The Ground Electronic State of Quadridentate Salicylaldehyde Schiff Base–Cobalt(II) Complexes in Non- and Weakly Co-ordinating Solvents

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The isotropic shifts in the ^{1}H n.m.r. spectra of *NN'-o*-phenylenebis(salicylideneiminato)cobalt(II) have been observed in solutions of [^{2}H]chloroform, [$^2H_7$]dimethylformamide, [$^2H_6$]dimethyl sulphoxide, and [$^2H_5$]pyridine. The contact shifts derived from the isotropic shifts revealed that the unpaired electron spin is delocalized onto the ligand through the highest-filled π molecular orbital. Formation of more than one species is observed in solutions of [$^2H_7$]dimethylformamide and [$^2H_6$]dimethyl sulphoxide as evidenced by the electronic absorption spectra in the near-i.r. region and by the large deviation from the Curie law of the temperature dependence of the isotropic shifts. The solvent-dependent isotropic shifts indicate that π-spin delocalization in chloroform solution is an intrinsic property of the planar four-co-ordinate complex and that the ground state of the complex is $|^2A_2, yz\rangle$. Co-ordination of weakly co-ordinating solvent molecules changes the ground state to $|^2A_1, z^2\rangle$.

The electronic state of low-spin cobalt(II) complexes with quadridentate ligands has been extensively investigated by many experimental and theoretical techniques. Among cobalt(II) complexes it is well established that porphyrin complexes and vitamin B_{12r} have a ground electronic state with the unpaired electron in the d_{z^2} orbital [1–5] and the orbital occupied by the unpaired electron is not altered by ligation at the fifth and sixth co-ordination sites.[6,7] Cobalt(II) complexes with quadridentate Schiff-base ligands are also of interest as model compounds for dioxygen carriers and vitamin B_{12r} because of their reversible dioxygen addition [8] and Co–C bond formation with organic compounds.[9] For Schiff-base complexes which possess five-co-ordinate structures containing an additional base molecule, it has been established through e.s.r. and other measurements that the ground electronic state is $|^2A_1, z^2\rangle$ with the unpaired electron in the d_{z^2} orbital [10,11] as in the case of the porphyrin complexes. For four-co-ordinate structures, however, the situation is more complicated; the alternative $|^2A_2, yz\rangle$ and $|^2A_1, z^2\rangle$ ground electronic states have been presented and discussed.[10,11] At the present time, on the basis of the relative magnitudes and orientations of the g and A tensors, it is accepted that the ground electronic state of the four-co-ordinate complexes diluted in a single crystal of diamagnetic nickel(II) complexes or in frozen solutions of non-co-ordinating solvents is $|^2A_2, yz\rangle$.[10,11]

Although e.s.r. measurements on these four-co-ordinate cobalt(II) complexes in fluid solutions at room temperature are not possible due to the short electron-spin relaxation time, measurements of the electronic and n.m.r. spectra are possible. In particular, the ^{1}H n.m.r. isotropic shifts of the co-ordinated ligands provide information on the spin distribution in the ligand molecules,[12] which can be used to clarify not only the ground electronic state of the cobalt(II) complexes but also the metal–ligand bonding.

We have previously [13] measured ^{1}H n.m.r. spectra and obtained isotropic shifts for these quadridentate Schiff base–cobalt(II) complexes in chloroform and in pyridine and observed that the isotropic shifts were remarkably dependent on the co-ordinating ability of the solvents. Since the contact shift pattern in chloroform suggested that the unpaired spin was delocalized through the π systems, the ground electronic state in non- and weakly co-ordinating solvents at room temperature seems to be $|^2A_2, yz\rangle$.[13a] In strongly co-ordinating solvents such as pyridine, the spin delocalization in the five-co-ordinate complexes occurred through both σ and π systems.[13b] Therefore, the ground electronic state can be considered to be $|^2A_1, z^2\rangle$, in contrast to the conclusion drawn from analysis of the e.s.r. spectra in frozen solutions.[10,11] In such solvents, however, six-co-ordinate complexes with two solvent molecules are also formed, and believed to possess high-spin ground states.[14,15]

On the other hand, Srivanavit and Brown [16] have reported that the spin delocalization in cobalt(II) complexes in dimethyl sulphoxide (dmso) occurs principally through the π systems, in spite of the fact that the e.s.r. spectra of the complexes in frozen dmso solution strongly suggest the $|^2A_1, z^2\rangle$ ground electronic state.[17] They proposed that the ground electronic state of these complexes at low temperatures and the resultant π-spin delocalization would be caused by the low-lying excited quartet state.[16c] However, another interpretation is also possible: since dmso is a co-ordinating solvent but not so strong as pyridine, the complex in dmso solution would have a five-co-ordinate structure with a dmso molecule at low temperatures, while at high temperatures an equilibrium would exist between the five- and four-co-ordinate complexes, the latter of which contributes to the π-spin delocalization.

The present work aimed to elucidate the ground electronic state of four-co-ordinate cobalt(II) complexes with Schiff bases in various solvents of different co-ordinating abilities. We chose *NN'-o*-phenylenebis(salicylideneiminato)cobalt(II) as the Schiff-base complex, as it is sensitive to axial perturbation, and the ^{1}H n.m.r. spectra of this complex in several solvent systems with different co-ordinating abilities have been recorded and analysed.

Experimental

NN'-o-Phenylenebis(salicylideneiminato)cobalt(II), [Co(salphen)], was synthesized by West's method.[18] Methyl-substituted complexes, which were used for signal assignment in the n.m.r. spectra, were synthesized by the same method using methyl-substituted *o*-phenylenediamines and salicylaldehydes, where the latter were obtained by the Duff reaction.[19] The numbering of the carbon atoms of [Co(salphen)] and definition of the co-ordinate system are shown in Figure 1. The deuterium-labelled solvents, [^{2}H]chloroform, [^{2}H$_7$]dimethylformamide, [^{2}H$_6$]dimethyl sulphoxide, and [^{2}H$_5$]pyridine, for n.m.r. measurements were dried with 3A molecular sieves and evacuated on a vacuum line. The solvents for the measurements of electronic absorption spectra were spectral grade chloroform, dimethylformamide (dmf), and dmso, which were used after the same drying and evacuation procedure.

Proton n.m.r. spectra were recorded on a Bruker CXP 300 FT n.m.r. spectrometer operating at 300.066 MHz and equipped with a variable-temperature probe and a temperature controller which was precalibrated with methanol. Between 1 000 and 10 000 transients were collected by using a 3.0-μs 90° pulse and 125-kHz bandwidths. Tetramethylsilane was used as the internal calibrant. Isotropic shifts (p.p.m.) were referenced to the corresponding diamagnetic nickel(II) complexes; high-frequency shifts are defined as positive. Since the nickel(II) complex became paramagnetic in pyridine, the diamagnetic shifts of the nickel(II) complex in pyridine were replaced with those in dmso solution. Sample solutions for ^{1}H n.m.r. measurements were prepared by dissolving the complexes (*ca.* 3 mg) in degassed solvents (*ca.* 0.4 cm^3) on a vacuum line.

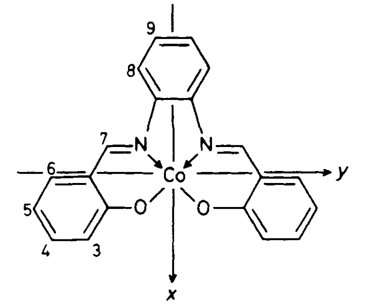

Figure 1. Numbering of the carbon atoms of [Co(salphen)] and definition of the co-ordinate system. The z axis is normal to the xy plane

A Hitachi EPS-3T recording spectrometer was used for the measurements of electronic spectra. E.s.r. spectra were measured on a Varian X-band E112 e.s.r. spectrometer equipped with an Oxford e.s.r. 9 continuous helium-flow cryostat and on a JEOL JES FE1X e.s.r. spectrometer using an insertion-type liquid-nitrogen dewar. Sample solutions for e.s.r. and electronic spectra were prepared by dissolving the cobalt(II) complexes in degassed solvents on a vacuum line.

Results

Proton n.m.r. spectra of [Co(salphen)] in [^{2}H]chloroform, [^{2}H$_7$]dmf, [^{2}H$_6$]dmso, and [^{2}H$_5$]pyridine at 293 K are shown in Figure 2 and isotropic shifts are listed in Table 1. In chloroform solution, we observed marked low-frequency shifts for H^5 and H^7, while large high-frequency shifts were observed for H^8. Relatively small high-frequency shifts were observed for H^3, H^4, and H^9. The isotropic shifts observed in pyridine are quite different from those in chloroform solution; only H^5 showed small low-frequency shifts, but the other protons showed relatively large high-frequency shifts. Such a change in the isotropic shifts of [Co(salphen)] with solvent is similar to that observed for *NN'*-ethylenebis(salicylideneiminato)-cobalt(II), [Co(salen)]. In dmso, the isotropic shifts of

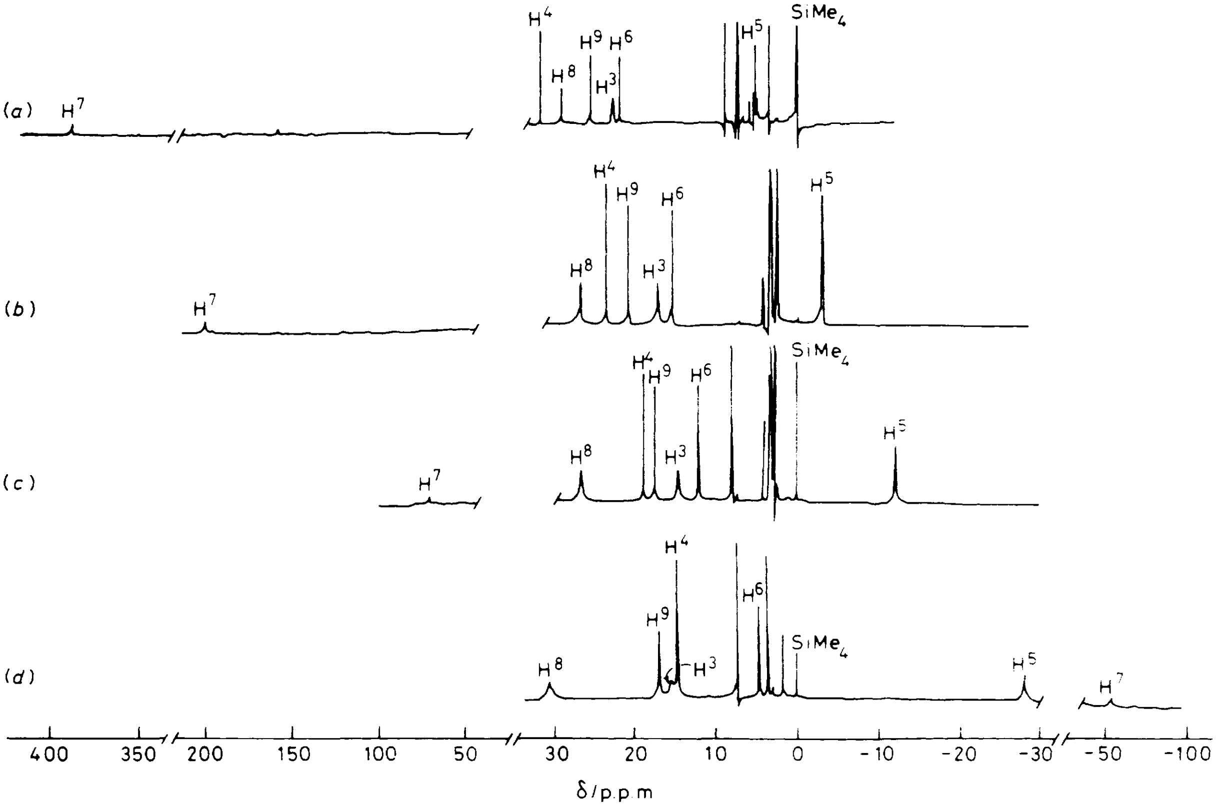

Figure 2. 300-MHz Proton n.m.r. spectra of [Co(salphen)] at 293 K in [^{2}H$_5$]pyridine (*a*), [^{2}H$_6$]dmso (*b*), [^{2}H$_7$]dmf (*c*), and [^{2}H]chloroform (*d*)

Table 1. Proton n.m.r. isotropic shifts * for [Co(salphen)] at 293 K

Position	[^{2}H]Chloroform	[$^2H_7$]dmf	[$^2H_6$]dmso	[$^2H_5$]Pyridine
3	8.24	7.69	10.19	15.84
4	7.41	11.46	16.06	24.35
5	−34.63	−18.73	−9.67	−1.54
6	−2.70	4.45	7.70	14.26
7	−63.2	60.0	194.7	381.3
8	22.89	18.47	18.55	20.94
9	9.74	10.18	13.40	18.12

* Shifts in p.p.m. referenced to the diamagnetic nickel(II) complex in the corresponding solvents. Diamagnetic reference resonances with respect to $SiMe_4$ are: H^3, 7.173; H^4, 7.284; H^5, 6.657; H^6, 7.323; H^7, 8.255; H^8, 7.723; H^9, 7.248 in [^{2}H]chloroform; H^3, 6.909; H^4, 7.355; H^5, 6.677; H^6, 7.655; H^7, 8.976, H^8; 8.231; H^9, 7.364 in [$^2H_7$]dmf; and H^3, 6.893; H^4, 7.329; H^5, 6.674; H^6, 7.611; H^7, 8.898; H^8, 8.152; H^9, 7.352 in [$^2H_6$]dmso. Diamagnetic reference resonances in [$^2H_5$]pyridine were replaced by those in [$^2H_6$]dmso.

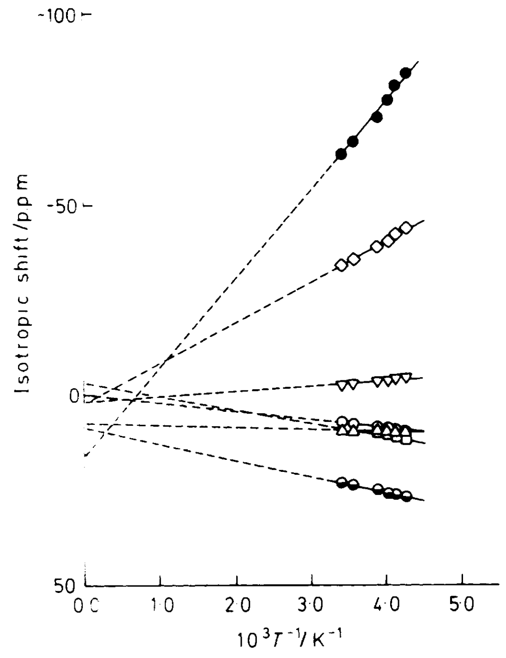

Figure 3. Temperature dependence of the n.m.r. isotropic shifts for [Co(salphen)] in [^{2}H]chloroform [H^3 (□), H^4 (○), H^5 ( ), H^6 (▽), H^7 (●), H^8 (◒), and H^9 (△)]

[Co(salphen)] are not similar to those of [Co(salen)], but rather those of [Co(salen)] in which the ligand contains electron-withdrawing groups. As the co-ordinating ability of the solvent increased, the magnitude of the low-frequency shifts of H^5 and H^7 decreased. In particular, H^7 showed high-frequency shifts except in chloroform and the magnitude of the shifts also increased as the co-ordinating ability increased.

Plots of the isotropic shifts *vs.* the reciprocal of temperature are shown in Figures 3—6. The isotropic shifts for each proton of [Co(salphen)] in chloroform showed a linear variation similar to the Curie law when plotted *vs.* $1/T$ (Figure 3). A linear variation was also found in pyridine but the intercepts at $1/T = 0$ were definitely not zero (Figure 6), an indication of the deviation from the Curie law. Since coalescence phenomena were not observed in the n.m.r. spectra, the non-linear variation does not arise from a change in the exchange rate constants with temperature. Large deviations from the Curie law were found for the isotropic shifts of [Co(salphen)] in dmf and dmso (Figures 4 and 5).

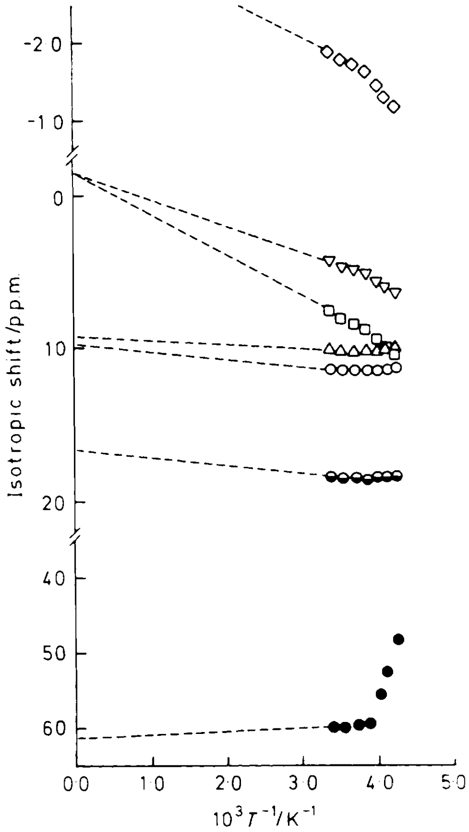

Figure 4. Temperature dependence of the n.m.r. isotropic shifts for [Co(salphen)] in [$^2H_7$]dmf. Key as in Figure 3

The electronic absorption spectra in the near-i.r. region of [Co(salphen)] in chloroform, dmf, and dmso are shown in Figure 7. A relatively sharp absorption peak at about 1 200 nm, characteristic of planar four-co-ordinate cobalt(II) complexes,[20] was observed in chloroform solution. Red shifts and broadening were recognized when the co-ordinating ability of the solvents increased.

The e.s.r. spectra of [Co(salphen)] and [Co(salen)] in frozen dmf solution have been recorded. Although the spectra were not glassy and were partially crystalline and oriented, it was found that two species existed in [Co(salphen)] solution, but only one in [Co(salen)] solution.

Discussion

Spin Delocalization of [Co(salphen)] *in* [^{2}H]*Chloroform.*—Since [Co(salphen)] in chloroform showed a temperature dependence of the isotropic shifts which approximated the Curie law and a characteristic band near 1 200 nm corresponding to planar cobalt(II) complexes, the complex in chloroform seems to exist as a single species with a planar four-co-ordinate structure.[20] Therefore, the isotropic shifts are worth analysing. The dipolar contributions to the isotropic shifts in chloroform were calculated according to equation (1) [where $(\Delta v/v)^{\mathrm{dip.}}$ = dipolar contribution to the isotropic shift, R = distance from the metal to the ligand nucleus, θ = angle between the z axis and the vector, σ joining the

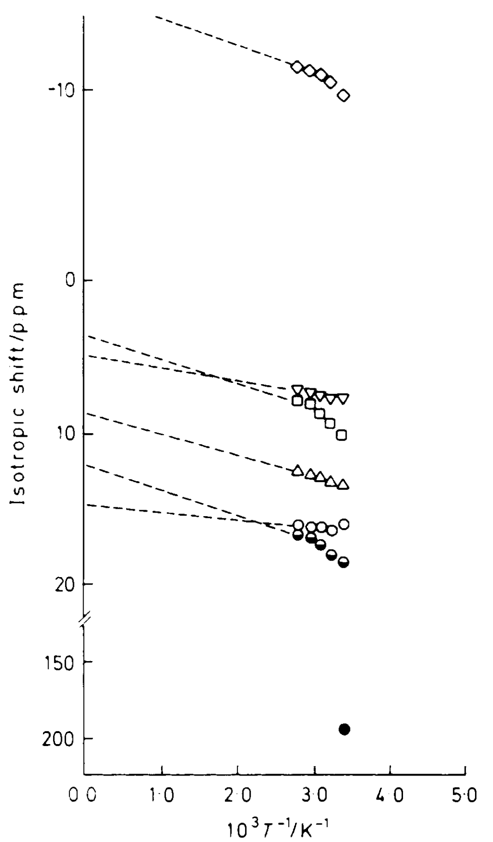

Figure 5. Temperature dependence of the n.m.r. isotropic shifts for [Co(salphen)] in [$^2H_6$]dmso. Key as in Figure 3

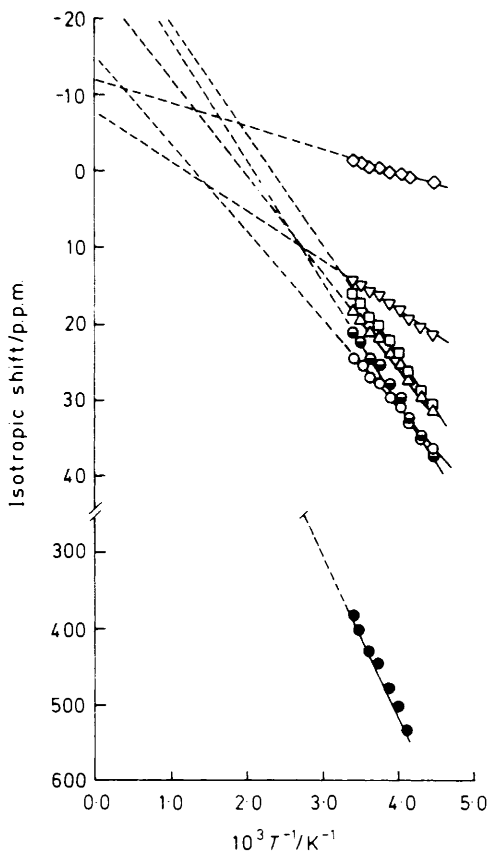

Figure 6. Temperature dependence of the n.m.r. isotropic shifts for [Co(salphen)] in [$^2H_5$]pyridine. Key as in Figure 3

Table 2. Dipolar and contact contributions to the isotropic shifts and hyperfine coupling constants of [Co(salphen)] in [^{2}H]chloroform at 293 K

	Shift/p.p.m.		
Position	Dipolar *	Contact	a_N/MHz
3	19.09	−10.85	−0.330
4	−1.35	8.76	0.267
5	−6.73	−27.90	−0.849
6	−12.99	10.29	0.313
7	−3.5	−59.7	−1.815
8	24.38	−1.49	−0.045
9	16.25	−6.51	−0.198

* The g values used in the calculation are $g_{xx} = 3.845$, $g_{yy} = 1.73$, and $g_{zz} = 1.75$ taken from ref. 21. The structural parameters are taken from ref. 22.

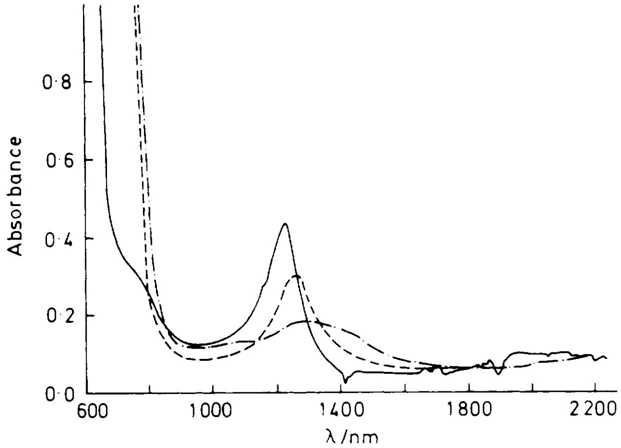

Figure 7. Absorption spectra of [Co(salphen)] in chloroform (——), dmf (- - - -), and dmso (— • — • —) at room temperature

metal and the ligand nucleus, and Ω = angle between the x axis and the projection of σ in the xy plane],[12] using the reported g values [21] and structural parameters [22] (Table 2).

$$(\Delta\nu/\nu)^{\text{dip.}} = [\beta^2S(S+1)/18kTR^3][(g_{xx}^2 + g_{yy}^2 - 2g_{zz}^2)(1 - 3\cos^2\theta) + 3(g_{xx}^2 - g_{yy}^2)\sin^2\theta\cos2\Omega] \quad (1)$$

$$a_N = 9h\gamma_N kT(\Delta\nu/\nu)^{\text{con.}}/\beta S(S+1)(g_{xx} + g_{yy} + g_{zz}) \quad (2)$$

Table 2 shows contact shifts calculated by subtracting the dipolar shifts from the isotropic shifts, and hyperfine coupling constants, a_N, calculated from equation (2) [where $(\Delta\nu/\nu)^{\text{con.}}$ = contact shift and γ_N = gyromagnetic ratio of the nucleus] [12] by using the resultant contact shifts. Comparing the contact shifts with dipolar shifts, the main contribution to the isotropic shift of H^8 comes from the dipolar interaction whereas that of H^7 comes from the contact interaction. The significantly negative values found for the hyperfine coupling constants are expected since the unpaired spin is delocalized through the highest-filled π molecular orbital of the salicylaldehyde Schiff-base ligands. Spin densities at the protons were derived from the values of the hyperfine coupling con-

Table 3. Observed and calculated spin densities at the protons of [Co(salphen)]

Position	Observed	Calculated *	
		$|^2A_2, yz\rangle$	$|^2A_1, z^2\rangle$
3	−0.000 23	−0.000 25	−0.000 22
4	0.000 19	0.000 39	−0.000 30
5	−0.000 60	−0.000 81	−0.000 88
6	0.000 22	0.000 69	0.000 81
7	−0.001 28	−0.000 28	−0.001 10
8	−0.000 03	−0.000 02	0.001 52
9	−0.000 14	−0.000 24	−0.001 41

* By MINDO/3.[23]

stants and were compared with those calculated theoretically by the MINDO/3 method [23] on the assumption that the ground state is $|^2A_2, yz\rangle$ or $|^2A_1, z^2\rangle$ (Table 3). The characteristic feature of the observed spin density is the alternation in sign at the benzene-ring protons and the large negative value at H^7. The $|^2A_1, z^2\rangle$ ground state resulted in much different spin densities when compared to the observed ones; the alternation in signs was not reproduced and large differences between observed and calculated spin densities were found at the protons of the phenylene bridge. Excellent agreement was found between the experimental and calculated spin densities based on the $|^2A_2, yz\rangle$ ground state, except for the large difference in spin density at H^7. Therefore, π-spin delocalization is established for the complex in chloroform solution. This feature was also observed for [Co(salen)] and related complexes in solutions of non-co-ordinating solvents,[13a] and for some complexes in weakly co-ordinating solvents.[16]

The Ground Electronic State of Planar Four-co-ordinate Schiff Base–Cobalt(II) *Complexes*.—The ground electronic state of planar four-co-ordinate Schiff base–cobalt(II) complexes has been the subject of controversy.[10,11] Among many proposals, the $|^2A_1, z^2\rangle$ and $|^2A_2, yz\rangle$ states are likely.[10,11] As to the determination of the ground electronic state, e.s.r. is the most powerful method, and n.m.r., electron nuclear double resonance, and other measurements complement it. The fact that $g_{yy} < g_{zz} < 2.0$ and the relative values of the hyperfine coupling constants strongly support the $|^2A_2, yz\rangle$ ground state.[10,11] The cobalt(II) complexes diluted in a single crystal of the corresponding nickel(II) complexes and in frozen solutions of non-co-ordinating solvents have $g_{yy} < g_{zz} < 2.0 < g_{xx}$ and $A_{yy}, A_{zz} << A_{xx}$ and therefore are suspected to have the $|^2A_2, yz\rangle$ ground state.[10] This is supported by photoelectron spectroscopy [24] and recent electron nuclear double resonance studies [25,26] as well as theoretical studies.[10,11,27]

Although the ground state of the complexes in non-co-ordinating solid matrices is now established, that in fluid solution is still uncertain. Since the e.s.r. spectra of the cobalt(II) complexes in fluid solutions cannot be measured, spin delocalization derived from the contact shifts in the n.m.r. spectra is the most informative in determining the ground electronic state of the complexes. The $|^2A_2, yz\rangle$ ground state is also supported by the spin-delocalization patterns of the complexes in solutions of non-co-ordinating solvents.

Spin delocalization through π orbitals is now undoubtedly confirmed but several mechanisms are possible. (1) The complex has the $|^2A_2, yz\rangle$ ground state where the unpaired electron resides in the molecular orbital which comes from linear combination of the highest-filled π molecular orbital of the ligand molecule and the d_{yz} orbital of the cobalt(II) ion.[13a] (2) The complex has the $|^2A_1, z^2\rangle$ ground state and the stepped or umbrella conformation, the unpaired electron in the d_{z^2} orbital being delocalized over the ligand π orbital through non-zero overlap between them.[16a,b] (3) The electronic state of the complex is the quantum-mechanically mixed state between the $|^2A_1, z^2\rangle$ and $|^2A_2, yz\rangle$ states through spin–orbit or configuration interaction, where the former gives positive spin density at H^5 and the latter negative. (4) The complex has the $|^2A_1, z^2\rangle$ ground state, but the low-lying excited quartet states are accessible.[16c]

Since the observed spin density at H^5 of [Co(salen)] and [Co(salphen)] in chloroform is negative, mechanism (3) through the spin–orbit interaction is precluded. Our experimental results show that base co-ordination brought about a decrease in π-spin delocalization. On the other hand, distortion from the planar structure to the stepped or umbrella conformation is facilitated by the co-ordination of an additional base molecule.[28] In the case of mechanism (3) through the configuration interaction, base co-ordination would result in a lowering of the molecular symmetry of the complex and a consequent increase in π-spin delocalization owing to mixing of the d_{z^2} and d_{yz} orbitals. This is not observed. In the case of mechanism (2), base co-ordination would increase the direct overlap of d_{z^2} and ligand π orbitals, which is not in accord with observation. Therefore, neither mechanism (2) nor (3) through the configuration interaction can explain the origin of the π-spin delocalization. As the ligand field of the axial base increases, the energy levels of the excited quartet states are lowered and become closer to that of the ground state.[6,7,10,27] Consequently, mechanism (4) is also unlikely. The mechanism (1) is quite reasonable and is supported by the agreement between the calculated and observed spin densities (Table 3). Therefore, the ground state of the Schiff-base complexes in the non-co-ordinating solvents is $|^2A_2, yz\rangle$ at room temperature [13a] as well as in frozen solutions of non-co-ordinating solvents at low temperatures.[10,11]

The Structure and Electronic State of [Co(salphen)] *in Weakly Co-ordinating Solvents*.—In weakly co-ordinating solvents it is difficult to determine the electronic state of [Co(salphen)] because the solvent molecules are weakly co-ordinated and the bonding is not stable enough to maintain the co-ordination structure over a wide temperature range. One of the species found in the e.s.r. spectra of [Co(salphen)] in frozen dmf solution is the four-co-ordinate complex with $|^2A_2, yz\rangle$ as ground state and the other may be the five-co-ordinate complex with $|^2A_1, z^2\rangle$ as ground state. On the other hand, [Co(salen)] in the same solution is solely the four-co-ordinate complex with the $|^2A_2, yz\rangle$ ground state. This difference arises from the acidity of the complexes. The co-existence of more than one species was revealed by the electronic absorption spectrum of [Co(salphen)] in the near-i.r. region at room temperature as a red shift and broadening of the peak, characteristically found in chloroform solution at *ca.* 1 200 nm (Figure 7);[25] also by the isotropic shifts which deviated considerably from the Curie law (Figure 4).

In frozen dmso solution, [Co(salphen)] shows an e.s.r. spectrum corresponding to the five-co-ordinate complex with the $|^2A_1, z^2\rangle$ ground state. In addition, the electronic absorption spectrum in dmso solution at room temperature is also different from that in chloroform (Figure 7). The isotropic shifts deviated from the Curie law as found in dmf solution, so that the complex cannot exist solely as a single species, *i.e.* the five-co-ordinate complex at room temperature.

Analysis of the isotropic shifts by neglecting the large deviation from the Curie law gives the π-spin delocalization for the complexes in weakly co-ordinating solvents. The complex [Co(salen)] in dmso shows an e.s.r. spectrum corresponding to the $|^2A_1, z^2\rangle$ ground state at low temperatures.[11] These facts led to a great confusion in estimating the ground state of four-co-ordinate cobalt(II) complexes with quadridentate Schiff bases. Such complexes act as Lewis acids towards solvent molecules, and their acidity increases when electron-withdrawing substituents such as nitro-groups are introduced into the ligand. When cobalt(II) complexes which are relatively strong Lewis acids are dissolved into weakly co-ordinating solvents such as dmso a five-co-ordinate complex with the $|^2A_1, z^2\rangle$ ground state forms, as confirmed by e.s.r. at low temperatures.[17] However, since [Co(salen)] is a rather weak Lewis acid in this series of complexes, the co-ordination of solvent molecules is not significant. Generally, the electronic state at room temperature or above is not necessarily the same as that determined at low temperatures. The complex [Co(salphen)], which is a stronger acid than [Co(salen)], is much more susceptible to axial co-ordination [15] and easily forms a five-co-ordinate complex with a solvent molecule and, in fact, showed distinct solvent-dependent isotropic shifts as already described. When substituted by a methyl group at the ethylene bridge, the isotropic shifts [16b] of [Co(salen)] showed only a slight solvent effect even when the solvent was varied from chloroform to dmso, because of steric hindrance of the methyl groups of the complex to axial co-ordination.

The solvent dependence of the isotropic shifts (*e.g.* Figure 2 and Table 1) clearly indicates that [Co(salphen)] in weakly co-ordinating solvents does not always exist as a single species, *i.e.* the four-co-ordinate complex, but as a mixture of the four- and five-co-ordinate complexes. Another species must also be taken into account in some cases.[14,15] In addition to the existence of more than one species, the amount of the five-co-ordinate complex retaining a solvent molecule changes with temperature and affects the apparent isotropic shifts because of the effect on the bond length between the metal ion and solvent molecule. This is the reason why the isotropic shifts of [Co(salen)] are almost the same in chloroform and in dmso [16b] in spite of the fact that the e.s.r. spectra are quite different in these solvent systems.

On the other hand, Srivanavit and Brown [16c] proposed another explanation for the π delocalization in dmso. Since the ground state of [Co(salen)] in frozen dmso solution is established to be $|^2A_1, z^2\rangle$ from e.s.r. measurements by Ochiai,[17] Srivanavit and Brown [16c] suggested that this ground state may remain even at room temperature, although spin delocalization into π orbitals on the ligand was observed from the n.m.r. spectra.[16b,c] They attributed this π-spin delocalization to the contribution of the excited quartet states,[16c] and proposed that the ground state of this complex in chloroform would also be $|^2A_1, z^2\rangle$ since the isotropic shifts in chloroform resemble those in dmso solution.[16b] The drastic change in the isotropic shifts, especially of H^7, with the substituents in the ligand system, was ascribed to the variation in the energy differences between the $|^2A_1, z^2\rangle$ ground state and the excited quartet states. Here, they included the case where the ground state changes from the doublet to the quartet state. However, solvent-dependent isotropic shifts were not observed, since the solvent was usually restricted to dmso. Therefore, the experimental results indicating the co-existence of four- and five-co-ordinate complexes in weakly co-ordinating solvents negates Srivanavit and Brown's version of mechanism (4): the effect of the ligand substituents is only to make one of the quartet states the ground state, without changing the four-co-ordinate structure. The isotropic shifts can satisfactorily be explained by an equilibrium between the four- and five-co-ordinate species, or in some cases,[14,15] by an equilibrium between the five- and six-co-ordinate species.

The Ground Electronic State of the Schiff Base–Cobalt(II) *Complexes in Basic Solvents*.—When the acidity of the complexes and/or the basicity of the solvent molecule increases, high-spin ground states are easily generated,[14,15] so that the situation in basic solvents is somewhat different from that in non- and weakly co-ordinating solvents. Previously,[14,15] we reported that cobalt(II) complexes with this ligand system adopt spin-quartet ground states in solutions containing N-heterocyclic bases, and the high-spin species have six-co-ordinate structures with co-ordination of N-heterocyclic bases at both the fifth and sixth co-ordination sites. The degree of the formation of the high-spin species increases as the basicity of the additional ligands increases.[14,15] When electron-withdrawing substituents such as nitro-groups are introduced into the ligand of [Co(salen)] or [Co(salphen)] the acidity of the complexes increases appreciably. In this case, Srivanavit and Brown also regarded the nitro-substituted complexes as high-spin complexes with four-co-ordinate structures. E.s.r. measurements revealed that in dmf, nitro-substitution at position 3 resulted in the high-spin ground state, not at position 5.[15] Unfortunately, the nitro-derivatives show poor solubility in non-co-ordinating solvents. Therefore, it is difficult to determine whether the high-spin ground state is intrinsic to the four-co-ordinate complexes or arises from the formation of five- and/or six-co-ordinate species.

Conclusions

The complex [Co(salphen)] showed a distinct solvent dependence of the isotropic shifts in the n.m.r. spectra, whereas [Co(salen)] was less sensitive to the solvent. This sensitivity depends on the acidity of the complex: as the acidity increases, the amount of the five-co-ordinate complex with a solvent molecule can increase and this is reflected as a drastic change in the isotropic shifts.

The solvent dependence of the isotropic shifts of [Co(salphen)] indicates that this complex undergoes appreciable co-ordination by solvent molecules even in weakly co-ordinating solvents and forms a five-co-ordinate complex in addition to the four-co-ordinate complex, which hinders the analysis of the isotropic shifts. Since the amount of each species changes with temperature, e.s.r. results at low temperatures do not necessarily give useful information on the electronic state at room temperature. This is true for [Co(salen)] in dmso: the e.s.r. spectrum implies the $|^2A_1, z^2\rangle$ ground state, but the n.m.r. spectrum reveals apparent spin delocalization through the highest-filled π molecular orbital, indicating $|^2A_2, yz\rangle$ as ground state. This discrepancy can be explained in terms of a change in the co-ordination number of the complex: five-co-ordinate at low temperatures and predominantly four-co-ordinate above room temperature, due to dissociation of the solvent molecules.

On the basis of the facts that chloroform possesses the least ability to co-ordinate to the fifth site of the complex among the solvents studied, the characteristic band of the complex in the electronic spectrum, and the temperature dependence of the isotropic shifts which approximates to the Curie law, implying the existence of a single species and π-spin delocalization in the ligand, the ground state of [Co(salphen)] in chloroform at room temperature is concluded to be $|^2A_2, yz\rangle$.

Similar π-spin delocalization observed for the quadridentate Schiff base–cobalt(II) complexes seems to be an intrinsic property of the four-co-ordinate complex in this ligand system. Consequently, it is natural to conclude that the cobalt(II) complexes with planar four-co-ordinate structures have $|^2A_2, yz\rangle$ ground states. The nitro-derivatives are exceptions whose ground state is still under investigation.

Moreover, it has been revealed that the isotropic shift of H^7 can be regarded as an indicator of the ground state of the complexes: a relatively large low-frequency shift for H^7 corresponds to the $|^2A_2, yz\rangle$ ground state, whereas a high-frequency shift refers to the formation of species with different ground states

We would stress that careful attention should be paid to the choice of solvent when studying the electronic state of cobalt(II) complexes.

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