Unusual Magnetic Behaviour of Some Iron(II)-Bis-(1,10-phenanthroline) Complexes

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BAKER and BOBONICH have recently reported[1] the observation of an unusual change of the magnetic moment with temperature for the compounds [Fe $phen_2(NCS)_2$] and [Fe $phen_2(NCSe)_2$]. On the basis of infrared-spectral investigations, exchange interaction between two iron(II) ions through bridging SCN groups was suggested.

We had previously shown[2] that, depending upon the strength of the ligand X, two magnetically different types of complexes may be prepared within the series [Fe $phen_2X_2$]: (a) high-spin compounds with $^5T_2$ ground states and room-temperature magnetic moments of 5·0—5·3 B.M., if X = Cl^-, Br^-, I^-, N_3^-, OCN^-, HCO_2^-; (b) low-spin compounds with $^1A_1$ ground states, diamagnetic, if X = CN^-, CNO^-, NO^{2-}. For ligands X having a field strength close to the cross-over point of $^5T_2$ and $^1A_1$ states, spin-state equilibria might be expected. We report some of our recent results which demonstrate that such equilibria occur for the ligands X = NCS^- and $NCSe^-$. In what follows, the compound [Fe $phen_2(NCS)_2$] will be used as an example. Similar conclusions were arrived at for [Fe $phen_2(NCSe)_2$].

Accurate magnetic-susceptibility measurements give a high-temperature limit for the moment of 5·20 ± 0·05 B.M. at 430°K. At ~170°K, the moment value decreases from 4·91 to 1·70 B.M. within ~3° and finally approaches 0·65 ± 0·01 B.M. at 77°K. The observed variation of magnetic susceptibility with temperature has been compared with plots obtained from the susceptibility expression for two antiferromagnetically interacting centres with spin $S = 2$. No reasonable fit could be obtained for any value of the exchange integral J, thus ruling out the explanation proposed previously.[1]

On the other hand, we derived an expression for the temperature-dependence of the magnetic susceptibility for a $^1A_1$ state separated by ΔE from a thermally accessible $^5T_2$ state. Reasonable agreement with the measured susceptibility is achieved, if $\Delta E \sim 350$ cm.$^{-1}$ The sudden decrease of susceptibility is not reproduced in complete detail for reasons specified previously.[3]

The electronic spectra measured at 298 and ~77°K show major differences as expected for a change in electronic configuration. In the region characteristic for *d–d* transitions, the room-temperature spectrum shows a band at 11,900 cm.$^{-1}$ which corresponds to the $^5T_2 \rightarrow {}^5E$ transition. At 77°K, the transition $^1A_1 \rightarrow {}^3T_1$ of the low-spin configuration is observed at ~10,400 cm.$^{-1}$

Infrared spectra were studied between 4000 and 280 cm.$^{-1}$ both at 298 and ~105°K. Several bands assigned to skeletal vibrations of the 1,10-phenanthroline ligand,[4] the C–N and C–S stretching modes and the NCS bending mode are shifted or changed in intensity on cooling. The changes observed are such as expected from a marked decrease in the ionic radius and an increase in the strength of the metal–ligand bond, both of which are associated with the transition from the high-spin to the low-spin state in iron(II).[5]

The possibility of a phase change has been ruled out by *X*-ray studies at 298 and 77°K. A change from a *trans-* to *cis*-configuration is extremely unlikely on the basis of infrared spectra. The NCS ligands are *N*-bonded and *cis*, independent of temperature.

Finally, measurements of the ^{57}Fe Mössbauer spectra were used to determine directly the electronic configuration of the iron ion in the two magnetically different states. From a spherical ground state like $A_1(t_2^6)$, a zero electric field gradient and, therefore, a very small quadruple splitting ΔE_Q will be expected. Finite values of ΔE_Q, however, are obtained from T_2 terms in absence of octahedral symmetry. Likewise, the spin polarization of core electrons, and thus the isomer shift δ, should increase, for a given ion, with the number of unpaired electrons. For [Fe $phen_2(NCS)_2$], the following results were obtained:†

T, °K	ΔE_Q, mm./sec.	δ, mm./sec.
293	2·67 ± 0·03	0·98 ± 0·03
77	0·34 ± 0·06	0·37 ± 0·05.

These values may be compared with $\Delta E_Q \sim 0{\cdot}30$, $\delta = 0{\cdot}45$ mm./sec. obtained for the low-spin

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† The isomer shifts, δ, are measured relative to the mid-point of the spectrum of an iron-foil absorber. A source of ^{57}Co diffused into stainless steel has been used.

[Fe phen$_3$]$^{2+}$ ion[6] on one hand, and with the results on numerous high-spin iron(II) compounds which yield values of ΔE_Q between 1·7 and 3·1 and δ between 0·8 and 1·4 mm./sec. on the other.[7] Also, high-spin compounds from the series [Fe phen$_2$X$_2$] give values of ΔE_Q and δ similar to those obtained for [Fe phen$_2$(NCS)$_2$] at 293°K; low-spin compounds give values comparable to those of [Fe phen$_2$(NCS)$_2$] at 77°K.

These data provide conclusive evidence for the existence of spin-state equilibria between almost equi-energetic $^5T_2$ and $^1A_1$ states. To our knowledge this is the first report on quintet-singlet equilibria in transition-metal complexes.

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