

Infrared Spectra of Some Magnetically Anomalous Iron(II) Complexes

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EARNSHAW, KING, and LARKWORTHY have recently reported¹ the magnetic properties of the nitrosyl adduct of a planar iron(II) complex. The magnetic moment of the nitrosyl is about 3.6 B.M. at room temperature but drops abruptly near 180°K to 2.0 B.M. They also report that the infrared spectrum shows the nitrosyl stretching band to be at 1715 cm.⁻¹ at room temperature and shifted to 1630 cm.⁻¹ below the magnetic transition point.

We had previously reported² similar magnetic behaviour in three iron(II) complexes, [Fe(phen)₂(SCN)₂], [Fe(phen)₂(SeCN)₂], and [Fe(bipy)₂(SCN)₂]. We have now studied the infrared spectra of these compounds over the temperature range 77—300°K. The C-N stretching band of

the thiocyanate (or selenocyanate) appears at room temperature as a strong doublet at 2060—2070 cm.⁻¹ Upon cooling, the intensity of this doublet decreases and a new doublet appears around 2100—2110 cm.⁻¹ A representative spectrum is shown in Figure 1.

In Figure 2 we show the relative intensity of the 2100 cm.⁻¹-doublet as a function of temperature for the three compounds. The similarities between these curves and the plots of magnetic moment against temperature² leave little doubt that the 2100 cm.⁻¹-doublet is associated with a low-spin species while the one at 2060 cm.⁻¹ is due to the high-spin form. The similarity is evident in both the temperature ranges over which the maximum

¹ A. Earnshaw, E. A. King, and L. F. Larkworthy, *Chem. Comm.*, 1964, 180.

² W. A. Baker, Jr., and H. M. Bobonich, *Inorg. Chem.*, 1965, 3, 1184.

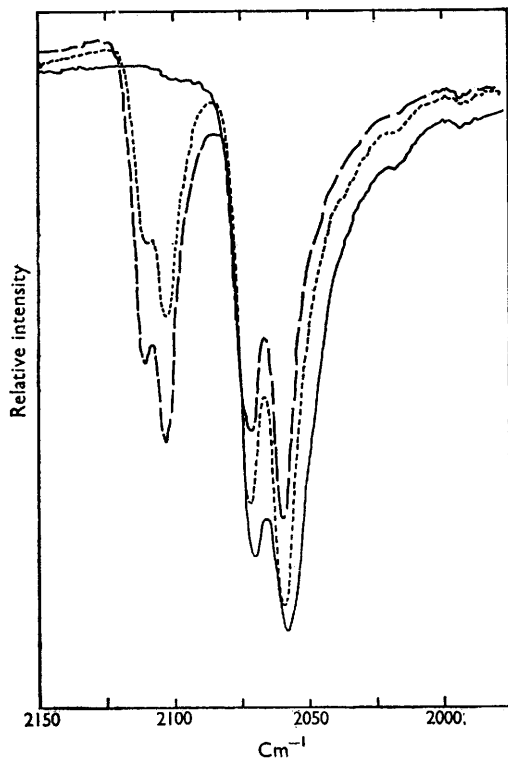


FIGURE 1. Infrared spectrum of $[Fe(phen)_2(SCN)_2]$ at room temperature (—), $172^\circ K$ (. . . .), and $160^\circ K$ (- - -).

change occurs as well as the sharpness of the transitions, the latter being more gradual for the selenocyanate.

The exact reason for the magnetic and infrared phenomena is still not clear. Our previous suggestion² of a polymeric species containing both co-ordinated and ionic anions now seems in error,

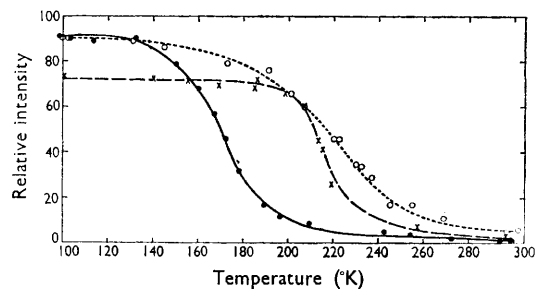


FIGURE 2. Relative intensity of the 2100 cm.^{-1} -doublet against temperature for $[Fe(bipy)_2(SCN)_2]$ (—), $[Fe(phen)_2(SCN)_2]$ (—) and $[Fe(phen)_2(SeCN)_2]$ (- - -).

however, since the ionic thiocyanate should show a band around 2060 cm.^{-1} whose intensity and position is essentially independent of temperature.

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