

**Figure 2.** Unpolarized emission and absorption spectra of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$  (crystal thickness  $\approx 0.1$  mm). A shoulder for line I can be detected in absorption even at  $H = 0$  T. Note that at  $T = 1.7$  K the emission from the lowest excited state (line I) is already dominant.

perature dependence of the emission intensities in the zero-phonon lines<sup>3</sup>—delivers a value of  $k_{\text{II}}/k_{\text{I}} \approx 40$ . Thus, the occurrence of this shoulder without magnetic fields is reasonable. (A group-theoretical classification for the transitions in  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$  cannot yet be presented due to the lack of crystal structure data.) With application of magnetic fields the absorbance of line I at  $H = 6$  T reaches approximately the same value as that of line II. Further, the energy separation between the lines increases from  $\Delta E = 8.5$   $\text{cm}^{-1}$  at  $H = 0$  T to  $11$   $\text{cm}^{-1}$  at  $H = 6$  T.

The reported effects can be interpreted on the basis of a two-states model and a mixing of the corresponding wave functions under magnetic fields. The amount of mixing of wave function  $\psi_{\text{II}}$  into  $\psi_{\text{I}}$  is determined by the mixing coefficient  $\beta$ . In first-order perturbation theory the value of  $\beta$  is proportional to the magnetic field  $H$  (e.g. see ref 6)

$$\beta = \mu_{\text{B}} H \frac{\langle \psi_{\text{I}} | \vec{L} + 2\vec{S} | \psi_{\text{II}} \rangle}{\Delta E} \sim H \quad (1)$$

with  $\mu_{\text{B}} H(\vec{L} + 2\vec{S})$  being the Hamiltonian of the magnetic-field induced perturbation.

From perturbation theory it follows<sup>6,7</sup>

$$\frac{k_{\text{I}}(H)}{k_{\text{II}}(H)} \approx \frac{\beta^2}{1 - \beta^2} \quad (2)$$

For  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ , for example, the measurements of the magnetic field dependence of the emission intensities of line I and line II deliver at  $H = 6$  T a value of about 0.45 for the ratio of the radiative rates.<sup>10</sup> Thus,  $\beta^2$  is determined to be  $\approx 0.3$  (see eq 2). As  $\beta^2 = 1/2$  means complete mixing of the two wave functions, we can conclude that the two lowest excited states of the compound and therefore the properties coupled to these states become very similar due to the magnetic field. Further, it is expected that the magnetic field induced interaction leads to a Zeeman effect. Indeed, this effect is also clearly observed in the  $H$  dependence of  $\Delta E$ .

In conclusion, it must be emphasized that the observed lines, which are found exactly at the same energies in emission and absorption and which exhibit the described magnetic field effects, represent zero-phonon lines. An assignment to impurity centers—as is speculated in the ref 12—is excluded. This is further substantiated by the fact that the two salts investigated in this paper exhibit very similar spectroscopic properties, which, however,

are displayed in slightly different energetical regions.

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### Effect of Particle Size on the High-Spin ( $^5T_2$ ) $\rightleftharpoons$ Low-Spin ( $^1A_1$ ) Equilibrium in Supported Spin-Crossover Complexes

Sir:

In a recent series of publications under the above (or similar) titles, Wei and Jean<sup>1-3</sup> have discussed an interesting observation related to the relative fraction of a given transition-metal compound present in the high-spin (HS) or low-spin (LS) form, depending on the adsorption and loading of the complex on a (presumed) inert support. Using  $^{57}\text{Fe}$  Mössbauer-effect spectroscopy, these authors have cited<sup>2</sup> evidence that a typical complex, for example  $\text{Fe}(\text{ppi})_2(\text{NCS})_2$  (where ppi = *N*-phenyl-2-pyridinecarboxaldimine), which exists at room temperature only in the HS form, on adsorption on carbon or MgO, gives rise to Mössbauer spectra which suggest that a significant fraction of the adsorbed material converts to the LS form at 298 K. This unexpected result has been ascribed to the state of subdivision of the complex on the support, with smaller sample size favoring the predominance of the LS fraction at a given temperature. In their experiments, at levels of less than 2-4% loading (defined as wt % Fe/wt % C or MgO), the samples showed evidence only for the LS form at 298 K. At higher loading levels, the spectra were interpreted in terms of an increasing fraction of the iron complex present in the (normal) HS form at room temperature, with spectral parameters corresponding to those of the neat (unsupported) sample at 298 K.

A great deal of data have been reported in the spin-crossover literature concerning the effects of stress and the concentration of deliberately introduced defects on the crossover temperature,<sup>4,5</sup> the effect of fine subdivision<sup>6</sup> and grinding<sup>7</sup> on both the transition temperature and its hysteresis, the influence of small crystallite size on the residual paramagnetism observed at low temperatures,<sup>8a</sup> and a number of related phenomena.<sup>8b</sup> A review of some of these effects has been published by Gütllich.<sup>9</sup> From these studies it is clear that the very sharp temperature dependence of the crossover phenomenon, which is observed in a number of systems, can be broadened by several of the above effects. At the same time, the crossover temperature, which can be defined as that temperature at which the HS and LS populations are equal, is

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invariably shifted to lower temperatures for both the cooling and heating cycles. The broadening effect may result in the existence of a small fraction of the compound in the low-temperature form, even at high (i.e. room) temperature, but in all cases so far reported, this fraction is considerably smaller than 0.5. In contrast, the results reported by Wei and Jean<sup>1-3</sup> clearly show the LS form of their complex to be the predominant species present at room temperature in their low-loading samples examined by <sup>57</sup>Fe Mössbauer spectroscopy.

Since these results would appear to be at variance with some of the effects discussed above,<sup>4-11</sup> as well as with the thermodynamic data of Sorai and Seki<sup>12</sup> and the relationship between the hysteresis observed for a first-order phase transition and the crystallographic phase change,<sup>13</sup> it was decided to explore the interesting phenomenon reported by Wei and Jean, making use of the variable-temperature Fourier transform infrared (VTFTIR) techniques described earlier.<sup>15</sup> In this context, it was considered appropriate to examine the adsorption on an inert support of crossover compounds whose temperature behavior (as a neat crystalline solid) had been well-documented in the existing literature<sup>14-16</sup> and had been studied previously, making use of both <sup>57</sup>Fe Mössbauer and VTFTIR spectroscopy. A further requirement for such studies is that such a crossover complex should be soluble in an appropriate solvent and be relatively inert to oxidative attack under the conditions of the experiment. The two samples used in this study that meet these requirements are Fe(2,2'-bpy)<sub>2</sub>(NCS)<sub>2</sub> (I) and Fe(pip)<sub>2</sub>(NCS)<sub>2</sub> (II) (where 2,2'-bpy = 2,2'-bipyridine and pip = 2-pyridinecarboxaldehyde *N*-isopyrimine).

In a typical experiment, a weighed quantity of the complex was dissolved in a small amount of anhydrous CH<sub>3</sub>CN and the solution then added dropwise to a weighed quantity of activated carbon in an appropriate ampule. The resulting sample was maintained at room temperature for 5 min with constant stirring, and then the ampule was transferred to a vacuum line and the volatiles distilled off into a liquid-nitrogen-cooled trap. The vacuum-dried sample was then milled with an inert grease (e.g. Kel-F) and spread as a thin layer onto a KBr disk, since this technique had been shown earlier<sup>15</sup> to permit VTFTIR study of the crossover phenomenon and to reproduce the heat capacity, susceptibility, and Mössbauer-effect data on well-characterized "neat" samples. In fact, the inert-grease mulling technique appears to introduce a minimal amount of the "stress" effect discussed by Hendrickson et al.<sup>4,5</sup>

In the case of unsupported, Kel-F-mulled I, it had been noted that the very intense and sharp CN stretch bands occur at 2068 and 2061 cm<sup>-1</sup> for the HS form (at 300 K) and at 2118 and 2111 cm<sup>-1</sup> for the LS form (at 80 K). Samples of the activated-carbon-supported material at low loading (2-4% Fe/C) showed no significant sharp absorbance either at room temperature or at 80 K in the range 2300-1900 cm<sup>-1</sup>, although there was a weak, broad absorbance observable at ~2050 cm<sup>-1</sup>. At higher loading (8-32% Fe/C), the room-temperature IR spectra showed the presence of bands at 2073, 2057 (broad), and 2034 cm<sup>-1</sup>, but these bands did not shift significantly on lowering the temperature to 80 K, being observed at 2081, 2062 (broad), and 2031 cm<sup>-1</sup>, respectively. These results are summarized graphically in Figure 1, in which 300 and 80 K IR data over the range 2200-1950 cm<sup>-1</sup> are shown for the unsupported sample (a and b) and for the sample supported on carbon (c and d).

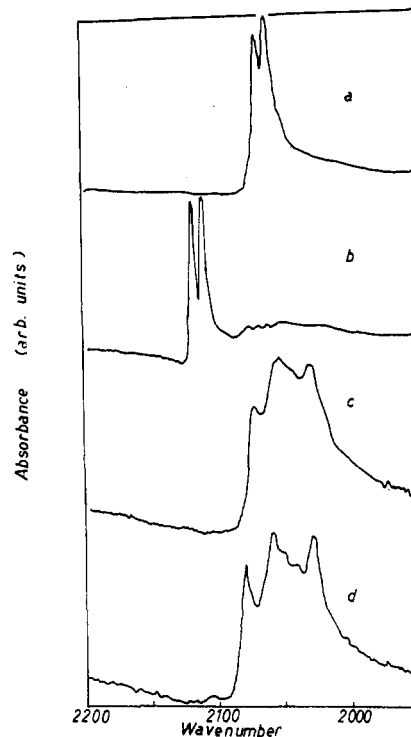


Figure 1. CN-stretch region of the infrared spectra of Fe(2,2'-bpy)<sub>2</sub>(SCN)<sub>2</sub> (I). The neat compound, dispersed in Kel-F grease, is shown in spectrum a (300 K) and spectrum b (80 K). A sample loaded to 32% Fe/C on activated charcoal is shown in spectrum c (300 K) and spectrum d (80 K). The absence of the LS form of I is clearly evident in spectra c and d, while the absorbance pattern at ~2050 cm<sup>-1</sup> suggests that a metathesis has occurred during the adsorption process.

In the case of sample II, the "neat", Kel-F-dispersed sample shows the IR-active CN bands at 2078 and 2063 cm<sup>-1</sup> (HS) and 2116 and 2108 cm<sup>-1</sup> (LS) at 300 K. The last two absorbances arise from the fact<sup>11</sup> that, even at room temperature, there has been a partial crossover to the LS form of the compound. When the temperature is lowered to 80 K, the absorptions ascribed to the LS form increase at the expense of the HS form absorbances, but again, the crossover conversion is incomplete at this temperature. The samples adsorbed on activated carbon (as for I, above) show no absorbances in the range 2300-2100 cm<sup>-1</sup> at either 300 or 80 K. At very high loading (16 and 32% Fe/C) a very weak absorbance appears in the room-temperature IR spectrum at 2109 cm<sup>-1</sup>, with a still smaller shoulder at 2116 cm<sup>-1</sup>. When the sample is cooled to 80 K, these bands become more distinct at 2112 and 2062 (broad) cm<sup>-1</sup>.

These data clearly indicate that, at low loading on activated carbon, the spin-crossover compounds do not give any IR evidence for the existence of either the HS or the LS forms, even at liquid-nitrogen temperature. (It should be noted that the other regions of the IR spectrum clearly showed the presence of the complex or its metathesis product, so that there can be little question that the solution species in some form had indeed been adsorbed on the support material.) At higher loadings, the IR spectra are consistent with the presence of some HS form at room temperature, but the conversion to the LS form on sample cooling is not significantly different from that observed for the "neat" samples. In this context, the present data suggest that, for the spin-crossover complexes I and II, a metathesis has occurred when solutions of the complexes are adsorbed on the activated-carbon supports. If, as seems likely, the Fe(II) complexes are converted by a heterogeneous oxidation process to a ferric form during this adsorption (and/or subsequent solvent evaporation) step, the <sup>57</sup>Fe Mössbauer signature of the resulting material will, of course, be different from that of the neat compounds. The usual Mössbauer isomer shift systematics<sup>17,18</sup> lead to the expectation that a collapse

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of the large quadrupole doublet associated with cis-octahedral Fe(II) configurations on oxidation to Fe(III) will lead to Mössbauer resonance absorptions in the range 0-0.8 mm s<sup>-1</sup> with respect to metallic iron, as observed in the data of Wei and Jean.<sup>2</sup>

It should be noted, however, that the present IR data pertain to spin-crossover complexes other than those examined in detail by Wei and Jean. While the present results indicate that the "particle size effect" is not a general phenomenon observable for complexes such as I and II, further detailed study by non-Mössbauer methods of the compounds discussed by Wei and Jean would appear to be appropriate.

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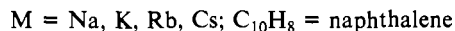
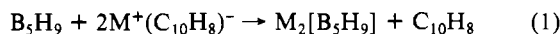
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### Reduction of B<sub>5</sub>H<sub>9</sub> by Alkali Metals. Preparation of the Dianion (B<sub>5</sub>H<sub>9</sub>)<sup>2-</sup> and a New Route to B<sub>5</sub>H<sub>11</sub>

Sir:

Although alkali-metal reductions to produce dianions have been successfully carried out with higher boron hydrides such as B<sub>10</sub>H<sub>14</sub><sup>1-4</sup> and B<sub>18</sub>H<sub>22</sub>,<sup>5</sup> reduction of the lower boron hydrides to dianions has not been demonstrated previously. While Stock<sup>6</sup> reported the reduction of pentaborane(9), B<sub>5</sub>H<sub>9</sub>, by potassium amalgam to give a compound he formulated as K<sub>2</sub>B<sub>5</sub>H<sub>9</sub>, later attempts to duplicate this work showed the product to contain a large amount of potassium borohydride and unidentified materials.<sup>4</sup> We have found that pentaborane(9) is cleanly reduced by two equivalents of sodium, potassium, rubidium, or cesium naphthalide in THF or glyme to form the nonahydropentaborate(2-) dianion, [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> (eq 1). Protonation of this dianion



provides a simple route from B<sub>5</sub>H<sub>9</sub> to B<sub>5</sub>H<sub>11</sub> in yields up to 38%.

In a typical reaction, 4.02 mmol of B<sub>5</sub>H<sub>9</sub> was condensed into a vessel containing 8.04 mmol of preformed potassium naphthalide in 10 mL of THF at -196 °C. Warming the mixture to room temperature and stirring for 30-45 min caused complete consumption of the naphthalide and produced the red-brown salt K<sub>2</sub>[B<sub>5</sub>H<sub>9</sub>]. No hydrogen was evolved in this reaction.<sup>7</sup> The salt was isolated by washing it with pentane on a filter to remove naphthalene and also by pumping away the naphthalene at room temperature under high vacuum. Other alkali-metal salts were

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- The possibility that the naphthalene was reduced in this reaction was tested by using perdeuterated naphthalene in the reaction. The reaction was carried out as described, and the product solution was examined by using <sup>2</sup>H NMR spectroscopy. The NMR spectrum revealed only minimal reduction of the naphthalene.

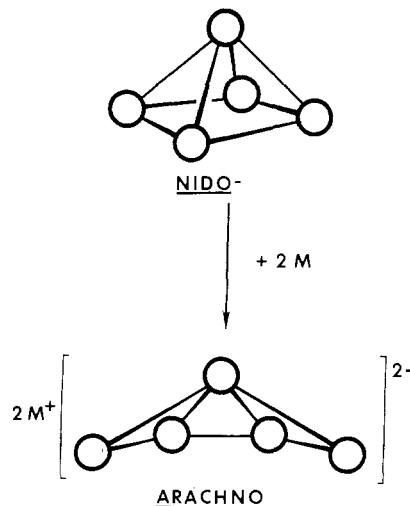


Figure 1. Expected structural change in the boron framework caused by a two-electron reduction of *nido*-B<sub>5</sub>H<sub>9</sub> to *arachno*-B<sub>5</sub>H<sub>11</sub>.

prepared similarly. The sodium salt is slightly soluble in THF and glyme while the potassium, rubidium, and cesium salts are insoluble.

In the presence of air, alkali-metal salts of [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> fume and are quickly discolored. They appear to be quite stable under vacuum in both the solid state and in solution, showing only minimal decomposition after 1 week, as judged from physical appearance, lack of gas evolution, infrared spectra, and boron-11 NMR spectra. IR spectrum of K<sub>2</sub>[B<sub>5</sub>H<sub>9</sub>] (Nujol mull, ν<sub>(B-H,terminal)</sub>, cm<sup>-1</sup>): 2407 (sh), 2359 (s), 2342 (s), 2335 (s). Bands in the B-H-B bridging region were unidentifiable due to overlap of Nujol bands. Boron-11 NMR spectrum of [K(dibenzo-18-crown-6)]<sub>2</sub>[B<sub>5</sub>H<sub>9</sub>] in THF (δ = 0.0 ppm for BF<sub>3</sub>·OEt<sub>2</sub>): -16.1 (J = 132 Hz, 4 B), -51.7 (J = 157 Hz, 1 B).

The crown ether (dibenzo-18-crown-6) complexes of the potassium, rubidium, and cesium salts of [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> are soluble in THF and glyme and thus could be used to obtain NMR spectra. These complexes were prepared by stirring equimolar quantities of alkali-metal and crown ether along with a small amount of naphthalene (ca. 5 mol %) in THF or glyme to form a yellow complex. This complex was then used to reduce B<sub>5</sub>H<sub>9</sub> to the dianion [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup>. The boron-11 NMR spectra of the [K(dibenzo-18-crown-6)]<sub>2</sub>[B<sub>5</sub>H<sub>9</sub>] complex and Na<sub>2</sub>[B<sub>5</sub>H<sub>9</sub>] are nearly identical. Boron-11 NMR spectra of [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> salts were clean and showed no other boron-containing species to be present. A two-electron reduction of *nido*-B<sub>5</sub>H<sub>9</sub> to the *arachno*-[B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> dianion is expected<sup>8</sup> to open the B<sub>5</sub>H<sub>9</sub> square pyramid to give a boron framework like that of B<sub>5</sub>H<sub>11</sub> (a pentagonal pyramid with one basal vertex site absent) as illustrated in Figure 1. The fact that only two NMR signals are observed indicates that the [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> molecule is highly fluxional at room temperature. Low-temperature (-70 °C) <sup>11</sup>B NMR spectra showed broadening of the signals; however, additional signals were not observed. Boron-11 NMR spectra of other pentaborane anions, [B<sub>5</sub>H<sub>8</sub>]<sup>-</sup>, [B<sub>5</sub>H<sub>10</sub>]<sup>-</sup>, and [B<sub>5</sub>H<sub>12</sub>]<sup>-</sup>, also show two doublets in a relative ratio of 4:1.<sup>9-12</sup> Although the <sup>11</sup>B NMR spectrum for [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> is very similar to that obtained for the [B<sub>5</sub>H<sub>8</sub>]<sup>-</sup> anion, the stabilities, solubilities, and IR spectra of [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> salts are very different from those of [B<sub>5</sub>H<sub>8</sub>]<sup>-</sup> salts. In addition, protonation of [B<sub>5</sub>H<sub>9</sub>]<sup>2-</sup> produces B<sub>5</sub>H<sub>11</sub> in good yield. No B<sub>5</sub>H<sub>9</sub> is obtained from this protonation.

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