Spin Equilibria in Iron(II) Hexa-amine Cages

Lisandra L. Martin,[a] **Karl S. Hagen,**[a] **Andreas Hauser,**[a] **Raymond L. Martin,**[b] **and Alan M. Sargeson**[a]*

[a] *Research School of Chemistry, The Australian National University, Canberra, A.C.T., 2601, Australia*

[b] *Department of Chemistry, Monash University, Clayton, 3168, Victoria, Australia*

Iron(II) cage complexes $[Fe\{(1\text{-}X, 8\text{-}Y)\text{-}sar\}]^{2+}$ (X = Y = H, NH_2, or NH_3^+, or X = Me, Y = H, sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane) show high-spin ($^5T_{2g}$ origin) $\rightleftharpoons$ low-spin ($^1A_{1g}$ origin) equilibria in solution, characterised by measurements of magnetism and visible and ^1H n.m.r. spectra.

The synthesis[1—4] of a series of first row transition metal ions encapsulated by the hexa-amine ligand 'sar' (Figure 1) offers an unusual opportunity to study their electronic properties in a saturated amine ligand field. Encapsulation of the central metal ion provides a magnetically dilute, co-ordinatively saturated, and kinetically inert environment and, in solution, the electronic properties should be determined by the intramolecular characteristics of the complex.[4]

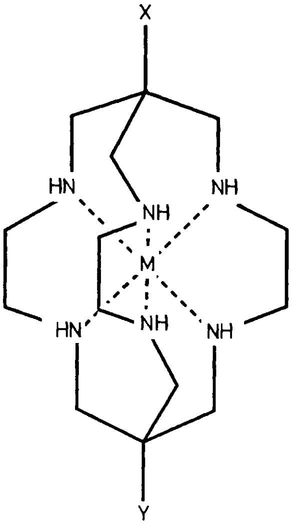

Figure 1. Structure of the cage complexes $[M\{(1\text{-}X, 8\text{-}Y)\text{-}sar\}]^{n+}$.
$[M(sar)]^{n+}$ X = Y = H
$[M\{(NH_3)_2\text{-}sar\}]^{(n+2)+}$ X = Y = NH_3
$[M\{(NH_2)_2\text{-}sar\}]^{n+}$ X = Y = NH_2

The temperature dependence of the magnetic susceptibility between 4 and 300 K has been measured[4,5] for the following polycrystalline complexes where the counter-anion is NO_3^-, Cl^-, ClO_4^-, $CF_3SO_3^-$, $S_2O_6^{2-}$, or $ZnCl_4^{2-}$:

$[M(sar)]^{n+}$	M = Cr^{III}, Mn^{III}, Mn^{II}, Fe^{III}, Fe^{II}, Co^{III}, Co^{II}, Ni^{III}, Ni^{II}, Cu^{II}, Zn^{II} (n = 2 or 3)
$[M\{(NH_3)_2\text{-}sar\}]^{n+}$	M = V^{III}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II} (n = 4 or 5).
$[M\{(NH_2)_2\text{-}sar\}]^{n+}$	M = Cr^{III} or Fe^{II} (n = 3 or 2)
$[M\{(NH_3)_2\text{-}sar\text{-}2H^+\}]^{4+}$	M = V^{IV}

The Fe^{III}, Co^{III}, and Ni^{III} complexes all exhibit low-spin behaviour whereas the Mn^{III} complex is a high-spin system. The M^{II} counterparts $[M(sar)]^{2+}$ and $[M\{(NH_3)_2\text{-}sar\}]^{4+}$ are all high-spin except for the deep blue Fe^{II} complex $[Fe\{(NH_2)_2\text{-}sar\}]^{2+}$. Surprisingly, this complex is diamagnetic, which implies that the ligand field generated by these saturated macrobicycles is close to that required for the low-spin (t_2^6) and high-spin ($t_2^4e^2$) crossover.[6] This situation has now been confirmed by studying the temperature dependence of the magnetic susceptibility and optical and ^1H n.m.r. spectra of the Fe^{II} cage complexes in solution, where the effects of intermolecular interactions are negligible. The magnetic moments at 20 °C determined by the Evans n.m.r. method[7] were found to lie between the values expected for

Table 1. Magnetic moments, measured at 293 K in solid and solution states, for Fe^{II} cages.

Compound	μ_{eff} in solid/ B.M.	μ_{eff} in solution/ B.M.	Solvent
$[Fe(sar)](CF_3SO_3)_2$	5.15[a]	2.15 ± 0.12	D_2O
		2.55 ± 0.04	CD_3CN
		2.27	DCl[b]
$[Fe\{(NH_3)_2\text{-sar}\}]Br_2Cl_2 \cdot 4H_2O$	5.42	4.23 ± 0.22	D_2O
		4.33	$(CD_3)_2NCDO$
$[Fe\{(NH_2)_2\text{-sar}\}](CF_3SO_3)_2$	Diamag.	2.33	CD_3CN
$[Fe\{(Me)\text{-sar}\}](CF_3SO_3)_2$	High-spin[c]	2.22	$(CD_3)_2NCDO$

[a] Measured at 230 K. [b] 0.1 M DCl in D_2O with t-butyl alcohol as reference probe. [c] Sample in solid state appears identical with the high-spin colourless $[Fe(sar)](CF_3SO_3)_2$ and $[Fe\{(NH_3)_2\text{-sar}\}]Br_2Cl_2 \cdot 4H_2O$; *cf.* the deep blue crystal of diamagnetic $[Fe\{(NH_2)_2\text{-sar}\}](CF_3SO_3)_2$.

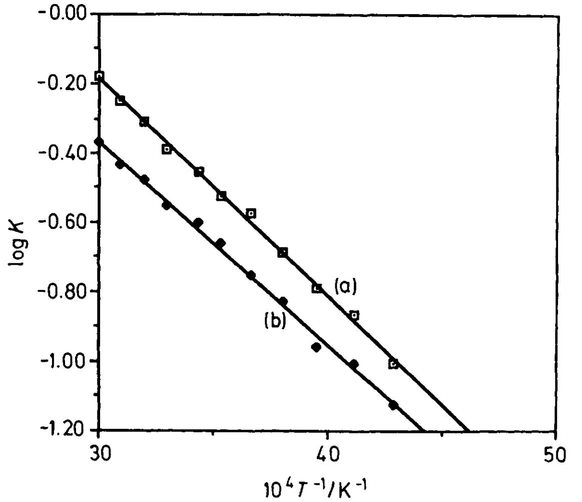

Figure 2. Temperature dependence of the spin equilibrium for $[Fe(sar)](CF_3SO_3)_2$ in CD_3CN formulated on the basis of (a) a spin-only value for the $t_2^4e^2$ state (K_{SO}) and (b) a spin-orbit coupled $t_2^4e^2$ state (K_{LS}).

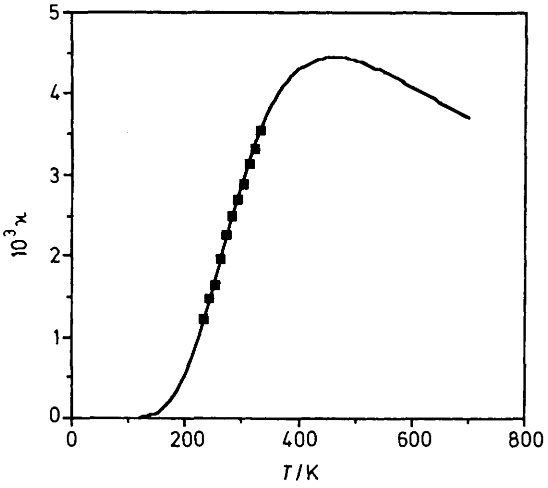

Figure 3. Calculated curve and experimental data for variation of magnetic susceptibility with temperature for $[Fe(sar)]^{2+}$ in CD_3CN based on a spin-only model for the $t_2^4e^2$ state.

low-spin and high-spin behaviour (Table 1). For the ions, $[Fe(sar)]^{2+}$, $[Fe\{(NH_2)_2\text{-sar}\}]^{2+}$, and $[Fe\{(CH_3)\text{-sar}\}]^{2+}$, χ_M and μ_{eff} vary markedly with temperature (*e.g.* Figure 3), whereas for $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ μ_{eff} is essentially temperature-independent. Equilibrium constants for the two states and other equilibrium parameters are deduced from equations (i) and (ii), where μ_{eff}^2 ($t_2^4e^2$) is taken as the spin-only value (24) (Figure 2).

The spin states can be considered as derived from the singlet $^1A_{1g}$ and quintet $^5T_{2g}$ ground states of octahedral symmetry, but the structural data available[8]† and the symmetry enforced by the ligand clearly require an effective symmetry less than O_h and almost certainly D_3 (on average) in solution. Given this constraint, it is reasonable to describe the singlet ground state as $^1A_1$ and the quintet ground state as $^5A_1$.

$$K_{eq} = [t_2^6]/[t_2^4e^2] = \mu_{eff}^2/(24 - \mu_{eff}^2) \tag{i}$$

$$\ln K_{eq} = -\Delta H/RT + \Delta S/R \tag{ii}$$

The interpretation of the magnetism is reinforced by the unusual absorption spectrum of $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ in D_2O (pH 4.5) (Figure 4), which displays a broad and weak band centred at *ca.* 11 000 cm^{-1} ascribed to the high-spin quintet transition of origin ($^5T_{2g} \rightarrow {}^5E_g$) split by a dynamic Jahn-Teller distortion of the excited state.[10] In addition, there are the expected strong absorptions for the low-spin isomer at 17 000 and 25 000 cm^{-1} originating from the $^1A_1 \rightarrow E, A_2$ and $^1A_1 \rightarrow E, A_1$ transitions in D_3 symmetry. Increasing the pH to 8.5 leads to deprotonation of the two NH_3^+ groups and an increase in the population of the low-spin form ($^1A_1$). In other solvents, the visible spectra are also temperature-dependent in a manner like that seen for the magnetism data.[4,9a] The simultaneous observation of the spectra of both high- and low-spin forms of $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ in solution clearly identifies the presence of both spin stereoisomers and the equilibrium condition. The temperature dependence of the visible spectrum of $[Fe(sar)]^{2+}$, for example, in solution is also consistent with marked changes in the low-spin population. The high-spin component in this system is more difficult to observe because its population is small and its spectral intensity very weak.[4,9a]

The magnitude and sign of the energy separation ΔH deduced from the solution magnetism indicates that the ^5A state lies *ca.* 1000 cm^{-1} above the diamagnetic $^1A_1$ state for $[Fe(sar)]^{2+}$, $[Fe\{(NH_2)_2\text{-sar}\}]^{2+}$, and $[Fe\{(CH_3)\text{-sar}\}]^{2+}$.

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† The expectation, in solution, is that the high-spin form (Fe–N~2.2 Å) will be roughly halfway between a trigonal prism and an octahedron for the ligating atoms whereas the low-spin isomer will be much closer to an octahedron (Fe–N~2.0 Å).

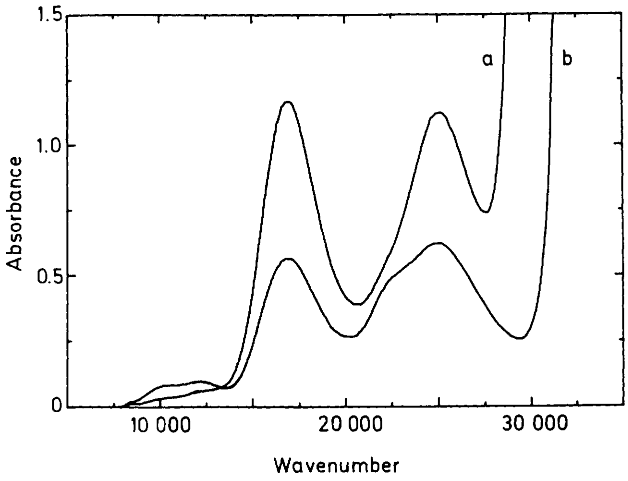

Figure 4. Variation of the visible absorption spectra with pH for $[Fe\{(NH_2)_2\text{-sar}\}]^{2+}$ in D_2O. At pH 8.5, the species in solution is $[Fe\{(NH_2)_2\text{-sar}\}]^{2+}$ (curve a) and at pH 4.5 it is $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ (curve b). (The shoulder around 22 000 cm^{-1} is due to a trace of di-imine complex arising from oxidation of $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ by traces of O_2.)

However for $[Fe\{(NH_3)_2sar\}]^{4+}$ the two states are nearly equi-energetic (ΔH *ca.* 100 cm^{-1}) and the equilibrium is therefore relatively temperature-insensitive.[4,9b] It can be seen from Figure 2 that although the choice of the spin-only or the spin-orbit coupled model affects the estimation of the equilibrium constant, it does not affect ΔH greatly. The χ and μ_{eff} data also fit either model equally well (*e.g.* Figure 3), except for $[Fe\{(NH_3)_2\text{-sar}\}]^{4+}$ where the data fit the spin-only model much better than the spin-orbit coupled model. It is also likely that the spin-orbit coupling is reduced considerably in the lowered symmetry, and therefore, a spin-only model is the most valid representation for the high-spin isomer in solution.

This is one of the few Fe^{II} thermal spin equilibrium systems for which d-d transitions can be observed. Usually, these ligand field bands have been obscured by charge-transfer bands associated with unsaturated ligands.[11—14] Moreover, it came as a surprise that the saturated amine ligands generate ligand fields which approach those in the unsaturated amine complexes. To a degree, this could arise from the strain induced in the ligand once bound to the metal ion.

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