Magnetic Isomers. *cis*-Bis(cyanotriphenylborato)bisphenanthrolineiron(II)

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Summary The complex *cis*-Fe(phen)$_2$(NCBPh$_3$)$_2$ (phen = 1,10-phenanthroline) exhibits synchronous spin- and stereo-isomerization in CH$_2$Cl$_2$, suggesting a previously unrecognized mechanism for spin-equilibria in octahedral complexes.

VARIABLE spin state phenomena for Fe^{II} complexes are thought to be an important aspect of the catalytic properties of certain bioactive complexes.[1] The phenomenon has been previously documented in the solid state[2] for non-bioactive complexes, where first and second order phase transitions are involved, but rarely in solution.[3] Here we report on Fe(phen)$_2$(NCBPh$_3$)$_2$ (phen = 1,10-phenanthroline), which exhibits dynamic spin isomerization in solution.

The complex is prepared from Fe(phen)$_2$Br$_2$ and NaNC-BPh$_3$ in CHCl$_3$ in > 90% yield. The molecular weight, after *in situ* conversion into Fe(phen)$_3$(NCBPh$_3$)$_2$, is 947 (theory, 953) based on the charge-transfer (CT) absorption

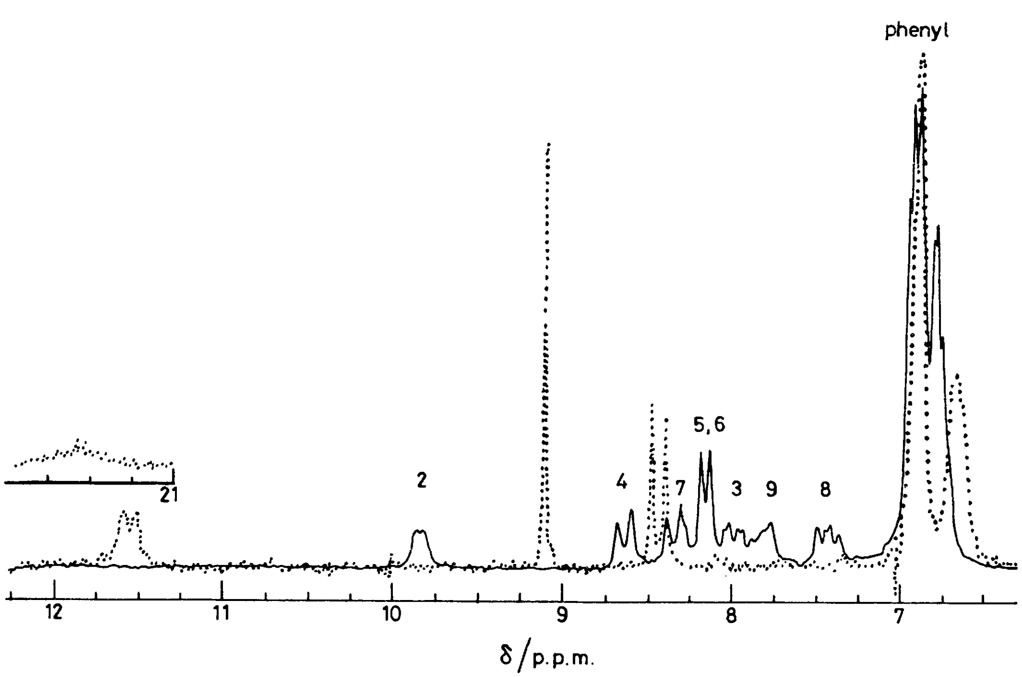

Figure 1. Pulsed Fourier 100 MHz ^1H n.m.r. spectra of $Fe(phen)_2(NCBPh_3)_2$ in CH_2Cl_2 at 221 K (—) and at 306 K (...) (rel. to Me_4Si).

of the latter. Decomposition of the complex in $(CD_3)_2SO$ to liberate phen and $NCBPh_3^-$ gives a phenyl proton: phenanthroline proton ratio of 2·1:1 (theory, 1·9:1). Chemical analysis gives C, 76·8; N, 8·7; and H, 5·0% (theory: 78·2, 8·8, and 4·9% respectively; low carbon results are characteristic of this class of compounds). In the solid state, Gouy and ^{57}Fe Mössbauer measurements indicate the red complex to be low-spin [μ (298 K) = 1·0 B.M., δ = 0·27 mm s^{-1}, ΔE = 0·30 mm s^{-1} relative to Fe].

At 221 K in CH_2Cl_2 the phenanthroline proton resonances are characteristic[4] of a low-spin complex of C_2 symmetry (Figure 1). At 306 K, rapid site exchange occurs to give averaged signals for each of the formerly non-equivalent (2,9; 3,8; 4,7; and 5,7) resonances. That the solute has become paramagnetic is indicated by the strong shifts of the 2,9, 3,8, and 5,6 resonances and by an effective magnetic moment for the complex of 4·8 B.M. (determined by Evans' method[5] using Me_4Si as reference). The very low solubility of the complex precludes reliable determination of μ_{eff} at lower temperatures and prevents us from determining thermodynamic parameters for the $S = 0 \rightleftharpoons S = 2$ equilibrium.

The synchronous loss of C_2 symmetry and the onset of paramagnetic shifts is shown in Figure 2. Here we find that the 4,7 chemical shifts experience very little contact shift but simply collapse owing to the stereoisomerization of the complex. The δ *vs.* temperature curves for the other resonances reveal the concurrent effects of site exchange and paramagnetic shifts. Were $k_{exch.} > k_{spin}$, the resonances would initially collapse and subsequently experience the contact shift. Conversely, $k_{spin} > k_{exch.}$ would lead to nearly parallel shifts followed by coalescence. The data thus indicate that k_{spin} = *ca.* k_{exch}. From the stopped-exchange shift difference of 38 s^{-1} for the 4,7 resonances, $k_{exch.}$ = *ca.* 10^2 s^{-1} is required for coalescence and this condition is met at *ca.* 275 K. We have determined that there is no appreciable dissociation of $NCBPh_3^-$ at room temperature (Beer's law is followed by the CT band at *ca.* 500 nm) and addition of $NaNCBPh_3$ to the complex in CH_2Cl_2 at 306 K reveals separate proton resonances for free

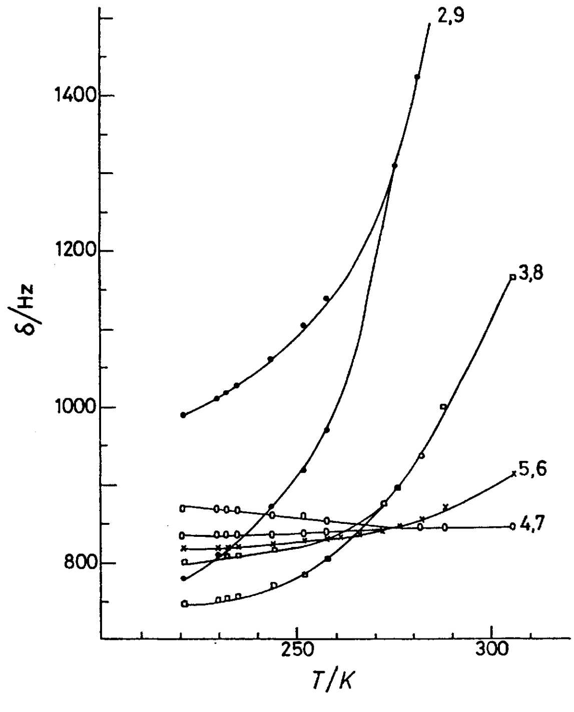

Figure 2. The variation with temperature of the phenanthroline proton resonances in the ^1H n.m.r. spectrum of $Fe(phen)_2(NCBPh_3)_2$ in CH_2Cl_2.

and complexed NCBPh$_3^-$. These findings argue against a *D* mechanism. On the other hand, a trigonal twist pathway is disfavoured by severe steric interactions between the 2,9 protons of adjacent phenanthroline ligands. Only the rhombic twist path survives.[6] This path is also supported over the dissociative paths by AOM arguments.[7]

The spin- and stereo-lability of this complex compared to that of Fe(phen)$_3^{2+}$ is remarkable.[8] Undoubtedly, the singlet–quintet surfaces are much closer when phen is replaced by NCBPh$_3^-$. Surface hopping in this case requires a triplet surface to lie close to the quintet and singlet surfaces at their intersection in co-ordinate space. The properties of Fe(phen)$_2$(NCBPh$_3$)$_2$ certainly raise the question as to whether this intersection is not in fact achieved by molecular distortion along a twisting co-ordinate. Questions such as these will be studied by configuration interaction–spin orbit calculations as a function of the twisting co-ordinate.

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