The High-spin Ground State of Quadridentate Salicylaldehyde Schiff-base Complexes of Cobalt(II) in *N*-Heterocyclic Solvents †

Kouto Migita *
School of Education, Yamaguchi University, Yamaguchi, Yamaguchi 753, Japan
Makoto Chikira
Department of Industrial Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112, Japan
Masamoto Iwaizumi
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan

Formation of species with a high-spin ground state ($S = \frac{3}{2}$) has been observed by e.s.r., n.m.r., and magnetic susceptibility measurements for quadridentate salicylaldehyde Schiff-base complexes of cobalt(II) in solution containing *N*-heterocyclic bases. It was found that a bidentate base, 1,10-phenanthroline, also gave similar high-spin species. The high-spin species were shown to be the base adducts having a six-co-ordinate structure. Magnetic susceptibility measurements revealed that 22% of *NN'*-ethylenebis(salicylideneiminato)cobalt(II) exists as the high-spin base di-adduct in pyridine at 295 K. The thermodynamic parameter ΔH° for the formation of this high-spin species was found to be -4.25×10^3 J mol^{-1}. The amount of the high-spin species increased as the temperature decreased. The analysis of the isotropic shifts in ^{1}H n.m.r. revealed that the unpaired electron spins in the high-spin species mainly delocalize through σ orbitals.

It is widely known that many quadridentate planar Schiff-base complexes of cobalt(II) react reversibly with molecular oxygen both in the solid state and in basic solvents.[1] Although there have been many investigations about the mechanism of oxygenation [2] and the ground state electronic configuration of these complexes,[3-7] most of the investigations have dealt almost exclusively with the low-spin ground state ($S = \frac{1}{2}$). There are several reports in which the high-spin state ($S = \frac{3}{2}$) was proposed for cobalt(II) complexes with quadridentate planar ligands at room temperature.[8-11] However, most of these complexes have a low-spin ground state with low-lying excited high-spin states, and the magnetic moment of these complexes is reduced to the value of the low-spin complexes at low temperatures.[10,11]

So far, little is known about the species with a high-spin ground state in solution,[8,9] although they have been expected to play some role in reaction with organic halides [10,12] or molecular oxygen. In the previous communication,[13] we reported that an appreciable amount of the high-spin species of cobalt(II) complexes is formed in *N*-heterocyclic solvents such as pyridine and its methyl derivatives. The high-spin state reported was undoubtedly the ground state of the complex, because the e.s.r. signal of the high-spin species was observed at an extremely low temperature (4.2 K). Recently, we found that the high-spin species were also formed in solutions not only with unidentate *N*-heterocyclic bases but also with bidentate bases such as 1,10-phenanthroline.

In order to investigate quantitatively the formation of high-spin species in *N*-heterocyclic solvents, magnetic susceptibility measurements were carried out on complexes in different solvents. The temperature dependence of the magnetic susceptibility gives valuable information on the change in the electronic state of the complexes as well as on the equilibrium between the low-spin and high-spin species. Isotropic shifts in the ^{1}H n.m.r. spectra for the complexes also provide valuable information on the mechanism of the spin transfer, which can afford an insight into a specific electronic state of the cobalt(II) complexes.

In this paper, we discuss extensively the formation and structure of the high-spin species of cobalt(II) complexes with various quadridentate salicylaldehyde Schiff bases.

Experimental

The cobalt(II) complexes were prepared according to the methods reported previously.[14,15] Methyl-substituted salicylaldehydes used in the preparations were obtained by the Duff reaction.[16] Imidazole and 1,10-phenanthroline were purified by sublimation *in vacuo*. Pyridine, *NN*-dimethylformamide (dmf), dimethyl sulphoxide (dmso), chloroform, and methylene dichloride were spectral grade and dried with 3A molecular sieves. Reagent grade aniline and 1-methylimidazole were dried with 3A molecular sieves. Reagent grade 2-, 3-, and 4-methylpyridine were dried with sodium hydroxide and distilled. All of the solvents were kept *in vacuo*. Sample solutions for e.s.r., n.m.r., and magnetic susceptibility measurements were prepared by dissolving these cobalt(II) complexes in degassed solvents in a vacuum line.

E.s.r. spectra were measured on a Hitachi model 771 *X*-band e.s.r. spectrometer using an insertion type liquid-nitrogen and liquid-helium dewar [17] and on a Varian *X*-band E112 e.s.r. spectrometer equipped with an Oxford e.s.r. 9 continuous helium flow cryostat. N.m.r. spectra were measured with a JEOL PS-100 n.m.r. spectrometer which was operated at 100 MHz and equipped with a variable temperature probe and a temperature controller. $SiMe_4$ was used as an internal reference. Isotropic shifts are referenced against the corresponding free ligands.

Magnetic susceptibility measurements of the solutions were determined using the Evans method through n.m.r. measurements.[18] Diamagnetism of the ligands was corrected using the reported value, -182×10^{-6} cm^3 mol^{-1}, for *NN'*-ethylenebis(salicylideneiminate) and the calculated value, -205.5×10^{-6} cm^3 mol^{-1}, for 1,1-dimethylethylenebis(salicylideneiminate) with Pascal's constants.[19] The density of the solutions used for the magnetic susceptibility determination was corrected for temperature using equation (1) [20] where t is the temperature in centrigrade and α is the expansion coefficient.

$$\rho(t) = \rho(15)[1 - \alpha(t - 15)] \qquad (1)$$

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† *Non-S.I. unit employed:* B.M. = 0.927×10^{-23} A m^2.

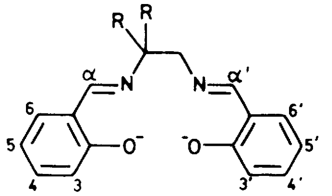

Figure 1. Numbering of the carbon atoms of salen^{2-} (R = H) and saldmen^{2-} (R = Me)

The values of density at 15 °C, $\rho(15)$/g cm^{-3}, and the expansion coefficient, α, are as follows: pyridine, $\rho(15) = 0.987\,83$, $\alpha = 0.001\,03$; aniline, $\rho(15) = 1.02613$, $\alpha = 0.000\,84$; chloroform, $\rho(15) = 1.498\,45$, $\alpha = 0.001\,28$; and 1-methylimidazole, $\rho(15) = 1.027\,89$, $\alpha = 0.000\,61$.

Abbreviations for the ligands used in this paper are as follows: salen^{2-} is the dianion of *NN'*-ethylenebis(salicylideneimine); 3,3'-Me$_2$-salen^{2-}, 4,4'-Me$_2$-salen^{2-}, 5,5'-Me$_2$-salen^{2-}, α,α'-Me$_2$-salen^{2-}, 3,3'-(NO$_2$)$_2$-salen^{2-}, 5,5'-(NO$_2$)$_2$-salen^{2-}, and 3,3'-(MeO)$_2$-salen^{2-} are the 3,3'-dimethyl, 4,4'-dimethyl, 5,5'-dimethyl, α,α'-dimethyl, 3,3'-dinitro, 5,5'-dinitro, and 3,3'-dimethoxy derivatives of salen^{2-}, respectively; salphen^{2-} is the dianion of *NN'-o*-phenylenebis(salicylideneimine); saldmen^{2-} is the dianion of 1,1-dimethylethylenebis(salicylideneimine). Numbering of the carbon atoms of salen^{2-} and saldmen^{2-} is shown in Figure 1.

Results

E.S.R. Spectra.—An intense e.s.r. signal observed near 300 mT for the frozen pyridine solution of [Co(salen)] at 77 K [Figure 2(*a*)] has been attributed to the well known low-spin base mono-adduct.[21,22] Sharp peaks found around 200 and 350 mT are characteristic of a planar low-spin four-co-ordinate cobalt(II) complex. When the solution was cooled to 4.2 K, a broad signal around 150 mT was intensified [Figure 2(*c*)]. This signal was assigned to a species with a high-spin ($S = \frac{3}{2}$) ground state from its g value (*ca.* 4).[13] Cooling to 4.2 K lengthened the electron spin-relaxation time of the high-spin species sufficiently to be clearly detected in the e.s.r. spectrum. Unfortunately, any ^{59}Co hyperfine splitting was not observed in the spectrum of the high-spin species. On cooling, e.s.r. signals of both the low-spin pyridine mono-adduct and the planar four-co-ordinate complex were partially saturated even at a few milliwatts of the microwave power.

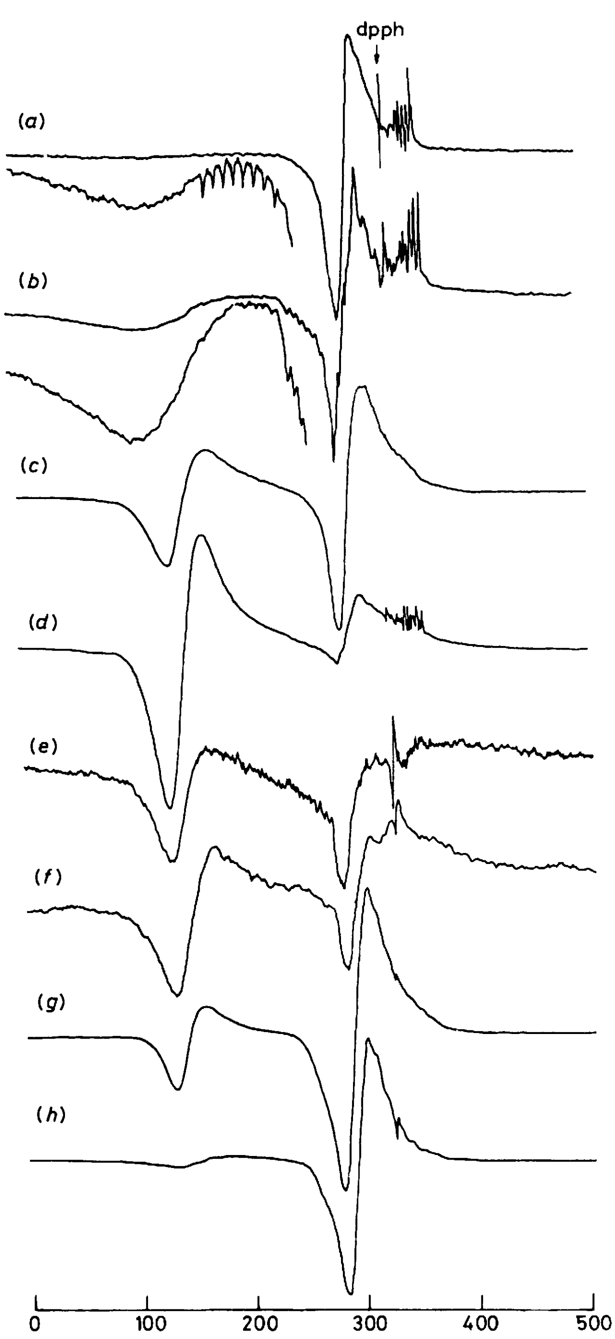

Figure 2. E.s.r. spectra of salicylaldehyde Schiff-base complexes of cobalt(II) in frozen pyridine solution: (*a*) [Co(salen)] and (*b*) [Co(3,3'-Me$_2$-salen)] at 77 K; (*c*) [Co(salen)], (*d*) [Co(3,3'-Me$_2$-salen)]; (*e*) [Co(4,4'-Me$_2$-salen)], (*f*) [Co(5,5'-Me$_2$-salen)], (*g*) [Co(α,α'-Me$_2$-salen)], and (*h*) [Co(saldmen)] at 4.2 K; dpph = diphenylpicrylhydrazyl

The high-spin signal is also observed for pyridine solutions of the cobalt(II) complexes with substituted salicylaldehyde Schiff bases [Figure 2(*c*)—(*h*)]. As is shown in Figure 2(*c*)—(*h*), the relative intensity of high-spin to low-spin signals varies from complex to complex; the high-spin signal is barely observed for [Co(saldmen)] but is intensely observed for [Co(3,3'-Me$_2$-salen)]. For the complexes with a phenylene-bridged ligand such as salphen^{2-}, the high-spin signal is more intense than those with ethylene-bridged ligands. Furthermore, the methyl substituent at the α position or at the ethylene bridge inhibited formation of the high-spin species, while the substituents at position 3 increased the high-spin product. Substitution with electron-withdrawing nitro-groups at position 3 of [Co(salen)] gave both high-spin and low-spin signals simultaneously in dmf solution even when no *N*-heterocyclic bases were added, whereas substitution at position 5 did not produce the high-spin signal in dmf solution without additional bases. The addition of excess base to the dmf solution of the nitro-substituted complexes resulted in the increase of the high-spin signal and the complete disappearance of the low-spin signal.

When the isolated pyridine mono-adduct of [Co(salen)] was dissolved in chloroform or toluene, no high-spin signal was observed but the typical e.s.r. signal for low-spin cobalt(II) complexes was detected. A titration of [Co(salphen)] with imidazole in methylene dichloride solution showed a continuous change in e.s.r. spectra. Only the low-spin signal of the base mono-adduct was observed in the equimolar solution

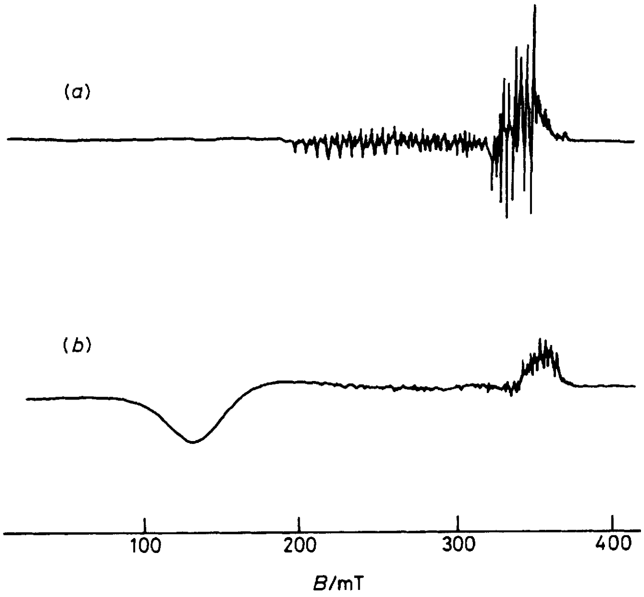

Figure 3. E.s.r. spectra of the frozen dmf solution of [Co(3,3′-Me_2-salen)] at 4.2 K. (*a*) With no additional base; and (*b*) with a large excess of 1,10-phenanthroline

of [Co(salphen)] and imidazole. With an increase in the relative concentration of imidazole, the high-spin signal appeared and intensified, whereas the low-spin signal decreased. The solution containing a large excess of imidazole showed only the high-spin signal, and the low-spin signal completely disappeared.

On co-ordination of bidentate bases such as 1,10-phenanthroline to the planar complexes, the cobalt(II) ions suffer six-co-ordination through distortion of the quadridentate Schiff bases from the planar structure. The frozen dmf solution of [Co(3,3′-Me_2-salen)] showed many sharp e.s.r. signals in the range 200—380 mT [Figure 3(*a*)], which are specific to the planar four-co-ordinate low-spin cobalt(II) complexes. Excessive addition of 1,10-phenanthroline to the dmf solution gave rise to an intense e.s.r. signal due to a high-spin species [Figure 3(*b*)]. It should be noted that no e.s.r. signal corresponding to the low-spin base mono-adduct was observed. The sharp signals due to the low-spin four-co-ordinate species were still observed at the same position but with increased linewidths. Addition of 2,2′-bipyridine did not give any high-spin signal nor any signal of the low-spin base mono-adduct, but instead gave only the signal due to the four-co-ordinate complex with no axial ligand.

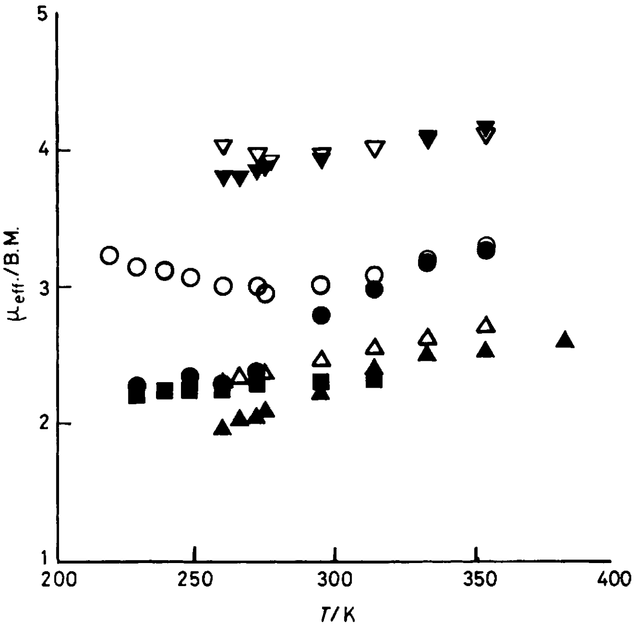

Figure 4. Temperature dependence of the magnetic moments for [Co(salen)] and [Co(saldmen)]. [Co(salen)] in aniline (△), pyridine (○), and 1-methylimidazole (▽); [Co(saldmen)] in chloroform (■), aniline (▲), pyridine (●), and 1-methylimidazole (▼)

Table. Temperature dependence of the magnetic susceptibilities[a] ($\chi_{obs.}$, χ_L, and χ_H), the mole fraction of the high-spin species, y_H, and the equilibrium constant, *K*, between the high-spin and low-spin species of [Co(salen)] in pyridine solution

T/K	$\chi_{obs.}$[b]	χ_L[c]	χ_H[d]	y_H	*K*
219	5.94	2.38	13.2	0.330	0.492
229	5.38	2.32	12.6	0.298	0.425
239	5.05	2.26	12.1	0.284	0.397
248	4.71	2.23	11.6	0.264	0.359
260	4.39	2.19	11.1	0.248	0.329
272	4.15	2.18	10.6	0.234	0.306
295	3.84	2.19	9.77	0.219	0.280
314	3.78	2.25	9.18	0.221	0.284

[a] The notation of $\chi_{obs.}$, χ_L, and χ_H is given in the text; values are expressed in units of 10^{-3} cm^3 mol^{-1}. [b] This work. [c] Ref. 23. [d] Ref. 24.

Magnetic Susceptibilities and Magnetic Moments.—The magnetic moments of [Co(salen)] and [Co(saldmen)] are plotted against temperature for several solvent systems in Figure 4. It is seen that each complex in the non-co-ordinating or weakly-co-ordinating solvents such as chloroform and aniline has a magnetic moment corresponding to low-spin cobalt(II) complexes at low temperatures,[8,10,23] but the moment increases considerably at high temperatures. When a strong basic solvent such as 1-methylimidazole was used, the cobalt(II) complexes showed large magnetic moments at low temperatures, and the value of [Co(salen)] was larger than that of [Co(saldmen)]. [Co(salen)] in pyridine solution showed larger magnetic moments than the ordinary low-spin cobalt(II) complexes over the entire temperature range observed (219—354 K). On the other hand, the magnetic moments of [Co(saldmen)] in pyridine solution are close to those of the ordinary low-spin species at low temperatures although the value increased exceedingly as the temperature increased.

By using the observed magnetic susceptibilities, the mole fraction of the high-spin species, y_H, can be calculated using equation (2) at different temperatures and are shown in the

$$y_H = (\chi_{obs.} - \chi_L)/(\chi_H - \chi_L) \qquad (2)$$

Table, where $\chi_{obs.}$ is the observed value of the magnetic susceptibility for the pyridine solution of [Co(salen)], χ_L is the value of the low-spin species extracted from the reported values for the single crystal of the pyridine mono-adduct of [Co(salen)],[23] and χ_H is the calculated value of the high-spin species assuming that the magnetic moment of the species is 4.8 B.M.[24] The value of y_H at a room temperature (20 °C) was 0.22 and this value increased as the temperature decreased.

In order to estimate the thermodynamic parameters ΔH°

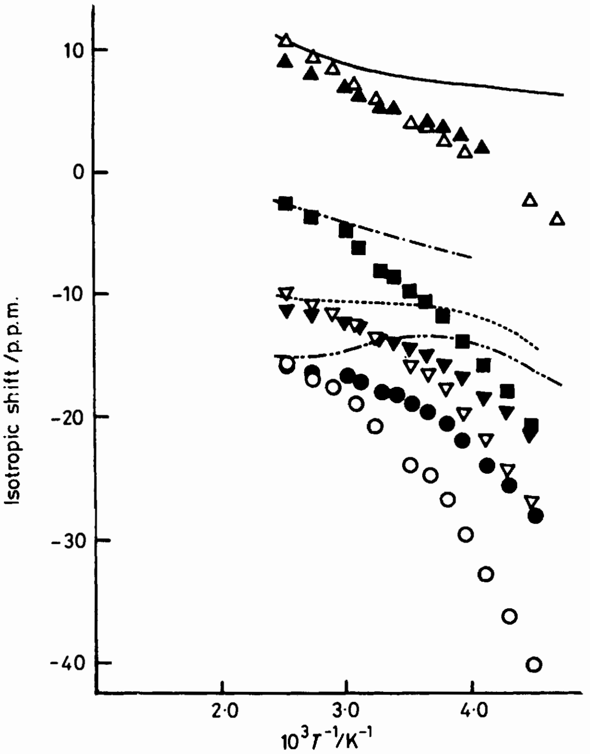

Figure 5. Temperature dependence of the n.m.r. isotropic shifts for [Co(salen)] [H^3 (■); H^4 (●); H^5 (▲); H^6 (▼)], [Co(3,3′-Me$_2$-salen)] [H^4 (○); H^5 (△); H^6 (▽)], and [Co(saldmen)] [H^3 (— · — · —); H^4 (— · · — · · —); H^5 (——); H^6 (- - - -)]

and $\Delta S^\ominus$ in the formation of the high-spin species, the equilibrium (3) was postulated and the constant, K, was calculated at different temperatures by equation (4) using y_H where B denotes a base. The calculated equilibrium constants are

$$\begin{array}{ccc} [\mathrm{Co(salen)B}] + \mathrm{B} & \overset{K}{\rightleftharpoons} & [\mathrm{Co(salen)B_2}] \qquad (3) \\ \text{(low-spin)} & & \text{(high-spin)} \end{array}$$

$$\begin{aligned} K &= [\text{high-spin}]/[\text{low-spin}] \\ &= y_H/(1 - y_H) \qquad (4) \end{aligned}$$

shown in the Table. The thermodynamic quantities $\Delta H^\ominus = -4.25 \times 10^3$ J mol^{-1} and $\Delta S^\ominus = -25.5$ J K^{-1} mol^{-1} were estimated from the slope and the intercept at $1/T = 0$ of the linear portion of the plots of ln$K$ *vs.* $1/T$.

^{1}H *N.M.R. Spectra.*—Proton n.m.r. spectra of all the cobalt(II) complexes in [^{2}H$_5$]pyridine were measured. The signal assignment was made by comparison with the spectra of the corresponding methyl-substituted complexes. Shifts to lower field were observed for all the ring protons of the complexes in [^{2}H$_5$]pyridine compared with the shifts in [^{2}H]chloroform.[25] Deviation from the Curie law was seen in the temperature dependence of the isotropic shifts. Some of the examples are shown in Figure 5. The corresponding protons among [Co(salen)], [Co(3,3′-Me$_2$-salen)], and [Co(saldmen)] showed markedly different isotropic shifts at the low-temperature region. The differences in the isotropic shifts from those of [Co(saldmen)] depend on the extent of high-spin species produced. In the high temperature region, the isotropic shifts for the corresponding protons among these complexes approached each other and nearly coincided at *ca.* 390 K.

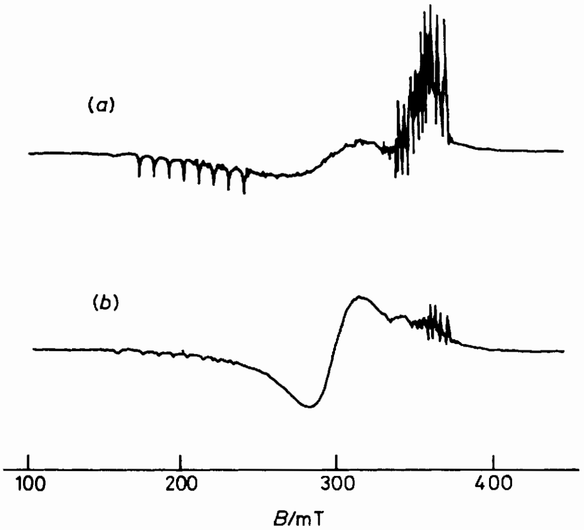

Figure 6. E.s.r. spectra of the frozen dmf solution of [Co{3,3′-(MeO)$_2$-salen}] at 15 K. (*a*) The main sharp signals around 200 and 370 mT are due to the low-spin anhydrous [Co{3,3′-(MeO)$_2$-salen}] and the broad signal around 300 mT is due to the remaining low-spin aqua mono-adduct; (*b*) the main broad signal around 300 mT is due to the low-spin aqua mono-adduct and the sharp signals around 200 and 370 mT are due to the remaining low-spin anhydrous complex

This tendency is compatible with that observed in the magnetic susceptibility measurements. The isotropic shifts of all the protons in pyridine solution have a lower field bias at high temperatures compared with those in chloroform solutions.

Discussion

Marzilli and Marzilli[10] isolated base mono-adducts of [Co(salen)] and related complexes and observed their magnetic susceptibilities. The magnetic moments of the adducts are fairly high for low-spin species at room temperature, but the value decreases and approaches the spin-only values of the low-spin state as the temperature decreases.[10] This behaviour implies that the high-spin state of the base mono-adducts is not a ground state but an excited state which is thermally populated or mixes with the ground state quantum mechanically at high temperatures.

The complex [Co{3,3′-(MeO)$_2$-salen}(H$_2$O)] in crystal form is exceptional in that this complex shows a magnetic moment of a high-spin species at 97 K.[8] This complex has a square-pyramidal geometry with a water molecule co-ordinated in the apical position. It should be noted, however, that a dmf solution of this complex does not show any high-spin e.s.r. signal but only two types of the low-spin signals, which are attributed to the five-co-ordinate aqua mono-adduct and the four-co-ordinate anhydrous complex (Figure 6). This indicates that, in dmf solution, the aqua mono-adduct does not have the high-spin ground state but the low-spin one, although the high-spin excited states may be close to the low-spin ground state. In the crystalline state, the spin-multiplicity of the ground state may not necessarily be the same as that in solution; the large magnetic moment of the crystal at low temperatures should be attributed to some specific effect of the molecular packing which may induce weakening of metal–ligand bond, stabilizing the high-spin state below the low-spin one. Thus, all the experimental results obtained so far tell us that the apical co-ordination of a single base molecule alone is not capable of altering the ground spin-

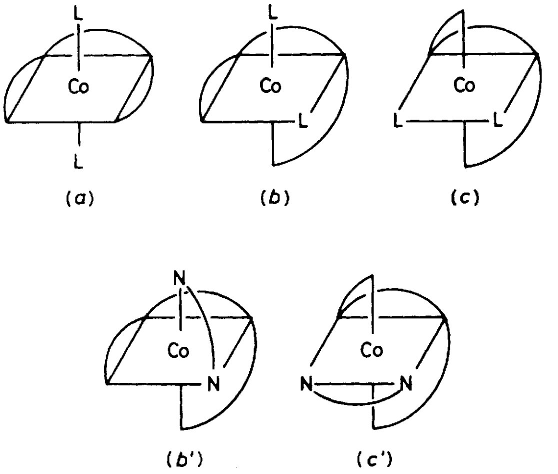

Figure 7. Schematic representation of the structures proposed for the high-spin species of the quadridentate Schiff-base cobalt(II) complexes: L is the unidentate base, N⌒N is the bidentate base

multiplicity of cobalt(II) complexes with quadridentate Schiff bases in solution.

The high-spin state of the species found in this study is undoubtedly the ground electronic state, because it was observed at sufficiently low temperatures (around 4.2 K), where thermal excitation to the high-spin state can be negligible. The increase in relative intensity of the high-spin to low-spin signal with increasing concentration of added bases suggested a six-co-ordinate structure for the high-spin species.[13] The formation of the high-spin species with 1,10-phenanthroline strongly supports this structure.

Three types of structure are expected for the high-spin six-co-ordinate complexes when unidentate bases are used as the additional ligands (Figure 7). The structures in Figure 7(*b*) and (*c*) show a distortion of the quadridentate Schiff bases from a planar structure. Such distortion of the in-plane ligands may cause a decrease in the ligand-field splittings among the *d* orbitals and a stabilization of the high-spin states. The co-ordination of 1,10-phenanthroline as a bidentate ligand inevitably needs a distortion of the Schiff bases from the planar structure [Figure 7(*b'*) or (*c'*)]. Similarly in the e.s.r. spectra between the 1,10-phenanthroline adduct and the unidentate base di-adduct also suggest a similar six-co-ordinate structure. Complexes with cyclic ligands such as di-oximes and various porphyrins did not show any high-spin signals at low temperatures. It is not clear whether the structure shown in Figure 7(*a*) can have a high-spin ground state or not. However, Kozuka and Iwaizumi [26] recently observed a low-spin e.s.r. signal having five-line superhyperfine splittings due to two identical nitrogenous ligands in a toluene–pyridine mixed solution of [Co(salen)]. This spectrum is in agreement with the structure in Figure 7(*a*) in which an unpaired electron resides in the d_{z^2} orbital and interacts with two axial pyridine molecules. This fact implies that the ground state of the species having the structure in Figure 7(*a*) is not high-spin but low-spin. Therefore, the structure in Figure 7(*a*) may be ruled out for the high-spin species found in this study.

There are several factors which govern the formation of high-spin species. The electron-withdrawing substituents such as nitro-groups will decrease the electron density on the co-ordinating atoms and will make rearrangement of the co-ordination structure easy. Bulky substituents near the cobalt(II) ion will make co-ordination of the second base molecule difficult. Naturally, the basicity of the added ligand is also important; the more basic the added ligand, the more the high-spin species are produced. The thermodynamic parameter $\Delta H^{\ominus} = -4.25 \times 10^3$ J mol^{-1} estimated for [Co(salen)] in pyridine solution is one order smaller than that (-6.3×10^4 J mol^{-1}) estimated for the oxygenation of *NN'*-ethylenebis(acetylacetonato)cobalt(II) in pyridine solution by Amiconi *et al.*[27] Therefore, the formation of the high-spin species will not interfere with the reversible oxygenation of these cobalt(II) complexes. However, the high-spin species (22%) may critically affect the quantitative analysis of various reactions of the cobalt(II) complexes in *N*-heterocyclic solvents.

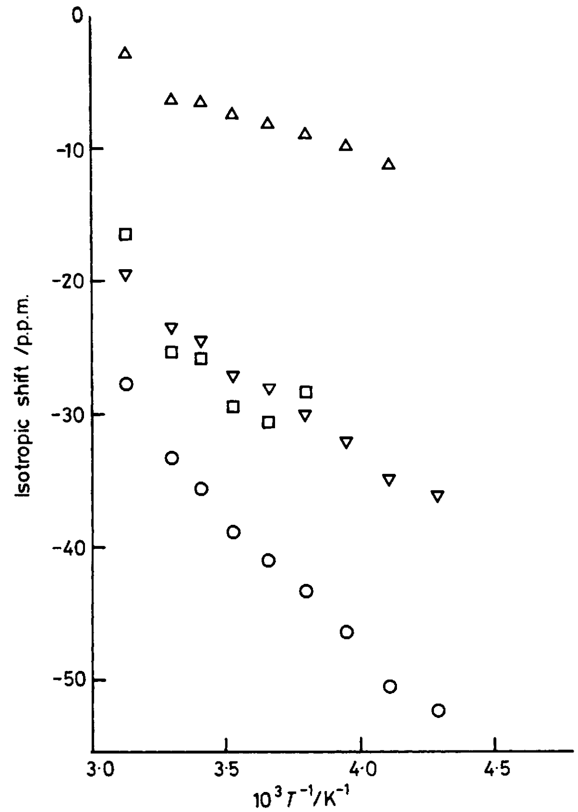

Figure 8. Temperature dependence of the n.m.r. isotropic shifts estimated for the high-spin species of the pyridine solution of [Co(salen)] [H^3 (□); H^4 (○); H^5 (△); H^6 (▽)]

The deviation from a straight line found in the high-temperature region of the plots of ln*K* *vs* 1/*T* (refer to the data in the Table) indicates that the assumed equilibrium of equation (3) is too restrictive in this temperature region, where the population of the high-spin base ' mono-adduct ' should be taken into account. Marzilli and Marzilli [10] proposed that the base mono-adducts have high-spin excited states very close to the ground state, while Murray and Sheahan [23] considered the weakening of the metal–ligand bond which causes an increase in the quantum mechanical mixing of upper high-spin states. In any event, the increase in the magnetic moment of the base mono-adduct at high temperatures is an intrinsic property of the complex. The n.m.r. isotropic shifts also reflect the anomalous electronic state at high temperatures in accord with the trends of the magnetic moment. Increasing the high-field shift of the proton at position 5 implies that the unpaired electron spin may delocalize through the highest occupied π molecular orbital,[25] and that the simultaneous increase in the low-field shift of the proton at position 4 suggests that σ delocalization is also significant.[28,29] The simultaneous increase in delocalization through both π and σ orbitals also suggests that the low-spin base mono-adducts have excited high-spin states close to the ground state and/or the ligand field drastically decreases with an increase in temperature.

As the exchange rate between high-spin and low-spin states is fast enough to observe their averaged spectrum, the isotropic shift (δ_H) of the high-spin di-adduct is estimated from equation (5), where $\delta_{obs.}$ is the observed isotropic shift

$$\delta_{obs.} = y_H\delta_H + (1 - y_H)\delta_L \qquad (5)$$

and δ_L is that of the base mono-adduct. Since [Co(saldmen)] barely showed the high-spin e.s.r. signal, δ_L was represented by the isotropic shift of [Co(saldmen)] in pyridine solution. The estimated values of δ_H are plotted in Figure 8. The magnitude and the low-field shift for all the protons are closely related to the contact interaction caused by the σ delocalization.[28,29] In addition to the contact interaction, the dipolar interaction may also make some contribution to the isotropic shifts, but the latter is not significant. High-spin cobalt(II) complexes having a tetrahedral structure show appreciable spin delocalization through π orbitals; the protons at positions 3 and 5 show high-field shifts and the protons at positions 4 and 6 show low-field shifts.[30] The high-spin di-adducts found in this study, however, did not show such a delocalization pattern. The octahedral symmetry in the co-ordination sphere enables the unpaired spin to delocalize through both π and σ orbitals, where σ delocalization predominates the observed isotropic shifts for the protons at those positions at least several bonds apart from the central paramagnetic metal ion. Thus, in view of the mechanism of spin delocalization, the high-spin base di-adducts are also quite different from the cobalt(II) complexes having the tetrahedral or square-pyramidal structure.

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