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DICD of Co(III) Complexes in Sugar Solutions

PIETER E. SCHIPPER and ALISON RODGER

Department of Theoretical Chemistry, University of Sydney, N.S.W. 2006, Australia

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Circular dichroism (CD) has proved to be a useful technique for studying magnetic dipole allowed transitions, and is therefore complementary to normal absorption (which probes predominantly electric dipole character) in probing the excited states through conventional one-photon absorption. However, CD vanishes for systems with an improper symmetry axis, and thus would appear to be ineffective as a potential probe of magnetic dipole allowed transitions of achiral systems. Fortunately, this is not the case. The CD technique may be extended to studying achiral systems by perturbing the achiral species with a chiral environment [1–3]. If this environment is a solution containing freely-rotating chiral species, the induced CD may be described in the context of the DICD (dispersion induced CD) model [4], in which the CD of the achiral species arises from orientationally-uncorrelated dispersive coupling with the chiral species.

The greatest problem in the practical application of the technique is the choice of chiral inducers. They should be transparent over the spectral range of interest of the achiral species, readily soluble in an achiral solvent which will also dissolve the achiral species, and unlikely to associate with the achiral species in solution in such a way as to lead to specific orientational correlation. In this paper, we report some studies which suggest that simple sugars are ideal for the investigation of the magnetic dipole allowed d–d transitions of water-soluble transition metal complexes.

Results

The normal absorption and DICD spectra of a range of Co(III) amine complexes (about 0.03 M) in an aqueous solution of fructose (1.0 M) are presented in Fig. 1 and 2 respectively. Only the energy region spanning the d–d transitions arising from the octahedral $^1T_{1g}$ band is shown. In order of decreasing symmetry the complexes whose spectra are shown are: $[Co(NH_3)_6]Cl_3$ (O_h); $[Co(NH_3)_5Br]Br_2$ (C_{4v}); *trans*-$[Co(en)_2Cl_2]Cl$ (D_{2h}); and $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ (C_{2v}).

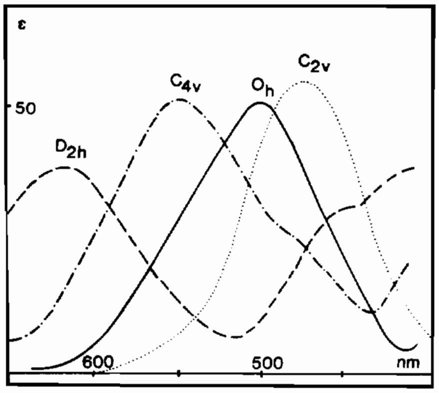

Fig. 1. Normal absorption spectra of the complexes in fructose solution.

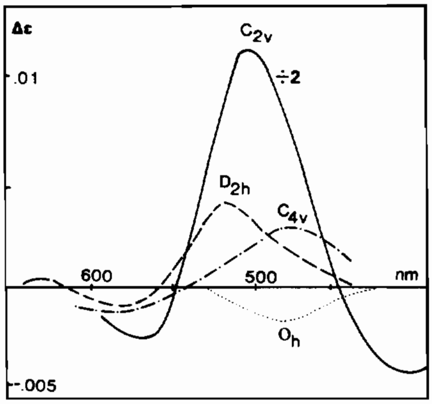

Fig. 2. DICD spectra of the complexes in fructose solution.

Discussion

The normal absorption spectra are unaffected by the presence or absence of the sugar, and are weak, with intensities characteristic of electric dipole forbidden transitions, even for those complexes with low enough symmetry to be formally electric dipole allowed. The intensities are therefore predominantly vibronically induced. The normal absorption spectra give little hint of the underlying symmetry variation for the complexes. The shapes of the O_h and C_{2v} normal absorption bands look much the same. However, we know from symmetry that they are composed of one and three component transitions respectively. The normal absorption of the C_{4v} and D_{2h} complexes suggests they both have two component transitions whereas the D_{2h} should, strictly speaking, have three. In fact, in crystal spectroscopy, *trans*-$[Co(en)_2Cl_2]Cl$ is generally considered to have a D_{4h} d–d chromophore [5].

The DICD spectra, in contrast to the normal absorption, vary dramatically as a function of the real

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symmetry of the complex. The number of peaks in each spectrum is consistent with that predicted on symmetry grounds based on a magnetic dipole selection rule. O_h has one peak; C_{4v} has two; D_{2h} has two large and a hint of a third smaller peak; and C_{2v} exhibits three clearly discernable bands. This enables an approximate determination of component transition energies, in addition to being a reflection of complex symmetry.

The spectra shown in Fig. 2 all have a DICD band at approximately 500 nm, in distinct contrast to the normal absorption which fails to resolve the components in any systematic way. In conjunction with the theoretical expression for the DICD, this provides a vital clue for the assignment of this transition.

The theoretical expression for the DICD depends on a scalar vector product of the transition moments on the achiral chromophore *i.e.* $\boldsymbol{\mu}^{oe} \times \boldsymbol{\mu}^{ed} \cdot \mathbf{m}^{do}$ [4]. $\mathbf{m}^{do}$ is the magnetic dipole transition moment of the transition $|o\rangle \rightarrow |d\rangle$ at whose energy the DICD band appears. $\boldsymbol{\mu}^{oe}$ and $\boldsymbol{\mu}^{ed}$ are electric dipole transition moments of the $|o\rangle \rightarrow |e\rangle$ and $|e\rangle \rightarrow |d\rangle$ transitions respectively. The $|e\rangle$ state is an excited state of the Co(III) ion through which the dispersive coupling to the chiral species occurs and may be taken to be a charge transfer state. The nature of the scalar triple product requires $\boldsymbol{\mu}^{oe}$ and $\boldsymbol{\mu}^{ed}$ to be in a plane perpendicular to $\mathbf{m}^{do}$. In addition, $\mathbf{m}^{do}$ involves a circulation of charge in the plane perpendicular to itself. Thus for systems dominated by σ-type bonding we may expect the scalar vector product to be most affected by substituents in the plane perpendicular to its axis. *This results in a qualitative correlation of the DICD of the transition with the chemical nature of the plane perpendicular to its direction of (magnetic) polarization.* So, if a series of complexes have a relatively invariant plane the DICD of the transition polarized perpendicular to the plane would be relatively invariant. This is precisely what we see in the 500 nm band of these complexes. The 500 nm band can therefore be assigned to a transition perpendicular to the 'amine' plane in each complex. This assignment agrees with the crystal assignment for the D_{2h} complex (the higher energy band being A_{2g}) [5], and with Hawkins assignment [6] for the C_{4v} complex (the higher energy band being A_2). In addition it enables the 500 nm band of the C_{2v} complex to be assigned to an A_2 transition. Thus from the normal absorption and the DICD together it can be deduced that the lowest energy transition in the C_{2v} complex is B_1, the middle is A_2, and the highest is B_2.

It is reasonable therefore to expect that sugars would be ideal DICD inducers for a wide range of water soluble complexes. More comprehensive studies on a range of sugars will be published elsewhere and suggest this is indeed the case.

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