Thermal Intersystem Crossing in Solids. Cophen$_2$(NCBR$_3$)$_2$, R = H and Phenyl

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Recent studies [1] in our laboratories have shown the complex Fephen$_2$(NCBH$_3$)$_2$ to exhibit intersystem crossing (often referred to as spin-equilibrium) above room temperature, with T_c = 360 K (T_c is defined as the temperature at which the fraction ratio of high to low spin molecules is 1). Although variable temperature infrared and magnetic susceptibility studies reveal only two electronic states are involved (the singlet and the quintet states of Fe(II)), variable temperature Mössbauer studies of the thermally induced transition indicate the presence of a third electronic state or, more probably, the existence of a third phase, a phase in which there is a rapid intersystem crossing equilibrium involving the two electronic states. Interestingly, the analogous BPh$_3$ complex is low spin and does not exhibit intersystem crossing as a solid [2], but does so on dissolution in dichloroethane [3]. In preparation for time resolved Mössbauer emission studies of the Fe complexes it is necessary to synthesize the analogous Co(II) complexes and to characterize their magnetic and electronic properties as solids. Of additional interest is whether or not the phen$_2$(NCBPh$_3$)$_2$ ligand field is sufficiently strong to confer the thermally accessible intersystem crossing phenomenon upon Co(II).

Experimental

In a 500 ml Schlenk tube, 0.766 g of CoCl$_2$·6H$_2$O and 1.277 g phenanthroline·H$_2$O were dissolved in approximately 200 ml of degassed, distilled water under an atmosphere of Ar. A solution of 2.21 g of NaNCBPh$_3$ in approximately 100 ml of degassed H$_2$O was slowly added through a purged, pressure equalizing dropping funnel to the clear brown solution in the Schlenk tube. With the first addition, there appeared a finely divided white-pink precipitate. After the addition was complete, the slurry was stirred for 45 minutes, the stirring bar removed and the solid collected on a Schlenk frit. The collected product was washed with distilled water and then with dry tetrahydrofuran and dried in vacuum overnight. The yield was 1.80 g (59%; some particles of product passed through the frit). *Anal.* Calcd. (found) for Cophen$_2$(NCBPh$_3$)$_2$: Co, 6.16 (6.20); C, 77.78 (77.79); H, 5.02 (5.00); N, 8.78 (8.70); B, 2.26 (2.42)% by Schwarzkopf Laboratories.

The same procedure was followed for synthesis of the BH$_3$ analog, using the following quantities: CoCl$_2$·6H$_2$O, 1.48 g, phenanthroline·H$_2$O, 2.46 g, and KNCBH$_3$, 1.09 g. The yield of the pale peach colored complex was 2.66 g (86%). *Anal.* Calcd. (found) for Cophen$_2$(NCBH$_3$)$_2$: Co, 11.81 (11.10); C, 62.58 (63.24); H, 4.41 (4.80); N, 16.85 (17.30); B, 4.34 (4.11)%.

Infrared spectra were recorded with the solids dispersed in KBr, using a Perkin-Elmer 180 spectrophotometer. Magnetic susceptibility measurements were made with a Cahn 7600-5 Faraday balance, over the range 190 K to 335 K. CoHg(SCN)$_4$ was used as the calibrant; diamagnetic corrections to the molar susceptibility were taken from the Mulay and Boudreaux monograph [4].

Results and Discussion

The infrared spectra are somewhat unusual for complexes containing *cis*-cyano linkages in the first coordination sphere of a metal in that only a single absorption band (2185 cm^{-1} for R = H and 2195 cm^{-1} for R = Ph) is recorded for the CN stretching modes, even under slow scan, expanded scale conditions. This same feature is found for the Fe(II) complex with NCBPh$_3^-$ as ligand; while two CN bands are observed at ambient temperature for the Fe-NCBH$_3$ analog, one corresponds to the low spin species, the other to the high spin species[†]. Two explanations can be advanced for failure to observe two CN bands: (a) the CN linkages have a *trans*-stereochemistry or (b) non-orthogonality of the CN linkages in a *cis*-configuration produces a kinetic coupling of the CN stretching motions which is

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[†] Reference 6 erroneously attributed the two CN bands to *cis*-CN oscillators in a triplet state complex.

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oppositely signed, and of comparable magnitude, to the coupling of electronic origin, resulting in uncoupled oscillators. It is currently accepted that interligand repulsions (from the *ortho* hydrogen atoms of the phen ligands) will confer a *cis*-stereochemistry upon bis-phen complexes of the 3d transition metal ions, although these repulsions do not control the stereochemistry of the heavier transition metal ion bis-phen complexes [5]. For this reason, we suppose all four complexes to have *cis*-configurations and the CN oscillator coupling is eliminated by kinematic factors. In all other respects the infrared spectra are perfectly normal for $Mphen_2X_2$ complexes.

The small shifts to higher frequency for the CN oscillators upon coordination to Co(II) is expected [6] and are nearly the same for the Fe(II)) analogs.

The magnetic susceptibility data, spanning the temperature range 190 K to 330 K, do not follow the simple Curie law, but plots of $1/X'$ *versus* T are linear, with large intercepts along the $1/X'$ axis corresponding to $\theta = -53.2$ K and -56.0 K for the cyanoborate and the cyanotriphenylborate ligands, respectively. The Curie-Weiss μ_{eff} values obtained from the slopes of the $1/X'$ *versus* T plots are, respectively, 4.28 and 4.49, indicative of high spin configurations for Co(II) down to 190 K. The large θ values indicate a complex situation [7] regarding the magnetic characteristics of the electronic quartet states populated at the temperatures spanned in our experiments and, together with the low μ_{eff} values, perhaps reflect the nearness of the doublet state. The present data do not merit a detailed discussion of the magnetic properties of these complexes, it being essential to chart in detail their magnetic behavior at temperatures lower than are accessible with our apparatus. We can conclude, however, that to temperatures nearly 200 K below T_c for the Fe(II)/$NCBH_3^-$ complex there is no indication of an intersystem crossing transition to a low spin state for either cyanoborate complex of Co(II). While the low spin state for Co(II) was not expected with R = H (see the following paragraph), its appearance for R = Ph was a possibility.

A closing comment is pertinent. Failure to observe the doublet state in the Co(II) complexes down to 190 K is consistent with either insufficiently stronger ligand interactions with Co(II) than with Fe(II) (so that the quartet state is the ground state at all temperatures) or with a doublet to quartet transition below 190 K. For a doublet to quartet transition to occur below 360 K (*i.e.*, T_c for the Fe/$NCBH_3^-$ complex) for the Co(II) complexes would require, first of all, stronger Co–ligand interactions than found for the Fe analogs so as to produce the doublet ground state; this expectation derives from the greater resistance to spin pairing for the d^7 than d^6 configuration [8] (for example, empirically one finds $Fephen_3^{2+}$ to be a low spin complex whereas the Co(II) analog is high spin). For the present complexes to exhibit a doublet ground state only below 190 K would require a rare balance of metal–ligand attraction and electron repulsion forces. Even in such a circumstance, $T_c < 190$ K is required, which in turn requires [9] a much smaller enthalpy and/or much greater entropy change on passing from low to high spin states than is found for the Fe(II) analogs. The entropy difference is not expected to be larger for the Co(II) complexes (one could reasonably argue that it should be smaller); the enthalpy change, however, could be smaller for the Co(II) species. The situation is further complicated by the realization that negative enthalpic and positive entropic intermolecular cooperativity contributions to a doublet to quartet transition, if operative, act to lower T_c. Thus, while the present Co(II) complexes are likely to be high spin cases, a definitive conclusion as to the true ground states of the Co(II) complexes must await magnetic studies at lower temperatures.

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