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Pressure-Temperature Relationships of the Spin-State Equilibrium in a Five-Coordinate Complex of Cobalt(II) Thiocyanate with an nnp Tridentate Ligand[a]

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Temperature dependent spin-state equilibria in five-coordinate complexes of nickel(II) and cobalt(II) thiocyanate complexes with nnp[c] tridentate ligands have been reported.[1,2] No pressure dependences have been reported for these systems to date. Recently it was possible to convert a high-spin, four-coordinate $NiBr_2(Bz\varphi_2P)_2$ (distorted tetrahedral) to a low-spin four-coordinate (square planar) with application of high-external pressures in the solid state.[3] There is considerable interest in the similarities and differences of the mechanisms operating on these spin-state equilibria at conditions of varying temperature and pressure.

Several experimental techniques have been used under non-ambient conditions of temperatures or pressure. The magnetic behavior, electronic transitions, mid-infrared spectra, and Mössbauer spectra have all been used. Recently, the skeletal region has been suggested as a technique to follow spin-state equilibria.[4] We have examined solid $Co(nnp)(NCS)_2$ under pressures up to 20 kbar, at 300° K and at 100° K. Figure 1 records the far infrared changes observed between the high-spin and low-spin forms. It may be observed that between 333–200 cm^{-1} sufficient difference exists between the high-spin form (spectra recorded at room temperature – curve (1)), and the low-spin form (spectra recorded at ~100° K – curve (2)). Pressure effects to 10 kbar at room temperature are observed to cause some conversion of high-spin to low-spin. At 20 kbar the spectrum washes out. At intermediate pressures (10–20 kbar) indications are that a mixture of high-and low-spin forms exist. If the solid under pressure is cooled to 100° K, complete conversion to low-spin occurs (curve (5)). Thus, both low temperature and high pressure favor the low-spin form. However, the effects of temperature seem to predominate. Pressure induces only some low-spin form at room

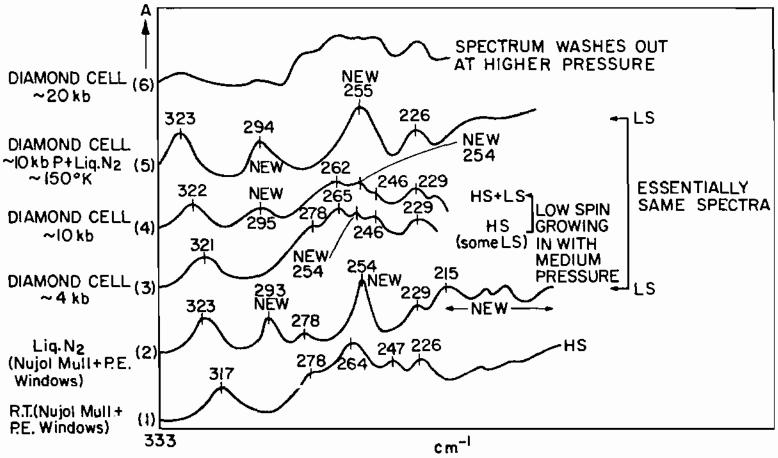

Figure 1. Pressure and Low Temperature Effects in the Metal–Ligand Skeletal Region for $Co(nnp)(NCS)_2$.

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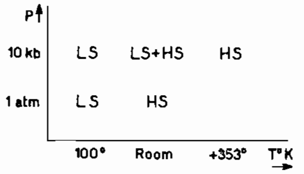
[c] nnp = $Et_2N\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2P\varphi_2$.

temperature. At high temperature only the high-spin form is favored. The following relationships between pressure and temperature for the system may be cited:



Similar results with pressure have been reported by Drickamer[5] for several six-coordinate, high-spin Fe^{II} complexes with *o*-phenanthroline using Mössbauer techniques.

Although the electronic spectrum was also recorded under pressure, the results were not too indicative of the changes occurring. However, blue shifts were observed, from which an increase in ligand-field energy may be inferred.

The results may be explained by the changes involving shifts in electrons in the system. It may be concluded that two mechanisms are in operation when the complex is placed under pressure. Some spin-pairing of electrons occurs initially because of the increase of Dq due to the increase in pressure. This is aided by the back-donation of metal electrons to the π^* orbitals in the organic and NCS^- ligands. At higher pressures this back-donation may be blocked because the π^* level becomes accessible to electrons from the ligands, decreasing the back-bonding and stopping the conversion toward low-spin.[5] It is entirely possible that in complexes involving ligands with empty π orbitals, pressure effects will only cause partial spin-state pairing, and thus the results are different than those occurring at low-temperature where high-spin complexes can be converted almost completely to low-spin.

The infrared experiments were conducted using a diamond-anvil cell and a 6X beam condenser. A Perkin–Elmer Model 301 far-infrared spectrophotometer was used to record the spectra. For the visible spectra, the same cell was used in a Cary 14 spectrophotometer. Further details of the technique are described elsewhere.[6]

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