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High Spin–Low Spin Crossover in Co(II) Complexes with Tris(2-diphenylphosphinoethyl)amine (NP_3) by Application of High External Pressures*

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Introduction

Although spin state conversions in solution with pressure [1] are more easily accomplished, a number of solid-state spin state crossovers have now been reported [2]. Fe(II) complexes of the type FeL_2X_2, where L = 1,10-phenanthroline or 2,2′-bipyridine and X = NCS^- or $NCSe^-$ have been converted from high-spin → low-spin with pressure [3]. For a discussion of Fe(II) conversions see Drickamer and Frank [2]. Several Fe(III) conversions have also been accomplished [2]. Recently, a high-spin → low-spin crossover has been observed for tri(N-ethyl-N-phenyldithiocarbamato iron(III) [4, 5]. By contrast, few Ni(II) and Co(II) systems have been studied for spin state crossover with pressure. The complex $Ni(Bz\Phi_2P)_2Br_2$ was converted from high-spin → low-spin at 12 kbar [6]. A five coordinate cobalt complex, $Co(nnp)(NCS)_2$, where nnp = $Et_2N{-}(CH_2)_2{-}NH{-}(CH_2)_2P\Phi_2$, has been converted to low spin [7].

Conversion of high spin → low spin states in transition metal complexes are of interest because of their relation to similar occurrences taking place in the Earth's mantle [8]. Since the transition metal coordination complexes can be converted at relatively low pressure, the crossovers are easily accomplished and investigated. The results may serve as a foundation to the results forthcoming from very high pressure studies of mantle, transition metal minerals.

In this paper we have investigated the crossover occurring with pressure in the Co(II) complexes of tris(2-diphenylphosphinoethyl)amine (np_3) of the type $[Co(np_3)X]B\Phi_4$, where X = Cl, Br or I. Both visible and far infrared [FIR] spectroscopy were used as the diagnostic tools.

Experimental

Syntheses

Details of the syntheses of the five-coordinate Co(II) complexes with tris(2-diphenylphosphinoethyl)amine (NP_3) have been discussed [9].

Spectroscopic Studies

Visible and near infrared spectra were obtained with a Cary 14R spectrophotometer. The measurements were made in a DAC interfaced with a beam condenser [10].

FIR measurements were made on a Beckman IR-11 using a 6X beam condenser [11], and a Beckman Model 4260 using a 4X beam condenser [12].

Results and Discussion

The complexes $[Co(np_3)X]B\Phi_4$, where X = Cl, Br, or I are all high spin. However, $[Co(np_3)I]I$ is also obtained in a low spin state. X-ray structural studies have shown that the high spin complexes are trigonal-bipyramidal [13], while the low spin complex is tetragonal-pyramidal [14]. Differences in the electronic spectra between the two spin states are noted. The high spin state spectrum is characterized by an intense absorption at $\sim$13,000 cm^{-1}, and a weaker absorption at $\sim$10,000–11,000 cm^{-1}. The low spin state spectrum shows an absorption at $\sim$10,600 cm^{-1} and the absorption at $\sim$13,000 cm^{-1} has diminished or disappeared. The presence or lack of the latter absorption may be used to differentiate spin states. In nitroethane solution a temperature dependent spin state equilibrium was found for $[Co(np_3)I]I$ [15]. It was of interest to ascertain whether a spin state crossover would occur for the $[Co(np_3)X]B\Phi_4$ complexes in the solid state with pressure.

Figure 1 illustrates the electronic spectra of the title complexes at ambient pressure and compares them with spectra obtained at 20 kbar. It may be observed that the $\sim$13,000 cm^{-1} absorption disappears in the $[Co(np_3)I]$ $[B\Phi_4]$ case, and is indicative of a crossover to a low spin state. However, in the case of the chloro- or bromo-analogue, some high spin state remains up to 35 kbar. The tendency to spin pair appears to be greatest for the iodine complex, and may account for the fact that both high and low spin states are found at room temperature for this complex and not for the chloro- or bromo-analogues.

Corollary data were obtained in the low-frequency vibrational spectrum of $[Co(np_3)Cl]B\Phi_4$. An absorption at $\sim$300 cm^{-1}, assigned to a cobalt–chlorine stretching vibration in the high spin state, weakens in intensity with pressure and an intensification of absorption occurs at $\sim$350 cm^{-1}. This is the direction

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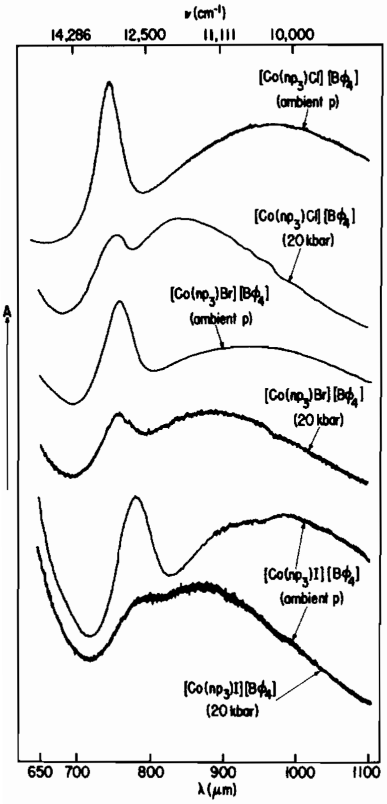

Fig. 1. Electronic Spectra of [Co(np$_3$)Cl]BΦ_4, [Co(np$_3$)Br]BΦ_4, [Co(np$_3$)I]BΦ_4 at ambient and 20 kbar pressure.

of the frequency shift that is observed for the metal-ligand vibration in going from high-spin → low-spin [2–5, 7]. Overlapping ligand absorptions precluded studying the Co–N, Co–P vibrations in the region >400 cm^{-1} and Co–Br, Co–I vibrations <250 cm^{-1}.

It may be concluded that high pressure favors the low spin state and the tetragonal pyramidal geometry in five-coordinate complexes of the type [Co(np$_3$)X][BΦ_4]. This system illustrates the behavior class type, where geometrical and spin state changes occur with pressure, but the coordination number and oxidation state remain unchanged [16]. The results parallel those obtained for [Cr(en)$_3$][Ni(CN)$_5$] where the geometry of the Ni(CN)$_5^{3-}$ changes from trigonal-bipyramidal to square-pyramidal with an increase in pressure [17], and for Co(nnp)(NCS)$_2$ where the low spin state is favored [7].

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