Some Spin-Free Iron Nitrosyls

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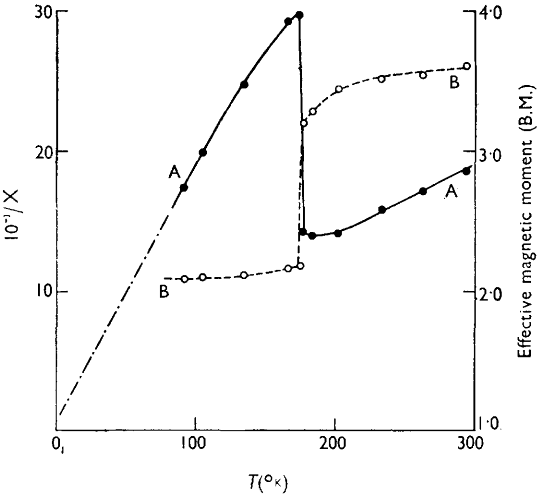
THE presumably planar iron(II) complex (I) is spin-free,[1] and obeys the Curie–Weiss law ($\theta = 3°$).[2] Like the corresponding cobalt(II) compound[3] it forms a mononitrosyl. The magnetic moment of the nitrosyl (Figure) corresponds to three unpaired electrons at room temperature, but changes abruptly to that for one unpaired electron near 180°K. Spin-free, spin-paired equilibria are fairly common, but we are aware of only one other example[4] of an abrupt change of this nature. Preliminary work has shown the only marked change in the infrared spectrum of the nitrosyl on cooling in liquid air to be the disappearance of a strong absorption at 1715 cm.$^{-1}$ Compound (I) does not absorb in this region so that the absorption may be assigned to the nitric oxide stretching vibration. On spin-pairing this absorption is believed to move to near 1630 cm.$^{-1}$ where an intense ligand absorption occurs.



Metal–metal or superexchange interactions would be expected to lead to a different temperature dependence of moment, with the moment tending to zero at lower temperatures. Several other effects could, singly or collectively, cause spin-pairing at low temperatures, *e.g.* contraction of the lattice, a change in NO orientation, or formation of bridging NO groups. Recent work indicates that a change from a linear to a bent M–N–O grouping could cause spin-pairing,[5] and be compatible[6] with a decrease in the nitric oxide stretching frequency.

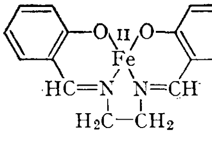
Other spin-free mononitrosyls obtained from 5,5′-disubstituted derivatives of (I), show no discontinuity in the temperature–susceptibility curve, the Curie–Weiss law being obeyed:

5,5′-dimethyl-nitrosyl, $\mu_{\text{eff}} =$ 4·0 B.M. at 296°K, $\theta = 6°$,

5,5′-dinitro-nitrosyl, $\mu_{\text{eff}} =$ 3·1 B.M. at 294°K, $\theta = 70°$.

The origin of the large Curie–Weiss constant for the nitro-compound is not known.

Each nitrosyl has been prepared several times and reproducible magnetic and spectral results have been obtained, although the magnitude of the discontinuity found for the nitrosyl of (I) does vary from preparation to preparation. When moist, (I) and its derivatives, and all the nitrosyls, are oxygen-sensitive. In certain solvents the nitric oxide rapidly oxidises the iron to the ferric state. The nitro-substituted nitrosyl soon loses nitric oxide, but these compounds generally seem to be the only reasonably stable solid spin-free nitrosyls so far reported. The nitric oxide adduct of bis-(salicylaldehydato)iron,[7] and the brown ring compounds,[8] readily decompose.



(I)

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