Proton Isotropic Shifts in Pseudo-tetrahedral Nickel(II) and Cobalt(II) Complexes with Salicylaldimines

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^{1}H N.m.r. spectra of pseudo-tetrahedral bis(*N*-alkyl-salicylaldiminato)cobalt(II) complexes have been recorded. Both Fermi-contact shifts and dipolar shifts have been found, by comparison with the analogous nickel(II) complexes, to contribute to the total isotropic shifts. For the latter complexes ^{1}H n.m.r. spectra have been reinterpreted on the basis of magnetic anisotropy data.

PROTON isotropic shifts of ligands attached to paramagnetic metal ions and the mechanisms of delocalization of unpaired spin density onto the ligands are of interest.[1-4] The pseudo-tetrahedral bis(*N*-alkylsalicylaldiminato)cobalt(II) complexes[5] have been investigated using a ^{1}H n.m.r. technique in solution.

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The ^{1}H n.m.r. spectra of the analogous nickel complexes have been reported and discussed,[6] however, anisotropic magnetic data on the bis(*N*-isopropylsalicylaldiminato)nickel(II) complex[7] have allowed us to estimate the contact and dipolar components of the isotropic shifts of this nickel(II) complex. A comparison between the contact shifts of nickel(II) and the isotropic shifts of cobalt(II) complexes has provided some information on the dipolar shift contributions to the total shifts of the latter complexes and on the spin-delocalization mechanisms.

EXPERIMENTAL

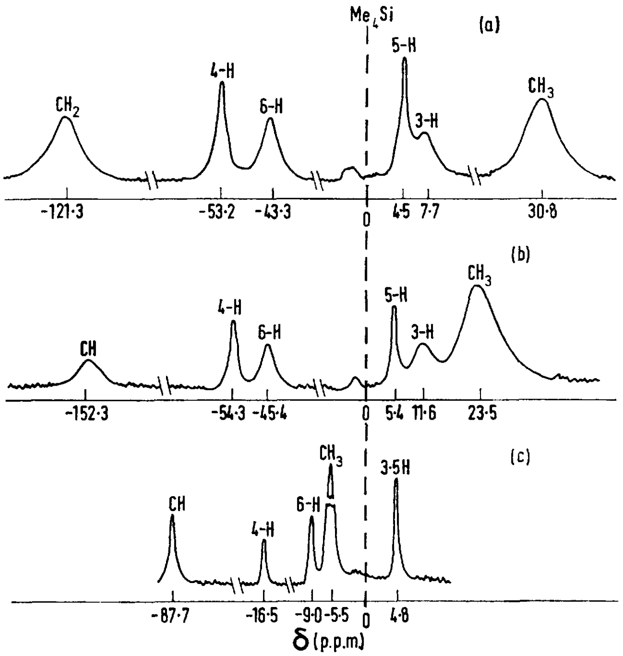
The complexes were prepared by the literature method[8] and analysed satisfactorily for C, H, and N.

^{1}H N.m.r. spectra were recorded with a Varian DA-60-IL spectrometer at 60 MHz and 26 °C. Shifts were calibrated from internal tetramethylsilane. The spectra were recorded both in the HR mode (side-band technique used for calibration) and in the HA mode in internal lock. $CDCl_3$ was used as solvent.

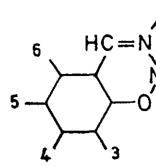
RESULTS AND DISCUSSION

The ^{1}H n.m.r. spectra of the bis(*N*-ethylsalicylaldiminato)cobalt(II) and bis(*N*-isopropylsalicylaldiminato)cobalt(II) complexes in $CDCl_3$ at 26 °C are shown in the Figure, together with the spectrum of the bis(*N*-isopropylsalicyaldiminato)nickel(II) complex for comparison. Aromatic protons have been assigned by recording the spectra of the 3-, 4-, 5-, and 6-chloro- and 5-methyl-substituted complexes. Assignment of the aliphatic protons is obtained from the isotropic shift directions and intensity considerations.[6,8,9] The 5-methyl signal of the cobalt *N*-ethyl-derivative is located at $-31{\cdot}1$ p.p.m. whereas the 5-H signal is at $+4{\cdot}5$ p.p.m. from internal tetramethylsilane. This indicates :[10–12] (i) Fermi contact interactions are strongly operative, (ii) the unpaired-spin density is mostly delocalized into the π-orbital system, as has been suggested for the analogous nickel complexes. The spectrum of the t-butyl-derivative differs from that of the isopropyl-analogue in the position of the aliphatic methyl group, which is at $+6{\cdot}5$ p.p.m. and overlaps the 3-H and 5-H peaks, the other aromatic peaks being at the same position as in the other *N*-alkyl-derivatives to within 3 p.p.m.

The bis(*N*-isopropylsalicylaldiminato)nickel(II) complex, is only 50% tetrahedral in solution.[6,13] The ^{1}H n.m.r. spectra of all the other α-branched alkylamine nickel complexes, which also give rise to planar–tetrahedral equilibria, are quite similar to that of the isopropyl-derivative save for corrections due to the different percentages of diamagnetic species.[6,13] Gerloch and Slade[7] recently published the three molar susceptibilities of the bis(*N*-isopropylsalicylaldiminato)nickel(II) complex which is fully paramagnetic in the solid state.

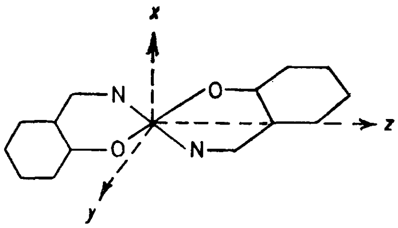


^{1}H N.m.r. spectra of bis(*N*-alkylsalicylaldiminato)metal(II) complexes in $CDCl_3$ at 26 °C (p.p.m. from internal tetramethylsilane)



(a) M = Co, R = Et
(b) M = Co, R = Pr^i
(c) M = Ni, R = Pr^i

The principal molecular susceptibility values, along the directions shown below, are: $\chi_{xx} = 5004$, $\chi_{yy} = 4551$, $\chi_{zz} = 3545$ (c.g.s.u. × 10^6, determined at 300 K). From



the susceptibility values, using equations (1) and (2), the dipolar shifts have been calculated for the limit situations of tumbling rates lower and higher

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than $|g_i - g_j|\beta H h^{-1}$, respectively;[14–18] the molecular tumbling time being much larger than the electronic relaxation time.[16,18]

$$\frac{\Delta\nu_i^{\mathrm{dip}}}{\nu} = \frac{1}{2N}\,[D_1G_i(\theta, r) + B_1H_i(\theta, \psi, r)] \tag{1}$$

$$\frac{\Delta\nu_i^{\mathrm{dip}}}{\nu} = \frac{1}{15N}\,[D_2G_i(\theta, r) + \tfrac{3}{2}B_2H_i(\theta, \psi, r)] \tag{2}$$

where: $D_1 = \frac{1}{3}(2\chi_{zz} - \chi_{xx} - \chi_{yy})$, $B_1 = \chi_{yy} - \chi_{xx}$, $D_2 = 3\chi_{zz} - \frac{3}{2}(\chi_{xx} + \chi_{yy}) + \frac{1}{2}\chi_{zz}^{\frac{1}{2}}(\chi_{xx}^{\frac{1}{2}} + \chi_{yy}^{\frac{1}{2}}) - (\chi_{xx}\chi_{yy})^{\frac{1}{2}}$, $B_2 = 3(\chi_{yy} - \chi_{xx}) + \chi_{zz}^{\frac{1}{2}}(\chi_{yy}^{\frac{1}{2}} - \chi_{xx}^{\frac{1}{2}})$, $G_i(\theta, r) = (1 - 3\cos^2\theta_i)/r_i^3$, $H_i(\theta, \psi, r) = (\sin^2\theta_i \cos 2\psi_i)/r_i^3$. In these formulae r is the modulus of the vector joining the metal atom to the i-th nucleus, θ is the angle made by this vector with the z axis and ψ is the angle between the x axis and the projection of r on the xy plane.

Calculated dipolar and contact shifts for the bis(*N*-isopropylsalicylaldiminato)nickel(II) complex are shown in the Table. These figures show that: (i) a dipolar contribution drastically affects the 6-H isotropic shift, (ii) corrected contact shifts are better alternating than isotropic shifts.

Isotropic, contact, and dipolar shifts [a] for the bis(*N*-isopropylsalicylaldiminato)nickel(II) complex

H	$\Delta\nu^{\mathrm{iso}}$	$\Delta\nu^{\mathrm{dip}}$ [b,c]	$\Delta\nu^{\mathrm{con}}$	$\Delta\nu^{\mathrm{dip}}$ [b,d]	$\Delta\nu^{\mathrm{con}}$
3	23·7	−1·4	25·1	2·6	21·1
4	−19·0	2·3	−21·3	2·2	−21·2
5	23·7	4·5	19·2	3·2	20·5
6	−3·7	8·4	−12·1	6·1	−9·8

[a] All the shifts are expressed in p.p.m. at 26 °C in $CDCl_3$. Isotropic shifts are determined relative to the reported shifts of the bis(*N*-alkyl-salicylaldiminato)zinc(II) complexes:[8] aromatic protons, −7·0 p.p.m. [b] Geometrical factors were calculated using structural data reported in M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Cryst.*, 1964, **17**, 1159: $G_3 = -0{\cdot}00165$, $H_3 = 0{\cdot}00683$, $G_4 = -0{\cdot}00401$, $H_4 = 0{\cdot}00010$, $G_5 = -0{\cdot}00663$, $H_5 = 0{\cdot}00012$, $G_6 = -0{\cdot}01244$, $H_6 = 0{\cdot}00019$ Å^{-3}. [c] Dipolar shifts calculated with equation (1). [d] Dipolar shifts calculated with equation (2).

Until now, for these and other pseudo-tetrahedral nickel complexes,[1,6,17] dipolar shifts have been considered negligible and spin densities calculated according to VB or MO theories have been directly compared to those expected from the isotropic shift values.[1,6,19,20]

The isotropic shift pattern of the cobalt complexes is different from the contact shift pattern of the nickel analogues (see Figure and Table) in that all of the aromatic proton signals of the former complexes are shifted downfield (the 3-H signal to a smaller extent) with respect to the corresponding contact shift values of the latter complexes. Since the G_i factors for protons 4, 5, and 6 have the same sign (the H_i's being negligible; see footnote to the Table), we conclude that the cobalt(II) complexes show evidence of a sizable dipolar shift similar to that shown to be present for other cobalt complexes.[16,17]

Anisotropic magnetic measurements are not available for these complexes, however, assuming that the contact shifts of nickel [*e.g.* those derived from equation (1)] and cobalt are in proportion and applying the ratio method[16–18,21,22] for the idealized axial D_{2d} symmetry,* an estimate of −3, −8, −13, and −24 p.p.m. for the 3-, 4-, 5-, and 6-H dipolar shifts for the cobalt complexes is obtained, leading to recalculated contact shifts of +21·5, −38·8, +22·8, and −14·2 p.p.m. for these protons. The pattern and magnitude of these contact shift values compare quite well with those of nickel; however, the ratios of shifts for nickel and cobalt agree only moderately owing to discrepancy in the 4-H contact shifts. This suggests that: (i) there is a relatively large error in the above calculated figures; (ii) the spin delocalization mechanisms for the two metal complexes are not quite identical.

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* D_{2d} symmetry requires $\chi_{xx} = \chi_{yy}$, that is $B = 0$. The negligibility of the term BH of equations (1) and (2) is justified also from the small H values in comparison with the G values for protons 4, 5, and 6. If the nickel complex is treated as having axial symmetry, *i.e.*, $\chi_{xx} = \chi_{yy} = \frac{1}{2}(5004 + 4551) \pm 4{\cdot}7\%$, the dipolar shifts calculated through equation (2) are: 0·8 (3-H), 1·9 (4-H), 3·1 (5-H), and 5·9 (6-H), p.p.m., in good agreement with the figures obtained without the assumption of axial symmetry.

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