

## Size-induced Spin Crossover in a Carbon-supported Iron-diimine Complex

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Mössbauer spectra for the diimine complex  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  provide clear evidence for high-spin iron(II) at room temperature; however for carbon-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  as the loading of the iron complex decreases the high-spin species is converted into the low-spin state.

We have recently described<sup>1,2</sup> the dependence of the high-spin(HS)  $\rightleftharpoons$  low-spin(LS) transition on the particle size of carbon- or MgO-supported  $\text{Fe}(\mathbf{1a})_2(\text{NCS})_2$ . At room temperature, as the iron complex loading decreases, the fraction of the HS species present approaches zero, until only LS species exist in the complex. In contrast, thermally-induced spin conversion in the non-supported complex is incomplete even at 4.2 K.<sup>3</sup>

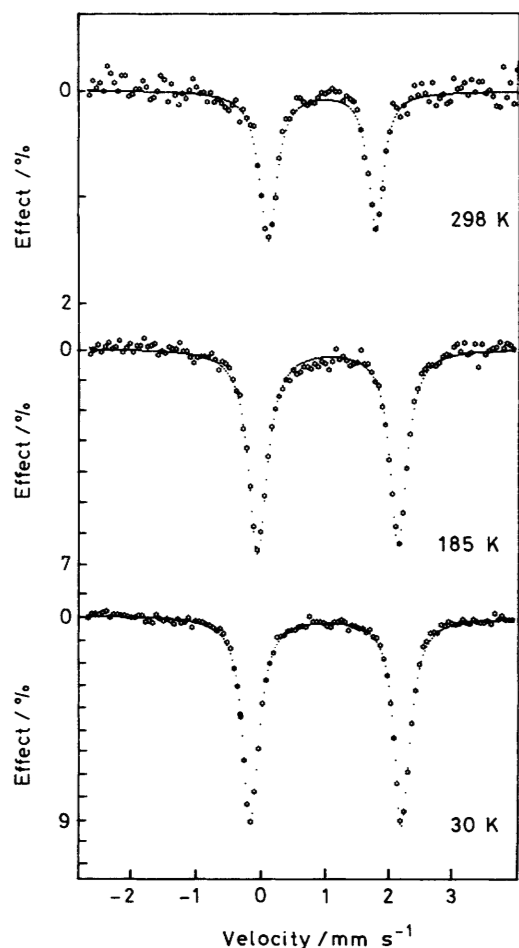
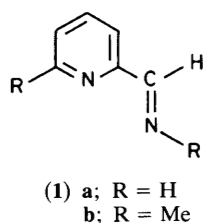


Figure 1. Mössbauer spectra of non-supported  $\text{Fe}(\mathbf{1b})(\text{NCS})_2$  as a function of temperature.

In this communication, we report a new example of the size-induced spin crossover at room temperature; that of the iron(II) complex with the diimine ligand ( $\mathbf{1b}$ ). The methyl group in the 6-position introduces a considerable steric effect into the resulting iron(II) complex. As a consequence of this,

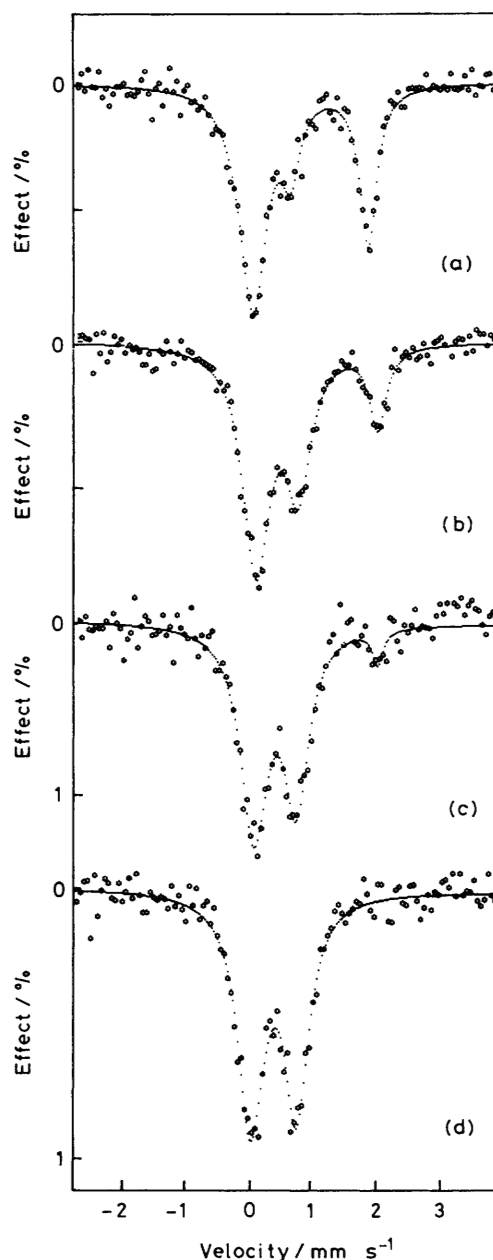
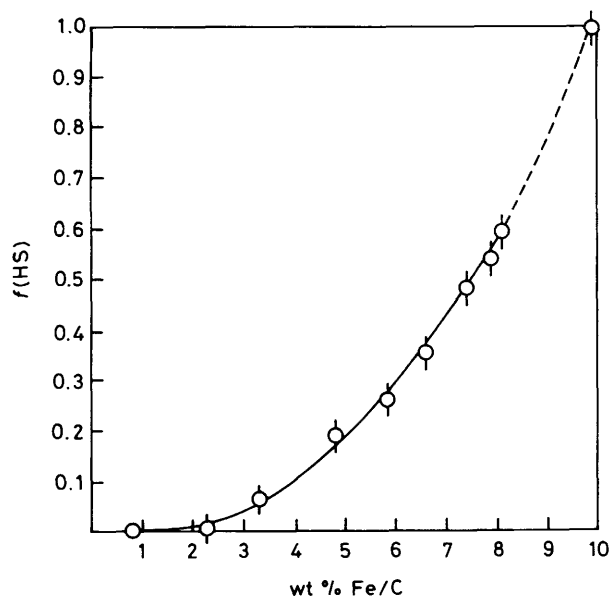


Figure 2. Mössbauer spectra at 298 K of carbon-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$ : (a) 8.0, (b) 4.9, (c) 3.3, and (d) 2.3 wt% Fe.



**Figure 3.** Variation of  $f(\text{HS})$  with iron loading (wt% Fe/C), for carbon-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$ .

the non-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  is expected to be in a high-spin ground state over the temperature range under study.

The non-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  was prepared using a standard method,<sup>4</sup> and purified by repeated recrystallization. Its composition was determined by elemental analysis and its i.r. spectrum. The magnetic moment at room temperature, determined using a Faraday balance, was found to be  $5.40 \mu_B$ . (The value published by Barth *et al.*<sup>4</sup> was  $5.18 \mu_B$  at  $20^\circ\text{C}$ .)

A series of samples containing various quantities of  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  supported on carbon were prepared *via* the incipient wetness technique. A known concentration of the solid iron complex was dissolved in 5 ml acetone, then added dropwise with stirring to pre-weighed, dry, purified and activated carbon (*ca.* 100 mesh). The impregnated samples were dried at room temperature in a high-vacuum, then sealed in polyacrylic sample holders. Complex loading is reported as Fe wt% of the dry sample, *e.g.* 2.3 wt% Fe/C.

Mössbauer absorption spectra of non-supported and carbon-supported iron complexes were measured using standard equipment described elsewhere.<sup>1,2</sup> The source was  $^{57}\text{Co}(\text{Pd})$  kept at room temperature. The isomer shifts (I.S.) are with respect to metallic iron at 298 K.

The Mössbauer spectra of non-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  between 30 and 298 K are shown in Figure 1, which shows only the quadrupole-split line of the HS state. Room temperature spectra for the carbon-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  samples (the iron loading was changed from 8.0 to 0.9 wt%) are shown in Figure 2. The sample with 2.3 wt% Fe/C, Figure 2(d), exhibits a spectrum consisting of only the quadrupole-split line of the LS state of iron(II). The sample size is small enough so that the spin conversion from the HS into the LS state is complete.

The Mössbauer parameters [quadrupole splitting (Q.S.) and I.S.] of the HS and LS iron(II) in the spectra of the carbon-supported  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  are independent of sample size, and have the same value (Q.S. =  $0.71 \text{ mm s}^{-1}$  and I.S. =  $0.44 \text{ mm s}^{-1}$  for the LS species and Q.S. =  $1.68 \text{ mm s}^{-1}$  and I.S. =  $0.95 \text{ mm s}^{-1}$  for the HS species) in all samples. The ratio of the HS to the LS fraction  $f(\text{HS})$  can be estimated by integration of the Mössbauer absorption lines. The  $f(\text{HS})$  values at 298 K so obtained are plotted in Figure 3 against the Fe wt%, where the maximum Fe wt% in bulk  $\text{Fe}(\mathbf{1b})_2(\text{NCS})_2$  is 9.87%. It can be clearly seen that, as the iron loading in the carbon-supported complex decreases to less than 2.0 wt%, the fraction of HS species approaches zero until only LS species exist in the complex. Thermally-induced spin crossover in the non-supported complex does not take place even at 30 K, and only the HS species is observed. This size-induced spin crossover phenomenon has not previously been reported in any spin crossover study.

We thank the National Science Council of Taiwan for the support of this work.

Received, 23rd April 1986; Com. 544

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