Infrared, Raman, and Magnetic Evidence for a $^4T \rightleftharpoons {}^2E$ Equilibrium in Bis[tri-(2-pyridyl)amine]cobalt(II) Perchlorate

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Summary The microsymmetry about the cobalt atom in the title compound is almost exactly octahedral, and the ligand in the complex is not extensively conjugated; nevertheless, a "crossover" situation is shown to exist in this complex, and use of this phenomenon is made in the assignment of its metal–ligand vibrations.

PREVIOUS treatments[1,2] of $^4T \rightleftharpoons {}^2E$ equilibria in d^7 systems have invoked electron delocalisation *via* π-bonding in order to explain the observation of "crossover" behaviour at values of Δ, the ligand-field splitting parameter, which are very much less than π, the mean electron-pairing energy.

We now report the confirmation of an earlier prediction[3] that bis[tri-(2-pyridyl)amine]cobalt(II) perchlorate (I) exists as a mixture of ^4T and ^2E spin isomers. *X*-Ray powder photographs show that this complex is isomorphous with the corresponding iron(II) complex, which has been found to have a negligible ($\Delta Eq = 0{\cdot}00$) quadrupole splitting in its Mössbauer spectrum.[4] We are therefore dealing with a complex in which the microsymmetry of the cobalt(II) ion must be almost exactly O_h, although the overall symmetry will probably be D_{3d}. Furthermore, the ligand does not contain the α-di-imine function, and the chelate rings in the complex are not planar, so we have shown that neither distortions from octahedral symmetry nor extensive conjugation are necessary prerequisites for the formation of low-spin cobalt(II) complexes with chelating heterocyclic ligands.

Figure 1 shows that the change in the spin state of the complex occurs mainly between 100 and 200°K: the changes in the susceptibility were reversible, and no time-dependence of this or any other property of the complex was detected.† By contrast, the analogous high-spin hexafluorophosphate salt obeys the Curie–Weiss Law: however, anion dependence is a common phenomenon in d^7 "crossover" systems.[1] Since the ^2Eg level in O_h remains unsplit in D_{3d} symmetry, we tentatively attribute the anion dependence observed here to the different abilities of the two lattices to accommodate the predicted Jahn–Teller distortion in the low-spin isomer.

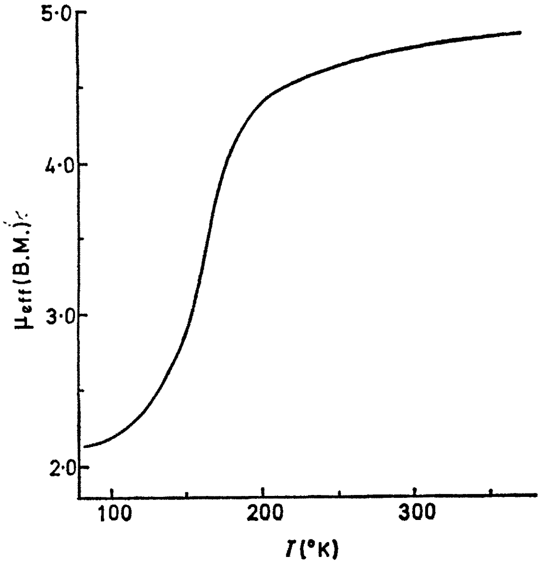

FIGURE 1. *Graph of μ_{eff} against absolute temperature for bis[tri-(2-pyridyl)amine]cobalt*(II) *perchlorate.*

The i.r. spectrum of (I) (Figure 2) (as a Nujol mull) changes markedly on cooling—the relative intensities of the bands are a smooth function of temperature—whereas, under similar conditions, the i.r. spectrum of the hexafluorophosphate analogue of (I) merely exhibits blue-shifts of the order of 4 cm^{-1} and some splitting of broad bands. The room-temperature i.r. spectra (500—195 cm^{-1}) of the bis-complexes of terdentate tri-(2-pyridyl)amine with zinc(II), copper(II), nickel(II), and cobalt(II) perchlorates are very similar, but the spectrum of (I) at 100°K resembles the room-temperature spectrum of bis[tri-(2-pyridyl)amine]-iron(II) perchlorate, which has bands at 309, 348, 381, and 486 cm.$^{-1}$ Also, in contrast to the other bands between 500 and 195 cm^{-1}, the band at 263 cm^{-1} in the spectrum of (I) at room temperature, which has no counterpart in its Raman spectrum, is sensitive to a change of metal in the series of complexes mentioned above. We therefore tentatively assign the pair of bands observed at 301 and 312 cm^{-1} in the spectrum of the low-spin cobalt(II) complex to the two components of ν_{as} Co–N (A_{2u}) which is shifted from 263 cm^{-1} and split on going from D_{3d} symmetry (high-spin, undistorted) to C_{2h} symmetry (low-spin, Jahn–Teller distorted) on cooling.

The Raman spectrum of (I) as a solid also changes markedly on cooling, and again, the spectrum of (I) at 100°K resembles the spectrum of the low-spin iron(II) complex at room temperature. Thus, a very strong line at Δν = 130 cm^{-1} in the room-temperature spectrum of (I) disappears on cooling, this change being accompanied by an increase in the breadth and intensity of a line at Δν = 170 cm^{-1}. The iron(II) complex has a very intense line at Δν = 180 cm^{-1} which is polarised in nitromethane solution: we therefore assign the lines observed at Δν = 130 and 170 cm^{-1} to the totally symmetric metal–ligand vibrations of the high- and low-spin isomers of the cobalt(II) complex, respectively.

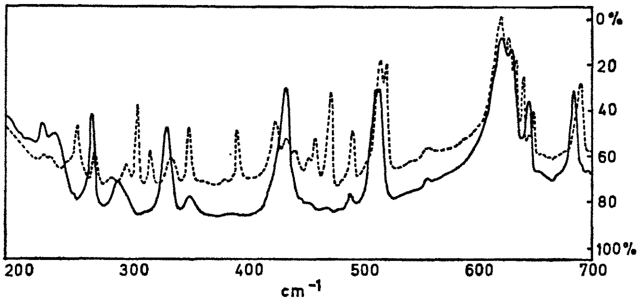

FIGURE 2. *I.r. spectra of bis[tri-(2-pyridyl)amine]cobalt*(II) *perchlorate at* 100°K (*broken line*) *and* 293°K (*full line*).

This constitutes the first application of vibrational spectroscopy to the study of spin-equilibria in d^7 systems, and it is the first application of Raman spectroscopy in any "crossover" system. Since the totally symmetric metal–ligand vibration in complexes of this type should be strongly dependent on spin-state, pressure, and temperature, further studies of the Raman spectra of these complexes are indicated. In this case, we have deliberately used the existence of a spin-equilibrium in the assignment of metal–ligand vibrations.

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† The observed susceptibilities were independent of the magnetic field strength.

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