The Complex $[Fe(phen)_2(CN)_2]$ (phen = 1,10-Phenanthroline) and its Solutions

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The different coloured solutions and solid forms of $[Fe(phen)_2(CN)_2]$ (phen = 1,10-phenanthroline) contain only this species. The n.m.r. spectra of representative red and blue solutions, in methyl alcohol and dichloromethane, have been analysed and it is shown that the change in position of the charge-transfer absorption is associated with changes in the magnetic environment of the ligand protons, especially those close to the nitrogen *trans* to a CN group.

Recent experience[1] with compounds of empirical formula $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline) suggested a similar explanation might account for the two apparently different forms of $[Fe(phen)_2(CN)_2]$ or, possibly, for the widely differing colours of its solutions in different solvents.

The compound obtained after dehydration *in vacuo* of the product from the normal aqueous preparation[2] of $[Fe(phen)_2(CN)_2]$ retains a bronze-like lustre and is easily distinguishable from the vacuum desolvated product from Soxhlet extraction of this material in chloroform. The latter product after vacuum removal of solvent is almost black and lacks metallic lustre. Schilt[3] indeed suggested that the two products might be *cis* and *trans* isomers. However, it has been shown that the Mössbauer parameters, especially quadrupole splittings, of the two products are practically the same.[4] However, the Mössbauer spectra of, for instance, *cis*-$[Fe(phen)_2(CN)_2]$, $[Fe(phen)_3][Fe(phen)(CN)_4]$, or $[Fe(phen)_3]_2[Fe(CN)_6]$, might not be too easily distinguished. Further, the differing absorption spectra in solution could be due to conversion of the first of these species to the second, and third, the absence of isosbestic points in the spectra excluding a simpler process.

Results and Discussion

Careful examination of the i.r. spectra of the two preparations of unsolvated $[Fe(phen)_2(CN)_2]$, $[Fe(phen)_3][Fe(phen)(CN)_4]$, and $[Fe(phen)_3]_2[Fe(CN)_6]$, in Nujol mulls and CsBr discs over the range 5 000—200 cm^{-1}, failed to reveal any significant difference between the two forms of $[Fe(phen)_2(CN)_2]$, but readily distinguished the other two compounds. The spectra agreed with data reported by Schilt[3] and Takemoto *et al.*[5] Measurements were made with CsI discs and also using Nujol mulls.

The blue-black form of $[Fe(phen)_2(CN)_2]$ dissolves in solvents more slowly than the bronze form, but both produce the same saturated solutions. As is well known,[6] the colour of these solutions varies from red to blue depending on the solvent. Conductivities were measured on solutions of both forms in methanol, nitromethane, nitrobenzene, and dichloromethane solutions, which span the range from the red to the blue solutions. No evidence of conducting solutions was obtained.

The n.m.r. spectra of the solutions confirmed that there is no evidence for formation of either of the electrolyte species mentioned above. However, heating anhydrous $[Fe(phen)_3]_2[Fe(CN)_6]$ did produce $[Fe(phen)_2(CN)_2]$. Nevertheless, the n.m.r. spectra throws some interesting light on the reasons for the widely different charge transfer spectra in different solvents, as Burgess *et al.*[6] have suggested. The solubility of $[Fe(phen)_2(CN)_2]$ in most solvents is low but by accumulating sweep data on the Brucker MH400 satisfactory data for detailed analysis could be obtained for solutions in dichloromethane, methyl alcohol, and acetone–water mixtures. The first of these gives a blue solution ($\lambda_{max.}$ 625 nm)[7] while the methyl alcohol solution is red ($\lambda_{max.}$ 541 nm). The acetone–water solution contained 10% by volume of water ($\lambda_{max.}$ 560 nm). An analysis of the spectra is shown in the Table. The data in CD_2Cl_2 solution could be fitted very satisfactorily as an AB, $X_1Y_1Z_1$, $X_2Y_2Z_2$ type of spectrum. The other two solvents fit an A_1B_1, $X_1A_2B_2$, X_2YZ pattern. In the analysis of the spectra of the two solvents giving XAB spectra frequency fits of calculated and observed spectra were very good, but the intensity fits rather less so.

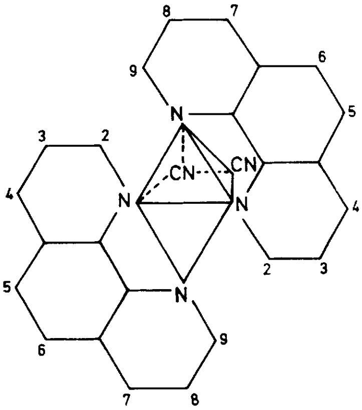

Figure. N.m.r. atom numbering and co-ordination sphere for $[Fe(phen)_2(CN)_2]$

First, it is clear that the solvent interactions do not destroy the equivalence of the protons on the two ligand moieties. As expected the 2,3,4-protons differ from the 7,8,9-protons on each ligand but the difference between the 5,6-protons is such that an AB spectrum results (group D lines, Table). The chemical shifts for this system are less sensitive to changes of solvent than found for the 5,6-proton singlet in different solutions containing $[Fe(phen)_3]^{2+}$, as reported by Van Meter and Neumann.[8]

Decoupling experiments established that the group A and B lines, or in the case of the solvent CD_2Cl_2, groups A and B′, are associated with the quartet E. The groups C, F, and G form an XYZ system in CD_2Cl_2, but in the other solvents the groups C and F comprise an XAB system. Clearly these two sets must correspond to the 2,3,4 and 7,8,9 sets of protons in the ligands. Numbering the ligand protons so that 2 is adjacent to the N *trans* to a CN ligand it is not possible to reach a rigorous assignment (see Figure). Miller and Prince[9] have found 2—3 (9—8) couplings of *ca.* 5 Hz and 3—4 (7—8) couplings of *ca.* 8 Hz in tris-phen complexes. These values have been confirmed in

Table. N.m.r. data for solutions of [Fe(phen)$_2$(CN)$_2$]

Solvent	CD_2Cl_2		CD_3OD		CD_3COCD_3–D_2O	
Line group	Chemical shift (τ)	Couplings (Hz)	Chemical shift (τ)	Couplings (Hz)	Chemical shift (τ)	Couplings (Hz)
A	10.22	5.14*	9.97	5.15*	9.93	5.18*
B			8.66	8.17*	8.66	8.31 0.9
C	8.42	8.15 0.6	X of XAB 8.42	See F below	X of XAB 8.41	See F below
B′	8.19	8.02 1.0				
D	AB type 7.99 δ_{AB} = 0.067†	8.88	AB type 8.14 δ_{AB} = 0.050†	8.91	AB type 8.14 δ_{AB} = 0.09†	8.90
E	7.88	8.11 5.22	8.00	8.15 5.23	8.02	8.12 5.23
F	7.43	5.12 1.0	XAB 7.47	J_{AB} 5.18 J_{AX} 8.17 J_{BX} 1.18 δ_{AB} = 0.032†	XAB 7.44	J_{AB} 5.18 J_{AX} 8.10 J_{BX} 1.02 δ_{AB} = 0.029†
G	7.29	5.21 8.03				

* Small unresolved further coupling observed. † Differences in chemical shifts of A and B nuclei.

other work.[1,10] Thus the groups A and F should arise from the 2- and 9-protons and the groups B and C from the 4- and 7-protons but they cannot be certainly assigned. The changes in chemical shift ($\Delta\tau$) on changing from methyl alcohol to dichloromethane can be tabulated as given below. If we tentatively suppose

Group	A	E	B	F	G	C	D
$100\Delta\tau$ (± 2)	25	−12	−47	4	−18	0	−15

that the 2,3,4-protons will suffer larger changes in magnetic environment than the 7,8,9-protons, this implies A,E,B ≡ 2,3,4 and C,G,F ≡ 7,8,9. The largest effect is seen on the proton *para* to the N *trans* to a CN ligand.

Comparatively small changes in n.m.r. parameters lead to the change from an XYZ to an XAB pattern. Finally, the solvent effects are reflected principally in changes in chemical shifts, the changes in coupling constant are much smaller, as might be expected, and are only a few times the probable error in the data.*

It is interesting to note that in both dilute aqueous acetone and nitromethane solutions the phen began to become labile. Some measurements in 30% aqueous acetone showed spectra that changed over 24 h. The lines in groups A and B broadened considerably although the other lines remained sharp. This may be due to one end of the chelate ligand becoming detached and reattaching on a suitable time-scale. Similarly, in nitromethane the lines at low τ were very broad and only the AB system (5,6-protons) and doublets at τ 6.96 and 8.08 remained sharp.

Experimental

[Fe(phen)$_2$(CN)$_2$] was prepared as described by Schilt;[2] [Fe(phen)$_3$][Fe(phen)(CN)$_4$] was prepared by the method of Driver and Walker.[12]

Preparation of [Fe(phen)$_3$]$_2$[Fe(CN)$_6$].—Hydrated iron(II) ammonium sulphate (6H_2O) (1.176 g) was dissolved in water (7 cm^3) and phen·H_2O (1.784 g) was added. K_4[Fe(CN)$_6$]·3H_2O (1.267 g) in water (5 cm^3) was then added. On cooling to −5 °C overnight very dark red crystals separated. Dehydration *in vacuo* at 80 °C led to the loss of *ca.* 18 molecules of water per molecule of complex and gave the anhydrous compound.

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* *Note added at proof.* Dove and Hallett[11] have reported n.m.r. data for a solution of [Fe(phen)$_2$(CN)$_2$] in the protonating solvent HF. Their spectrum is closer to my result for CD_3OD than is either the HF or CD_3OD spectrum to that found in CD_2Cl_2.