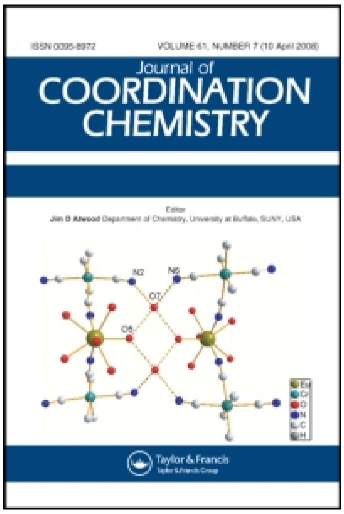

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OPTICALLY ACTIVE COORDINATION COMPOUNDS. PART 44.[1] ON THE INTERACTION OF LEWIS ACIDS WITH OPTICALLY ACTIVE DICYANO-BIS-(1,10-PHENANTHROLINE)IRON(II), $[Fe(PHEN)_2(CN)_2]$

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The electronic spectra and circular dichroism of adducts of several Lewis acids (Hg^{2+}, $Hg(CN)_2$, CH_3^+ and BF_3) with the optically active Schilt-Barbieri compound, $Fe(phen)_2(CN)_2$ in $CHCl_3$ solution is discussed. The sign pattern of the c.d. bands arising from the long axis $\pi \rightarrow \pi^*$ absorption is not changed by the various Lewis acids, confirming that this pattern reflects the optical configuration for the dicyano-compound. This finding strongly supports the occurrence of configurational inversion when $[Fe(phen)_3]^{2+}$ reacts with cyanide ion.

Keywords: inversion, octahedral, Schilt complexes, diimines, circular dichroism

INTRODUCTION

Optically active "ferroin", $[Fe(phen)_3]^{2+}$, undergoes a reaction with cyanide ion to yield the Schilt-Barbieri species $[Fe(phen)_2(CN)_2]$ with[2] apparent optical inversion. The extensive discussions of this finding turn on the question as to whether this inversion of sign pattern in c.d. (a real effect, despite a report[3] that the dicyano-compound can not be made optically active in this way in dilute cyanide solution at 0°) corresponds to a chemical (Bailar) inversion of octahedral configuration between tris and bis-chelate, or whether the change in ground state point group from D_3 (reactant) to C_2 (product) leads to alteration of the energy levels of the exciton bands such that the signs of the Cotton effects would be (from long wavelength) + then — for D_3 but — then + for C_2 of the *same* relative configuration.

The spectroscopic difficulty is that the coupled long-axis transitions of the diimine ligands (the "exciton" bands, useful in correlating chiralities of $[M(phen)_3]^{n+}$ and *cis*-$[M(phen)_2XY]$ where X and Y are "innocent" ligands like NH_3) may, in the compound[†] $[Fe(phen)_2(CN)_2]$ not be "pure" phenanthroline bands, but may involve some participation of the cyanide groups. Consequently, if that were the case, reliance on the sign of bands in the 280 nm exciton region would be misguided as a means of deducing the optical hand for complexes containing π-bonding ligands like CN^- in addition to the cis-bisdiimine.

Some earlier experiments have focussed on this point. For example, in order to alter the environment along the C_2-axis of $[Fe(phen)_2(CN)_2]$ (to remove or to decrease any

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[†] The structure of this compound has not been established with utter certainty. While crystals of $[Fe(phen)_2(CN)_2]$ often appear attractive, we obtain only a few diffraction spots in the X-ray record of this complex.

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contribution of cyanide to the exciton region) the c.d. spectrum was measured[4] in acid solution.

It is known from Schilt's work,[5] that purple $Fe(phen)_2(CN)_2$ can be recrystallized from its yellow solution in sulfuric acid by careful addition of water. It was originally suggested that the central metal ion might be protonated but it is now believed[6] that the nitrogen atoms of the cyanide groups are the most likely site of protonation. The salt $[Fe(CNH)_2(phen)_2](PF_6)_2$ has been characterized,[7] and the acid-base indicator properties for $[Fe(phen)_2(CN)_2]$ ("commonly referred to as ferrocyphen" — *sic*) have been described.[8]

The most striking feature of the spectrum in acid solution is the fact that while a c.d. band is observed in the visible region, that in the u.v. disappears completely. In a subsequent n.m.r. investigation it was not possible to ascertain whether or not the 1,10-phenanthroline ligands were involved in the reaction.

We have now studied several addition compounds of $[Fe(phen)_2(CN)_2]$ with various Lewis acids by means of c.d. with respect to the sign of the bands in the exciton region, to confirm that the "exciton" region may indeed be used in this case as non-empirical evidence for configuration in the Schilt-Barbieri compound.

RESULTS AND DISCUSSION

Reactions were carried out at 0° to minimize racemisation of the Λ-$[Fe(phen)_2(CN)_2]$ in $CHCl_3$. On addition of solutions (in chloroform) of $Hg(CH_3COO)_2$, $Hg(CN)_2$, $(CH_3)_2SO_4$ or BF_3, immediate colour changes of the violet solution of $[Fe(phen)_2(CN)_2]$ in $CHCl_3$ to red were observed. The resulting addition compounds have been characterized by their absorption spectra in the visible region and by means of circular dichroism. The results are summarized in Figures 1–4

All the addition compounds are of stoichiometry $[Fe(phen)_2(CN)_2]$:Lewis acid = 1:2.[10,11] It is therefore expected that both nitrogen atoms of the cyanide groups are involved in coordinative bonds, although the existence[9] of a complex $[Fe(phen)_2(CN)_2 \cdot Hg(CN)_2]$ has been suggested.

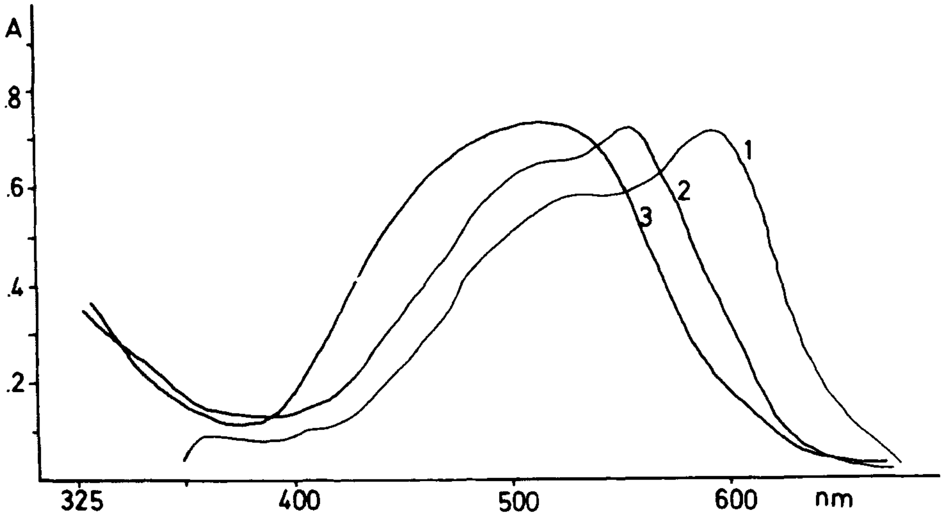

FIGURE 1 Absorption characteristics of $[Fe(phen)_2(CN)_2]$ (1) and the adducts with $[Hg(CN)_2]$ (2) and $[Hg(CH_3COO)_2]$ (3) in $CHCl_3$.

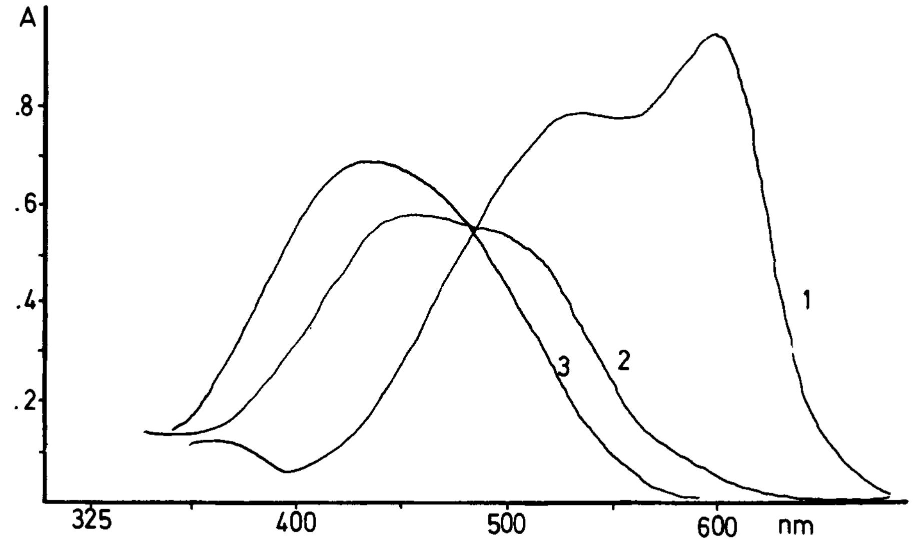

FIGURE 2 Absorption characteristics of [Fe(phen)$_2$(CN)$_2$] (1) and the adducts with [(CH$_3$)$_2$SO$_4$] (2) and [BF$_3$·(C$_2$H$_5$)$_2$O] (3) in CHCl$_3$.

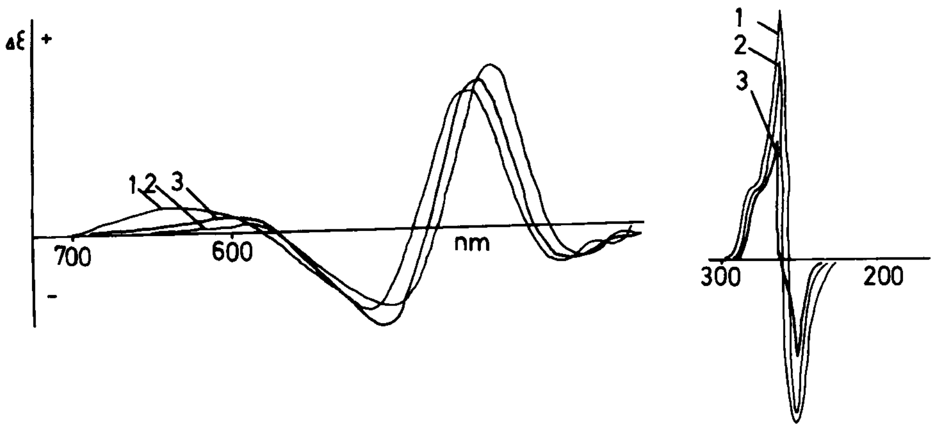

FIGURE 3 Comparative c.d. spectra (arbitrary units) of [Fe(phen)$_2$(CN)$_2$] (1) and of the reaction products of [Fe(phen)$_2$(CN)$_2$] (1) and of the reaction products of [Fe(phen)$_2$(CN)$_2$] with [Hg(CH$_3$COO)$_2$] (2) and [Hg(CN)$_2$] (3) in CHCl$_3$.

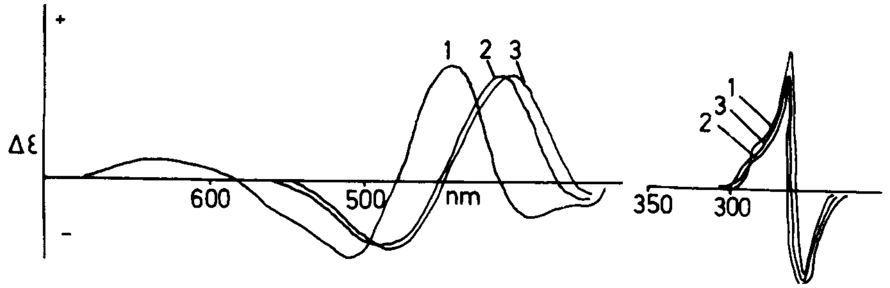

FIGURE 4 Comparative c.d. spectra (arbitrary units) of [Fe(phen)$_2$(CN)$_2$] (1) and the reaction products of [Fe(phen)$_2$(CN)$_2$] with [(CH$_3$)$_2$SO$_4$] (2) and [BF$_3$·(C$_2$H$_5$)$_2$O] (3) in CHCl$_3$.

The natures of the racemic compounds $[(phen)_2Fe(CNMe)_2]^{2+}$ and $[(phen)_2Fe(CN\cdot BF_3)_2]$ have already been established in the literature.[10,11]

Although there are significant shifts of the visible c.d. bands of the addition compounds with respect to $[Fe(phen)_2(CN)_2]$ the sign pattern of the Cotton effects in the region of the $\pi \rightarrow \pi^*$ long axis electronic transition remains unchanged. This sharp contrast between the sensitivity of the visible bands to adduct formation and the lack of sensitivity of the so-called "exciton" bands is informative. It confirms the assignment of the characteristic pair of Cotton effects at *ca* 280 nm to a transition independent of the metal and its ligands, that is, one located within the phenanthroline molecules. This characteristic +/— pair is insensitive to environment (it is — *pace* Fig. 4 — about the same in the Schilt-Barbieri compound and in its methylated adduct for example). This would support the idea that the sign pattern (+ at long wavelength, — at shorter wavelength) indicates configuration reliably.

These sign patterns of c.d. of the reactant and product have of course been considered[12–15] by many workers as non-empirical evidence of absolute configuration. We confirm here from the constant sign pattern of c.d. near 280 nm in a series of complexes of related constant configurations, that the observed change (apparent inversion)[2] of this pattern in this reaction

$$\Delta - [Fe(phen)_3]^{2+} + 2\ CN^- \rightleftharpoons \Lambda - [Fe(phen)_2(CN)_2] + phen$$

constitutes strong evidence that some (at least) optical inversion has occurred.

The behaviour of strong protonic acids is still anomalous; we have confirmed our earlier finding[4] that the ultraviolet pair of Cotton effects 'disappears' in acid. The structures of the protonic adducts are not known with certainty. However, if the protonation (like other additions, *e.g.* of CH_3 or BF_3) of $[Fe(phen)_2(CN)_2]$ is, as thought, upon the nitrogen atoms of the *C*-bonded cyanide ligands, giving $[Fe(phen)_2(CNH)_2]^{2+}$, like $[Fe(phen)_2(CNCH_3)_2]^{2+}$, it would be strange if that had a unique effect on the order or sign of the transitions within the phenanthroline ligands which we have shown to give rise to the c.d. around 280 nm. To put it in another way, the reversible disappearance of the c.d. exciton bands on acidification would be consistent with the energy separation of the already overlapping positive and negative c.d. bands (at *ca* 270 and 260 nm) being changed to about zero. Then the c.d. bands would cancel and no c.d. would be observed in the u.v. exciton region (although the compound remains optically active and the visible c.d. is, albeit different — actually enhanced — still observed).

Why should the proton be unique in this regard? Such explanations based on selective effects of a cyanide bound proton on spectroscopic levels of the coupled diimine ligands are untenable. We have shown that two *cis*-ligated H_3CNC molecules have no influence on the c.d. arising from the two *cis*-ligated phenanthrolines, so how could the analogous homologous HNC species produce the large observed effect?

In our continuing attempts to clarify the role of the proton in causing this chiroptical anomaly, we are evaluating solvatochromic effects on the c.d. of the Schilt-Barbieri compounds, and studying the structure of solids, both some adducts, *e.g.* (±) —$\{[Fe(phen)_2(CN)_2]\cdot 2Hg(CN)_2\}$ and the parent compounds, though some present crystallographic difficulties, as mentioned above.

EXPERIMENTAL

Δ-tris(1,10-phenanthroline)iron(II) perchlorate trihydrate was prepared according to the method of Dwyer and Gyarfas[16] while dicyanobis-(1,10-phenanthroline)iron(II) dihydrate was obtained by the method of Schilt.[5] All reactions were carried out at 273 K in $CHCl_3$ (2% v/v ethanol) to minimize racemisation. The concentration of metal complex throughout was 2.0×10^{-4} mol dm^{-3} and concentrations of Lewis acids ($Hg(CH_3COO)_2$, $Hg(CN)_2$, $(CH_3)SO_4$, BF_3. $(C_2H_5)_2O$) were 4.0×10^{-4} mol dm^{-3}.

Circular dichroism spectra were recorded on a Jobin-Yvon Dichrograph III, and electronic spectra were measured to identify products on a Unicam SP 8000 recording spectrophotometer with a Unicam SP 8005 Program Controller.

All chemicals used were from BDH Chemicals Ltd., Poole, England.

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