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Proton Magnetic Resonance Spectra of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes

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Proton magnetic resonance spectra of a series of bis(*N*-alkylsalicylaldiminato)copper(II) complexes have been recorded and the isotropic shifts have been factorized into their dipolar and contact contributions. The contact shift pattern has been compared with that of other bis(*N*-alkylsalicylaldiminato)metal(II) complexes. The PMR line width as well as the contact shift values are found to increase along the series from *N*-methyl to *N*-*tert*-butyl.

Introduction

It is generally believed that PMR spectra of copper(II) complexes are not useful owing to unfavorable electronic relaxation times which broaden up the signals.¹⁻⁷ However, the observation of proton signals for some bis(*N*-alkylsalicylaldiminato)copper(II) complexes^{5,8} (Cu(sal-*N*-R)₂) induced us to investigate a series of these complexes by means of PMR spectroscopy in order to determine the nature of the isotropic shifts and to investigate the factors which determine the PMR line width.

Experimental Section

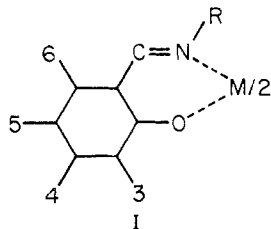
Materials. The complexes were prepared according to literature methods^{9,10} and analyzed satisfactorily for C, H, and N.

PMR Measurements. Proton magnetic resonance spectra were recorded with a Varian DA-60-IL spectrometer at 60 MHz. Shifts were calibrated from internal tetramethylsilane (TMS). The spectra were recorded both in HR mode (side-band technique used for calibration) and in HA mode in internal lock. Deuteriochloroform (Merck, 99.8%) was used as solvent.

ESR Measurements. ESR spectra of ca. 10⁻³ M "glassy" solutions of bis(*N*-alkylsalicylaldiminato)copper(II) complexes in chloroform were obtained with a Varian E-9 spectrometer, using diphenylpicrylhydrazone (DPPH) as external standard.

Results

All the investigated complexes give reasonably sharp PMR signals for the 4 and 5 protons of the salicylaldiminato ligand (I). In the cases of bis(*N*-methylsalicylaldiminato)- and



bis(*N*-ethylsalicylaldiminato)copper(II) complexes, broad signals, attributable to the 3 and 6 proton resonances, respectively, have been detected; however in the other cases investigated (R = *n*-propyl, isopropyl, *tert*-butyl) the resonance peaks of these protons were not detected, presumably because

Table I. Isotropic Shifts (ppm) of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes in CDCl₃ at 26°C^a

Alkyl group	3-H	4-H	5-H	6-H
Methyl ^b	16	-2.3	1.2	-23
Ethyl		-2.6	1.6	-29
<i>n</i> -Propyl		-2.7	1.8	
Isopropyl		-3.2	3.0	
<i>tert</i> -Butyl		-3.3	3.2	

^a The isotropic shifts are determined relative to the reported shifts for the bis(*N*-alkylsalicylaldiminato)zinc(II) complexes: J. D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, **5**, 1036 (1966). ^b Methyl isotropic shifts (ppm) of *n*-CH₃ derivatives: 3-CH₃, -0.2; 4-CH₃, 6.5; 5-CH₃, -2.7.

Table II. 4-H Signal Half-Widths (Hz) of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes in CDCl₃ at 26°C

Derivative	Derivative				
	Methyl	Ethyl	<i>n</i> -Propyl	Isopropyl	<i>tert</i> -Butyl
	90	100	110	150	250

Table III. Temperature Dependence of 4-H Signal Half-Width (Hz) for Bis(*N*-ethylsalicylaldiminato)copper(II) and Bis(*N*-*n*-propylsalicylaldiminato)copper(II) Complexes in CDCl₃

Derivative	Temp, °C			
	57	26	-11	-31
Ethyl	70	100	210	250
<i>n</i> -Propyl	75	110	220	270

they were very broad or were covered by intense *N*-alkyl resonances.

Assignments of the proton absorptions have been performed through substitution of the protons by methyl or halide groups. The broad and strong signals which appear near TMS in the spectra of all the complexes (with the exception of bis(*N*-methylsalicylaldiminato)copper(II)) are attributable to the β and γ protons of the aliphatic chains. The observed isotropic shifts of the aromatic protons are shown in Table I. The room-temperature PMR spectra of bis(*N*-methylsalicylaldiminato)- and bis(*N*-ethylsalicylaldiminato)copper(II) complexes are reported in Figure 1.

The signal half-widths strongly depend on the nature of the

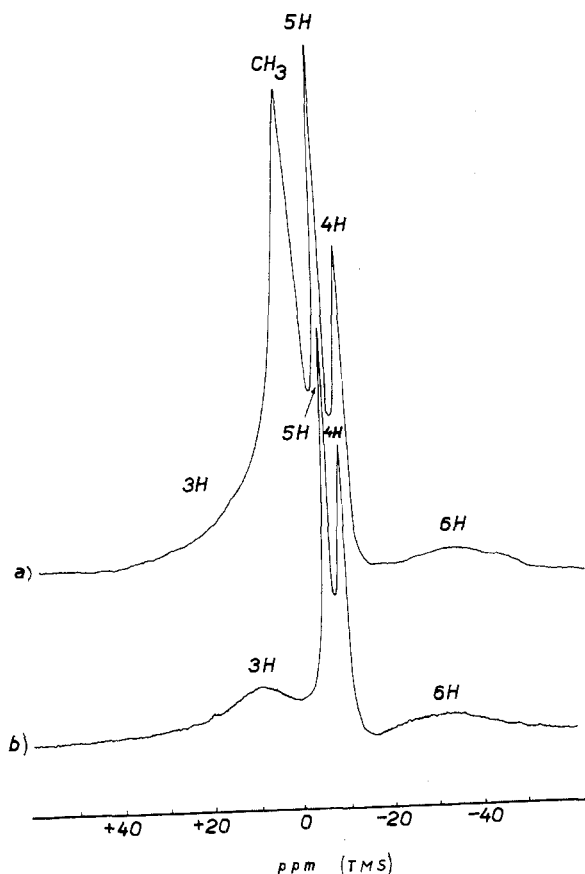


Figure 1. Proton magnetic resonance spectra at 26° of (a) bis(*N*-ethylsalicylaldiminato)copper(II) and (b) bis(*N*-methylsalicylaldiminato)copper(II) in CDCl_3 .

Table IV. g Values of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes^a

Alkyl group	g_{\parallel}	g_{\perp}	Alkyl group	g_{\parallel}	g_{\perp}
Methyl	2.22	2.05	<i>n</i> -Propyl	2.23	2.06
	(2.21) ^b	(2.05) ^b		(2.22) ^b	(2.05) ^b
Ethyl	2.21	2.06	Isopropyl	2.23	2.07
			<i>tert</i> -Butyl	2.27	2.08

^a For ca. $10^{-3} M$ "glassy" solutions (see also ref 11). ^b Single-crystal g values.¹⁵

alkyl substituent on the nitrogen donor atom and on the temperature, becoming sharper as the temperature increases (see Tables II and III). Both frequencies and half-widths of the various proton signals are substantially independent of the concentration of solutions within the range 5×10^{-2} – $5 \times 10^{-1} M$.

The temperature dependence of the isotropic shifts of the 4 and 5 aromatic protons of bis(*N*-ethylsalicylaldiminato)- and bis(*N*-*n*-propylsalicylaldiminato)copper(II) complexes is reported in Figure 2. Despite the error in locating the signal at low temperatures, it appears that the isotropic shifts do not follow the Curie-Weiss dependence, at least in the temperature range investigated. Such a behavior, however, has been found for other copper(II)-containing systems.^{11–14}

These compounds give ESR signals in the solid state¹⁵ and in solution.¹⁶ The molecular g values in CHCl_3 glassy solutions are reported in Table IV, together with the single-crystal g values¹⁵ for the methyl and *n*-propyl derivatives.

Discussion

The observation of both ESR and PMR spectra in pure copper(II) complexes is somewhat surprising and quite interesting. Usually PMR spectroscopy investigations on

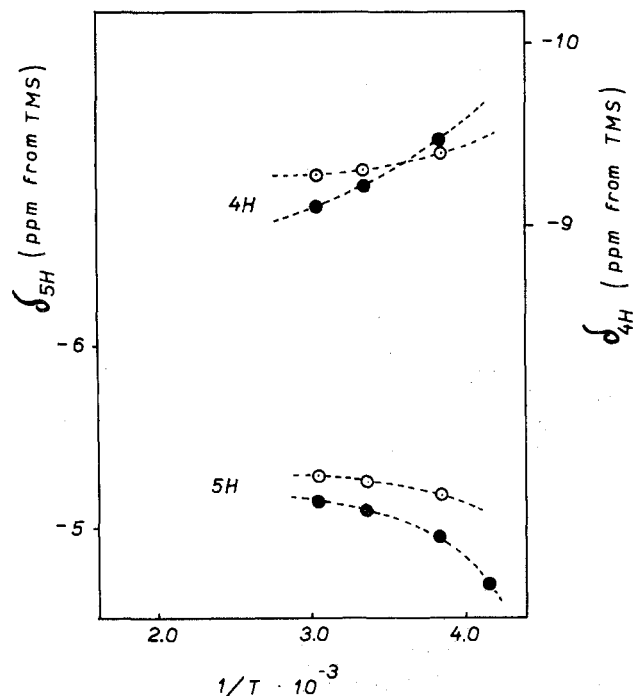


Figure 2. Temperature dependence for 4-H and 5-H chemical shifts of bis(*N*-ethylsalicylaldiminato)copper(II) (●) and bis(*N*-*n*-propylsalicylaldiminato)copper(II) (○) complexes in CDCl_3 .

Table V. Contact and Dipolar Shifts (ppm) in Bis(*N*-alkylsalicylaldiminato)metal(II) Complexes

Proton	Cu(sal- <i>N</i> - <i>n</i> -Pr) ₂		Cu(sal- <i>N</i> - <i>i</i> -Pr) ₂ ^a		Ni(sal- <i>N</i> - <i>i</i> -Pr) ₂	
	Dipolar	Contact	Dipolar	Contact	Dipolar	Contact
3	0.8		0.3		-1.4	25.1
4	0.3	-3.0	0.2	-3.4	2.3	-21.3
5	0.2	2.0	0.2	3.2	4.5	19.2
6	0.4		0.3		8.4	-12.1

^a Reference 22.

copper(II)-containing systems have been carried out under ligand excess and/or fast ligand-exchange conditions^{12–14,17,18} in order to reduce the effects of unfavorable electronic relaxation times. In the present case there is no fast ligand exchange as the spectra of solutions containing two different complexes show several signals for each aromatic position.

The resonance half-widths strongly depend on the geometry of the chromophore (Table III). The sharpest signals have been observed for the planar complexes (methyl, ethyl,¹⁹ and propyl derivatives), the broadest signals are observed in the spectra of the isopropyl and *tert*-butyl derivatives, which have been shown to have a flattened tetrahedral structure both in the solid state and in solution.¹⁰ This pattern is just the contrary of what was earlier postulated.⁵ It was also suggested that the ESR line width follows the very same order.¹⁶ This latter behavior was attributed to the extent of distortion from planarity and to the consequent availability of lower lying excited states.

The observation of the PMR signal is substantially restricted to protons experiencing a small hyperfine coupling. Presumably such small contact term, A , does not dramatically affect the transverse relaxation time of the proton, T_2 , as shown by the following eq 1¹ (where the symbols have the usual meaning). Furthermore, since the contact terms increase among the investigated complexes (Tables I and V), they may, at least in part, account for the observed line width pattern. The correlation time, τ_c , which mainly depends on the tumbling time, is not expected to be significantly affected by a minor change in the geometry of the molecule.

$$\frac{1}{T_2} = \frac{S(S+1)g^2\beta^2\gamma_I^2}{15r^6} \left(7\tau_c + \frac{13\tau_c}{1 + \omega^2\tau_c^2} \right) + \frac{S(S+1)A^2}{3h^2} \left(\tau_e + \frac{\tau_e}{1 + \omega^2\tau_e^2} \right) \quad (1)$$

A further mechanism which presumably contributes to the observed pattern is the electron spin exchange in the relatively concentrated solutions used to record the PMR spectra (ca. $10^{-1} M$). The effect of such mechanism has been demonstrated to be dramatic on the electronic relaxation time as it has been possible to measure the PMR spectra of organic radicals when the solvent is a radical itself.²⁰ This mechanism is expected to be more operative for planar than for pseudotetrahedral complexes since the former may allow a direct copper-copper interaction. Since the number of collisions between unpaired electrons is strongly affected by the temperature, this mechanism could also explain the dramatic effect of the temperature on the line width. A third mechanism able to account for the observation of the PMR signals as well as of their half-width pattern could be due to electron spin-spin superexchange interactions²¹ through a monomer-dimer equilibrium. The formation of dimers is, again, more probable for planar than for pseudotetrahedral complexes within this series.¹⁰ This mechanism could also account for the observed temperature dependence of the spectra as the equilibrium should be temperature dependent.²² It should be noted, however, that the percentage of dimers should be very low as it has not been possible to measure any sizable increase in the molecular weight on passing from 10^{-3} to $10^{-1} M$ solutions.

The availability of the g values for the same complexes allow us to factorize the isotropic shifts into their dipolar and contact contributions.^{23,24} Since the observed g values (Table IV) reproduce quite well the experimental susceptibility values, second-order Zeeman effects on the dipolar contributions presumably play an unimportant role.²⁴ This is consistent also with the actual low symmetry of the chromophores. We can assume, therefore, eq 2 to be valid to reproduce the dipolar contributions.^{14,18}

$$(\Delta\bar{\nu}_{\text{dip}})_i = \frac{\nu\beta^2 S(S+1)}{9kT} g(g_{\parallel} - g_{\perp}) \left(\frac{1 - 3 \cos^2 \vartheta_i}{r_i^3} \right) \quad (2)$$

These contributions have been calculated for the aromatic protons of both the planar bis(*N-n*-propylsalicylaldiminato)copper(II) and the pseudotetrahedral bis(*N-isopropylsalicylaldiminato*)copper(II) complexes, using the ϑ_i and r_i crystallographic values.^{25,26} The results of these calculations are reported in Table V.

The dipolar shift contributions are all positive and small in their absolute values, according to previous findings.¹⁴ Also, contact shifts are small relative to those observed for nickel(II) and cobalt(II) analogs,²⁷ consistent with the presence of only one unpaired electron; however, the contact shift pattern differs from that of other salicylaldiminato complexes. For example the contact shift values for the bis(*N-isopropylsalicylaldiminato*)nickel(II) complex, as calculated through a similar equation, are quite well alternating on passing from the 3 (upfield) to the 6 (downfield) positions (see Table V). In the

present copper(II) complexes protons 3 and 6 are respectively up- and downfield of a large amount (Table V), whereas protons 5 and 4, although up- and downfield, are close to the diamagnetic positions. This is a quite unusual contact shift pattern for the unpaired electron residing in a ligand π molecular orbital, since the shifts would not be expected to attenuate as the number of bonds between the paramagnetic center and the resonating protons increases. It should also be noted that methyl substitution on the salicylaldimine ring at positions 4 and 5 gives rise to isotropic shifts reversed with respect to the unsubstituted positions, whereas the 3-CH₃ resonance shows a very small isotropic shift (Table I). These data could be indicative of a spin density distribution not being due to a unique mechanism of spin delocalization.¹² Consistent with this, the contact shifts increase on passing from planar to pseudotetrahedral complexes although the copper-donor atoms distances do not follow the same pattern, being essentially constant.^{25,26}

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Registry No. Cu(sal-*N*-Me)₂, 26194-22-9; Cu(sal-*N*-Et)₂, 26194-23-0; Cu(sal-*N-n*-Pr)₂, 37703-49-4; Cu(sal-*N-i*-Pr)₂, 38956-95-5; Cu(sal-*N-t*-Bu)₂, 36508-99-3.

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