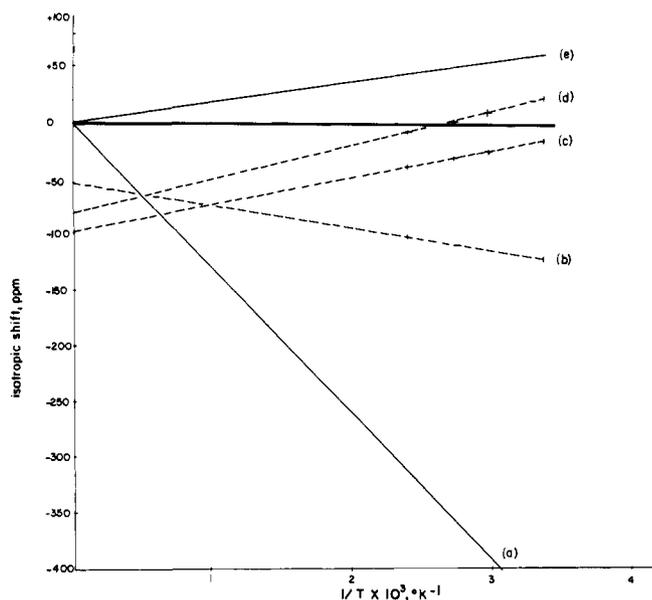


Figure 4. Calculated isotropic shifts. Lines (b), (c), and (d) are the isotropic shifts which would result from populating two electronic states each of which obeys the Curie law. Lines (a) and (e) are the isotropic shifts for these two "pure" states. The energy separation between the two states, $\Delta E = E_{(a)} - E_{(e)}$, is 514 cm^{-1} for (d), 354 cm^{-1} for (c), and 113 cm^{-1} for (b). Line (d) reflects the behavior observed for H-7 in Co(5-OCH₃-salen), line (c) reflects the behavior observed for H-7 in Co(4-OCH₃-salen) and Co(salen), and line (b) reflects the behavior observed for H-7 in Co(5-Cl-salen) and Co(5-Br-salen). See text for further discussion.

reflect expected behavior. For example, the complexes with more electron-withdrawing substituents in the ligand system show a smaller separation between the doublet and quartet states. These ligands provide a weak in-plane ligand field. Theoretical analysis has shown that a weaker in-plane ligand field will cause a significant energy lowering for a number of quartet states.^{8c}

Electronic States in Co(salen). In the previous section it was suggested that the two states responsible for the isotropic shifts were a quartet (q) state and a doublet (d) state. The two low-energy doublet states which have been assumed by various workers are 2A_1 and 2A_2 in which the unpaired electron is found in d_{z^2} or d_{yz} , respectively. In five-coordinate adducts the 2A_1 state is generally agreed to be the ground state. We have previously argued that 2A_1 is the correct ground state for Co(BAE) and Co(salen) in Me₂SO solution.^{7d,e} This is consistent with the fact that Co(salen) binds O₂ in Me₂SO and with the g values obtained from ESR of Co(salen) in Me₂SO. Migita et al. have suggested that 2A_2 may be the ground state in a Me₂SO solution of a closely related low-spin cobalt(II) system.^{7f} Nevertheless all current evidence points to a 2A_1 ground state for Co(salen) in Me₂SO solution. The quartet states in Co(salen) have also been discussed recently.^{8c} In four-coordinate Co(salen) it has been determined that a variety of quartet states lie $3000\text{--}4000 \text{ cm}^{-1}$ above the ground state. These quartet states drop significantly lower in energy upon formation of five-coordinate adducts primarily owing to a lengthening of the equatorial metal-ligand bonds. In the present study we have prepared several salen derivatives with electron-withdrawing substituents. Because of the resulting weaker equatorial ligand field in the cobalt complexes of these derivatives, the quartet state(s) should be even lower in energy and perhaps even become the ground state. We have measured the solution magnetic moments of three of the complexes studied under the same conditions as those under which the NMR spectra were obtained (Table II). Of note is the fact that the room temperature magnetic moment for Co(3-NO₂-salen) in Me₂SO is about $4.7 \mu_B$. Thus this compound is, in fact, high

spin. Since Co(3-NO₂-salen) and Co(5-NO₂-salen) exhibit very large negative shifts for the proton at position 7, it is clear that it is indeed a quartet state which is responsible for the substantial downfield contribution to the shifts for this position in compounds such as Co(5-Cl-salen), Co(5-Br-salen), and even Co(salen). We have found that the magnetic moment for Co(salen) in Me₂SO increases with increasing temperature indicating a significant quartet state population under the conditions of the NMR measurements. This is consistent with the non-Curie-law behavior of the isotropic shift of the proton at position 7 in Co(salen).

Spin Delocalization Pattern in the Co(salen) System. Previous reports have commented to some extent on the apparent spin delocalization in Co(salen). However, these comments have all assumed that a single electronic state (either 2A_1 or 2A_2) is responsible for the isotropic shifts. Unfortunately the isotropic shift of the proton at position 7 has been used particularly to argue for a particular spin delocalization mechanism. From the current work, we now see that the large downfield shift for this proton is in fact due to a significant population of a quartet state which allows both σ and π delocalization. On the other hand, it now appears that a "pure" doublet (d) electronic state for the Co(salen) system (e.g., Co(4,6-di-OCH₃-salen)) gives an *upfield* shift for the protons at position 7. This still leaves open the problem as to whether 2A_1 (d_{z^2}) or 2A_2 (d_{yz}) is the electronic ground state for Co(salen) in Me₂SO. For reasons previously described we believe that the 2A_1 (d_{z^2}) state is most reasonable.

Migita's most recent work in which the isotropic shifts of *N,N'*-1,1-dimethylethylenebis(salicylideneiminato)cobalt in pyridine were reported deserves comment. Here a large negative shift was observed for the proton at position 7. This was attributed to σ delocalization from 2A_1 (d_{z^2}). We suggest, based on the present work, that Migita's system may also have a significant contribution from a quartet electronic state. It is also interesting to note that Migita has reported a number of calculated ligand hyperfine coupling constants using an INDO MO calculation. Their analysis followed a procedure which we had earlier employed for the Co(BAE) system.^{7d} In our hands the INDO calculation on a salen-type ligand fragment did not converge with the unpaired electron in an orbital of interest because of a number of nearly degenerated π orbitals. No details of the calculation were given in Migita's report. However, their results are suggestive of a significant downfield shift for the proton at position 7 from σ delocalization. In view of our results which show that at least two electronic states are responsible for the isotropic shifts and the inseparability of the σ and π systems due to nonplanarity of the complex, it is doubtful that detailed analyses of the spin delocalization mechanisms can be made for Co(salen) and its derivatives.

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- (15) Abbreviations used for the ligand systems in this article are as follows: bis(salicylaldehyde)ethylenediamine, salen; bis(7-deuteriosalicylaldehyde)ethylenediamine, 7-*d*-salen; bis(5,7-dideuteriosalicylaldehyde)ethylenediamine, 5,7-di-*d*-salen; bis(4-methoxysalicylaldehyde)ethylenediamine, 4-CH₃O-salen; bis(5-methoxysalicylaldehyde)ethylenediamine, 5-CH₃O-salen; bis(3-ethoxysalicylaldehyde)ethylenediamine, 3-C₂H₅O-salen; bis(4,6-dimethoxysalicylaldehyde)ethylenediamine, 4,6-di-CH₃O-salen; bis(7-methylsalicylaldehyde)ethylenediamine, 7-CH₃-salen; bis(5-halosalicylaldehyde)ethylenediamine, 5-X-salen; bis(5-halo-7-deuteriosalicylaldehyde)ethylenediamine, 5-X,7-*d*-salen; bis(3-nitrosalicylaldehyde)ethylenediamine, 3-NO₂-salen; bis(5-nitrosalicylaldehyde)ethylenediamine, 5-NO-salen. All ligands are coordinated to the cobalt as the dianion.

Selenium-77 Nuclear Magnetic Resonance Studies. 1. Chemical Shifts, Coupling Constants, and Relaxation Times for *Se-dl*-Cystine, *Se-dl*-Methionine, and Several Se-Containing Transition Metal Complexes

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Abstract: ^{77}Se NMR spectra of 29 Se-containing compounds are reported. The ^{77}Se chemical shifts reported cover a range of ~ 1000 ppm. In dialkyldiselenocarbamate metal complexes, the magnetic anisotropy associated with d^8 nickel triad complexes contributes significantly to the ^{77}Se chemical shielding, giving rise to upfield shifts with respect to the anionic ligands and zinc and cadmium complexes. Electronic effects arising from the ligand also significantly contribute to the shielding. Solvent, temperature, and concentration dependence studies have also been carried out on a few of the diselenocarbamate complexes. Both P-Se and Pt-Se coupling constant data and an NMR trans influence argument have been utilized in making peak assignments. Spin-lattice relaxation times (T_1) of a few of the compounds are also reported and they range from 0.46 to 4-5 s in the temperature range -28 to 27°C . With $\text{Zn}(\text{Se}_2\text{CNET}_2)_2$ and $\text{Pd}(\text{Se}_2\text{CN-}i\text{-Bu}_2)_2$, the chemical shift anisotropy appears to be the dominant relaxation mechanism for the ^{77}Se nuclei.

Introduction

The use of Fourier transform ^{77}Se NMR was first reported by Gronowitz et al.^{1a} in 1973. Since then, these workers^{1b-d} have reported the ^{77}Se chemical shifts of a variety of organoselenium compounds. Recently, Odom and co-workers² presented spin-lattice relaxation time measurements on some diaryldiselenides, alkyl selenols, and dimethyl selenide. These studies have demonstrated the relative ease with which ^{77}Se NMR spectra can be obtained despite a number of potential drawbacks, including a low natural abundance of the ^{77}Se isotope (7.58%) and an NMR sensitivity of 6.97×10^{-3} with respect to the proton at constant field. Previously, ^{77}Se NMR studies of a number of inorganic and organic compounds had been carried out using the continuous wave^{3,4} and INDO⁵ techniques. The former technique suffers from the shortcomings mentioned above while the latter is useful only when protons are coupled to ^{77}Se . These studies and others published prior to 1972 have been reviewed by Lardon.⁶

Selenium compounds generally show structural properties

similar to those of their sulfur analogues. Hence, several years ago we became attracted to the use of ^{77}Se NMR for the study of the intramolecular rearrangements of coordination compounds of the type $\text{Pt}(\text{Se}_2\text{CNR}_2)_2\text{L}$ (where L is a phosphine and R an alkyl group). Our interest in ^{77}Se NMR was further stimulated by recent studies which have demonstrated the biological importance of selenium in the enzymes glutathione peroxidase,⁷ glycine reductase,⁸ and formate dehydrogenase.⁹ Selenium also has been implicated as a protective trace element against cancer^{10a} and heart disease.^{10b} Therefore considerable incentive exists to develop ^{77}Se NMR for the study of molecular structure, particularly in solution with metal-organic species. The first results of these investigations are reported here.

Our experience with dithiocarbamates²¹ has provided an excellent background for the study of diselenocarbamate complexes, the compounds we chose to initiate our ^{77}Se NMR studies generally. In this paper, we report some chemical shifts, coupling constants, and spin-lattice relaxation times (T_1) of a number of compounds which are in the main transition metal