Circular Dichroism of Diamagnetic d^6 Isoelectronic Tetracyanoferrate(II) and Tetracyanocobaltate(III) Complexes of (*R*)-1,2-Diaminopropane and (*RR*)-*trans*-1,2-Diaminocyclohexane

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Summary Circular dichroism (c.d.) spectra of the title compounds are essentially the same for the first and second absorption bands, confirming that the c.d. spectra of isoelectronic complexes are the same for *d–d* transitions.

CIRCULAR dichroism of *d–d* transitions of optically active diamagnetic Fe^{II} complexes has not been reported previously, in spite of many publications on the corresponding Co^{III} complexes.[1] Optically active Fe^{II} complexes can be used to study both the theory of c.d. of metal chelates and the structural chemistry of Fe^{II} complexes. The c.d. spectrum of a diamagnetic Fe^{II} complex of known configuration $[Fe(R\text{-pn})(CN)_4]^{2-}$ was compared with that of the corresponding Co^{III} complex $[Co(R\text{-pn})(CN)_4]^-$ [*R*-pn = (*R*)-1,2-diaminopropane].

The Fe^{II} complexes were prepared by a method similar to that of Goedken for preparing $Na_2[Fe(diamine)(CN)_4]$, using resolved *R*-pn and *R*-chxn [*R*-chxn = (*RR*)-*trans*-1,2-diaminocyclohexane].[2] The absorption and c.d. spectral data for $[Co(R\text{-pn})(CN)_4]^-$ were provided by Yano.[3]

The ^1H n.m.r. spectrum of $[Fe(R\text{-pn})(CN)_4]^{2-}$ [δ (p.p.m. from sodium 3-trimethylsilylpropanesulphonate = 0) 1·7 (3H, d, Me), 2·1 (1H, dd, *axial* CH_2 proton), and 2·7 (2H, m, *equatorial* CH_2 proton and *axial* CH)] is essentially similar to that of $[Co(R\text{-pn})(CN)_4]^-$ and indicates that the conformation of the chelate ring is fixed as λ.[3]

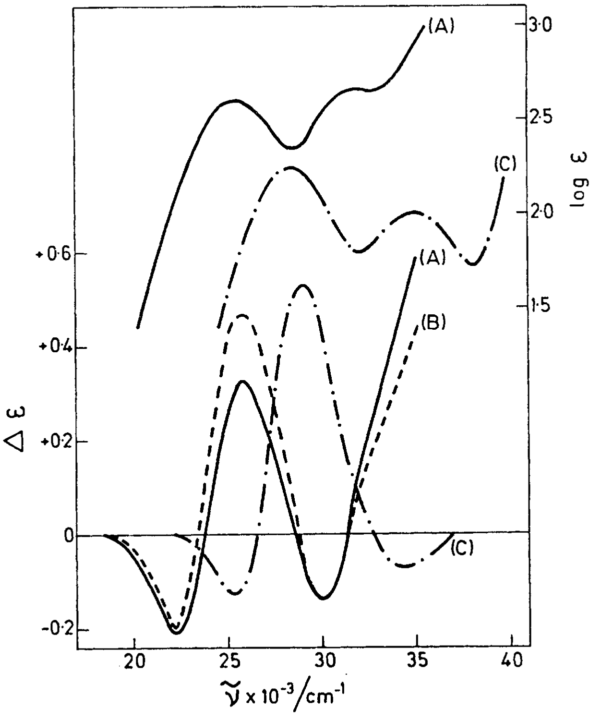

FIGURE. Visible and c.d. spectra of $[Fe(R\text{-pn})(CN_4)]^{2-}$ (A), $[Fe(R\text{-chxn})(CN)_4]^{2-}$ (B), and $[Co(R\text{-pn})(CN)_4]^-$ (C), in water.

The absorption and c.d. spectra of these complexes are shown in the Figure. The first absorption bands of $[Fe(CN)_6]^{4-}$ and $[Fe(NH_3)(CN)_5]^{3-}$ have been reported as having maxima at 31,000 and 25,400 cm^{-1}, respectively, and are assigned to *d–d* transitions.[4] Both maxima of the first absorption bands of $[Fe(R\text{-pn})(CN)_4]^{2-}$ and $[Fe(R\text{-chxn})(CN)_4]^{2-}$ are located at 25,500 cm^{-1} and are split into two components of opposite signs at 22,200 (negative) and 25,700 cm^{-1} (positive) in the c.d. spectra. These two components are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

The c.d. spectrum of $[Co(R\text{-pn})(CN)_4]^-$ shows two components having negative and positive signs in the region of the first absorption band at 25,400 and 29,100 cm^{-1}, respectively. The signs of the c.d. components of $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions for *trans*-$[Co(R\text{-pn})(X)_2]^{n+}$ are well established as being positive and negative, respectively. The c.d. spectrum of *trans*-$[Co(R\text{-pn})_2(CN)_2]^+$ has been reported as having two maxima in the region of the first absorption band at 21,000 ($\Delta\epsilon$, $-0{\cdot}25$) and 24,700 cm^{-1} ($\Delta\epsilon$, $+1{\cdot}07$).[5] The tetracyanodiamine complex, $[Co(R\text{-pn})(CN)_4]^-$, should show c.d. components of the same sign as in the case of *trans*-$[Co(R\text{-pn})_2(CN)_2]^+$; the Figure shows this clearly, the components having a magnitude almost a half of that of the latter complex.

The first absorption bands of the Fe^{II} and Co^{III} complexes are split into two c.d. components, a small negative one and a large positive one at lower and higher wavenumbers, respectively. These Cotton effects originate solely from the vicinal effect of the chelate ring in the λ conformation. The c.d. spectra of $[Fe(R\text{-pn})(CN)_4]^{2-}$ and $[Co(R\text{-pn})(CN)_4]^-$ are essentially the same, taking into account the difference in the ligand field splitting, *i.e.*, electronic transitions for the Fe^{II} complex occur at a lower energy than those for the Co^{III} complex by a difference of 3300 cm^{-1}. The same conclusion is obtained from the c.d. spectra in the region of the second absorption bands, where negative c.d. components are observed with both Fe^{II} and Co^{III} complexes. This observation confirms that the signs of the c.d. components of *d–d* transitions are the same if the electronic and structural configurations are the same, regardless of the individual metal ions.

The magnitude of the c.d. ($\Delta\epsilon$), for the major positive component, is larger in the Co^{III} complex than in the corresponding Fe^{II} complex, but the trend is reversed for the minor negative component. This reflects a slight modification of the structure of the metal chelates. The change may originate partly from the difference in metal–nitrogen bond length. The longer bond length for Fe^{II}–N than for Co^{III}–N allows the formation of less sterically constrained metal chelates. The magnitude of the c.d. of $[Fe(R\text{-chxn})(CN)_4]^{2-}$ is enhanced in the major positive component while that of the minor component remains constant as with $[Fe(R\text{-pn})(CN)_4]^{2-}$. The enhancement arises from the more rigid structure of the diaminocyclohexane chelate.

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