High-spin Quadridentate Salicylaldehyde Schiff Base Complexes of Cobalt(II) in N-Heterocyclic Solvents

By Makoto Chikira,* Kouto Migita, Toshio Kawakita, Masamoto Iwaizumi, and Taro Isobe

(*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai* 980, *Japan*)

Summary E.s.r. and magnetic susceptibility studies of the title complexes show that an appreciable amount of the high-spin base di-adduct is formed in N-heterocyclic solvents such as pyridine and its methyl derivatives.

It is well known that quadridentate salicylaldehyde Schiff base complexes of cobalt(II) react reversibly with molecular oxygen both in the solid state and in basic solvents.[1] The mechanism of the oxygenation and the ground electronic configurations of these complexes have been discussed extensively.[2,3] Most of the planar, quadridentate Schiff base complexes of cobalt(II) have magnetic moments corresponding to the $S = \frac{1}{2}$ low-spin state, and some base mono-adducts exhibit low-spin–high-spin equilibria with the low-spin ground state.[4] However, species with the high-spin ground state ($S = \frac{3}{2}$) have not been observed yet in basic solvents. We report here e.s.r. and magnetic susceptibility measurements which show that an appreciable amount of the high-spin species is formed in N-heterocyclic solvents such as pyridine and its methyl derivatives.

The Figure shows the e.s.r. spectra of *NN'*-ethylenebis(salicylidenaminato)cobalt(II), [Co(salen)], in γ-picoline at 77 and 4·2 K. The broad peak near 1·5 kG at 4·2 K, which disappears at 77 K, is a typical e.s.r. signal of high-spin Co^{II} complexes.[5] The sharp lines near 2·0 and 3·5 kG are characteristic of low-spin complexes in non-co-ordinating solvents such as toluene or chloroform.[2,6] The most intense peak near 3·0 kG is due to the base mono-adduct, as has already been discussed.[2] The high-spin signal was not observed for [Co(salen)] and other quadridentate Schiff base

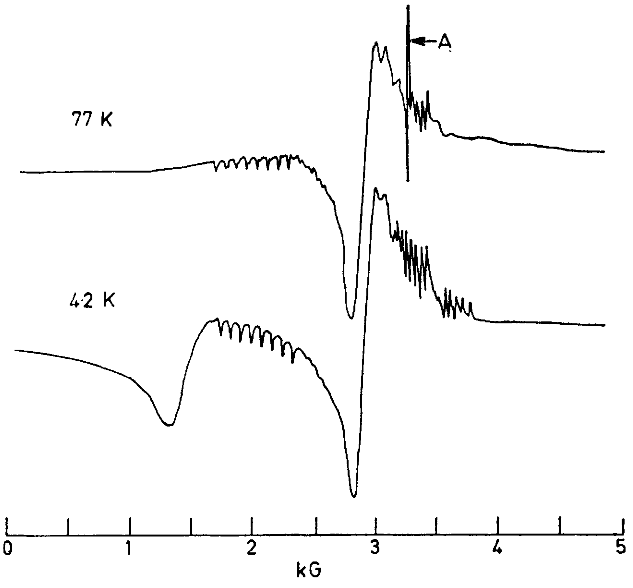

Figure. X-band e.s.r. spectra of [Co(salen)] in γ-picoline at 77 and 4·2 K. A = diphenylpicrylhydrazyl signal.

complexes of cobalt(II) in non-co-ordinating solvents, or in weakly co-ordinating solvents such as methanol, tetrahydrofuran, dioxan, and aniline.

Solutions of the pyridine mono-adduct of [Co(salen)] in toluene, and solutions of the imidazole mono-adduct of *NN'-o*-phenylenebis(salicylidenaminato)cobalt(II), [Co(saloph)], in CH_2Cl_2 did not show the high-spin signals, though they showed intense signals due to the low-spin base mono-adducts. The high-spin signals were observed on addition of the corresponding bases to the solutions, and their intensity increased with the amount of base added. For [Co(saloph)], the low-spin signals disappeared completely with a large excess of imidazole. The small anisotropy of the g tensor ($|g_{\parallel} - g_{\perp}| < 1$) for the high-spin species of [Co(saloph)] indicates that the ligand field around the high-spin cobalt(II) ions may be almost octahedral. We therefore conclude that the high-spin species are six-co-ordinated base di-adducts. Cobalt(II) complexes with cyclic ligands such as di-oximes and phthalocyanines showed no high-spin signals even at 4·2 K.

In order to estimate the amount of the high-spin species in solution near room temperature, the magnetic moments of [Co(salen)] in pyridine at different temperatures were measured by Evans' method.[7] The magnetic moment of 3·17 B.M. at 307 K gradually decreased with decrease in temperature to a minimum of 3·05 B.M. at 263 K, and then increased to 3·17 B.M. at 223 K. If we assume that the magnetic moments of the non-adduct, mono-adduct, and di-adduct are 2·5,[4] 2·35,[4] and 4·8 B.M.,[5] respectively, 20—25 % of [Co(salen)] in pyridine is estimated to be in the high-spin state near room temperature.

These results indicate that the existence of high-spin species cannot be neglected in spectral or kinetic investigations of these complexes in N-heterocyclic solvents, particularly at low temperatures.

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