

Characterization of a High Temperature Spin Equilibrium Compound, Bis[hydrotris(Pyrazol-1-yl)borate]iron(II)

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Summary Variable temperature magnetic susceptibility, Mössbauer, and far-i.r. spectral data are correlated to show that bis[hydrotris(pyrazol-1-yl)borate]iron(II) exhibits a low-spin, high-spin crossover at high temperature.

SEVERAL six-co-ordinate pseudo-octahedral iron(II) complexes are known which show spin-equilibrium below room temperature.¹ We report here the magnetic susceptibility, and far-i.r. and Mössbauer spectra of $[(\text{htpb})_2\text{Fe}]$ (htpb = hydrotrispyrazol-1-ylborate) between 298 and 463 K which show this compound to exhibit a reversible spin-equilibrium at high temperature. The preparation and initial suggestion of spin change based on the thermochromic nature of this compound were reported in 1968.²

Heating a crystalline sample of the $[(\text{htpb})_2\text{Fe}]$, recrystallized from hot toluene, from room temperature to 463 K results in a change of effective magnetic moment from 1.0 to 4.9 B.M. (Figure). These results indicate a change from primarily low-spin $^1A_{1g}$ to the high-spin $^5T_{2g}$ state which occurs upon initial heating with a sharp rise in effective magnetic moment at about 391 K. Upon cooling to room temperature the same sample exhibits an effective magnetic moment of 1.4 B.M. but shows no sharp decrease in moment. During second heating of the same sample the magnetic moment follows the cooling pathway. The sample composition was unchanged by the above process.

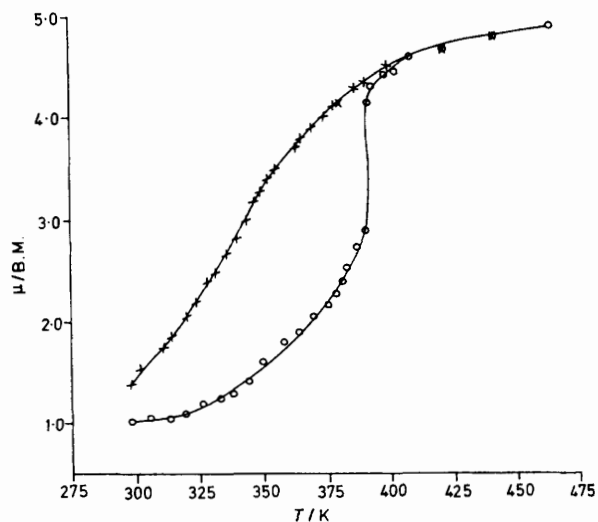


FIGURE. Temperature dependence of the effective magnetic moment of crystalline $[(\text{htpb})_2\text{Fe}]$. \circ initial heating; $+$, cooling.

The Mössbauer spectrum of $[(\text{htpb})_2\text{Fe}]$ at 4.2 K reveals two lines with an isomer shift of 0.48 mm/s and a quadrupole splitting of 0.22 mm/s. These lines result from the overlap of the quadrupole doublet resulting from each

crystallographically distinct iron(II) site.³ At this temperature, $H_{\text{internal}} = H_{\text{applied}}$ in an applied magnetic field of 6 T, as is expected for a low-spin iron(II) complex. At room temperature, a single broad line is observed with an isomer shift of 0.45 mm/s and a quadrupole interaction of 0.19 mm/s. At 423 K a two-line spectrum is observed with a isomer shift of 0.81 mm/s and a quadrupole splitting of 2.77 mm/s. Thus, at this temperature, the Mössbauer parameters indicate essentially complete conversion into a high-spin paramagnetic pseudo-octahedral iron(II) complex. The Mössbauer spectra also indicate that the spin-state transformation is essentially completely reversible after the initial heating and cooling. During the second and subsequent heatings between room temperature and 423 K the Mossbauer spectrum shows a gradually increasing quadrupole splitting and isomer shift with increasing temperature. The line width and intensity asymmetry goes through a maximum at *ca.* 370 K. This behaviour indicates that, within this temperature range, the rate of spin state interconversion is of the order of, or faster than, the lifetime of the Mössbauer isomeric excited state. Different behaviour, which is indicative of a co-operative transformation, is observed during initial heating. No indication of the formation of iron(III) was observed in any of the Mössbauer spectra.

Metal-isotope substitution of ⁵⁴Fe and ⁵⁷Fe in the complex gave isotope shifts of >5 cm⁻¹ for certain absorptions in the far-i.r. spectrum at 298 and 468 K. Other bands were not shifted by this change. Absorptions which shift upon metal isotopic substitution must involve significant metal movement in their vibration. Shifted bands occur at 459, 425, and 399 cm⁻¹ for the low-spin species and at 250 and 225 cm⁻¹ for the high-spin and are assigned as Fe-N stretching bands. The large difference in the position of the Fe-N stretching bands is due to the weakening of the Fe-N bond when the antibonding e_g orbitals are occupied, $t_{2g}^4 e_g^2$, compared to the low-spin form t_{2g}^6 .⁴ Bands in this spectral region which are unchanged by isotope substitution at 355 and 332 cm⁻¹ are due to ligand vibrations. The i.r. spectrum at intermediate temperatures indicates the simultaneous presence of varying amounts of high- and low-spin species through both types of Fe-N stretching bands.

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¹ H. A. Goodwin, *Co-ordination Chem. Rev.*, 1976, **18**, 293.

² J. P. Jesson, J. F. Weiher, and S. Trofimenko, *J. Chem. Phys.*, 1968, **48**, 2058.

³ B. B. Hutchinson, J. D. Oliver, D. F. Mullica, and W. O. Milligan, *Inorg. Chem.*, in the press.

⁴ B. B. Hutchinson, M. Hoffbauer, and J. Takemoto, *Spectrochim. Acta*, 1976, **32A**, 1785.