Vibronic Structure in Circular Dichroism

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EXAMPLES of vibronic structure in circular dichroism (c.d.) have been found in the carbonyl chromophore,[1] but none exist for transition-metal complex ions. Many theoretical studies[2-5] have been devoted to the c.d. of (+)-$Co(en)_3^{3+}$ ion, but confusion has arisen from the absence of the trigonal splitting[6] required by most of these. We now report a measurement of the circular dichroism of this ion at ~5° K. We have obtained both absorption and circular dichroism spectra with the same spectrometer,[7] without disturbing the sample. The crystal was (±)-$[Rh(en)_3Cl_3]_2$,$NaCl,6H_2O$ doped with ~1 mole % (+)-$Co(en)_3^{3+}$, and was aligned such that the optic axis of the hexagonal crystal was coincident with that of the instrument.

We find: (i) at room temperature the c.d. in the E_a band[3] agrees well with the results of Mason;[8] (ii) at 77° K and ~5° K the "red" side of this c.d. band is lost, just as in the absorption spectrum, and vibrational structure appears; (iii) a comparison of the c.d. and absorption spectra (Figure) of the first vibronic components shows that the same intensity mechanism is operating in both measurements. This is consistent with (ii); (iv) the energies of the components (Figure) agree well with the six skeletal vibrational frequencies of the Co–N_6 octahedron,[9] but the intensity bears no apparent relation to the *g*, or *u* character of the O_h vibrations.

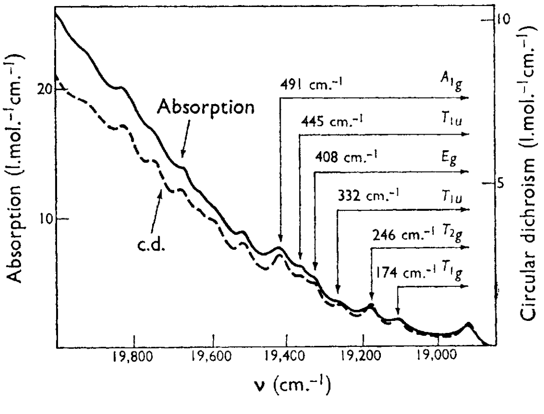

FIGURE. *The single-crystal circular dichroism ----- and absorption spectra ——— of the low energy portion of the* $^1T_{1g}(O_h)$ *band in* (+)-$Co(en)_3^{3+}$ *ion at* ~5° K

Moffitt and Moscowitz[10] predict that in an electrically "forbidden" band c.d. will occur only in totally symmetric modes, while absorption will appear in asymmetric modes and totally symmetric progressions thereon. These predictions have been used[11] to separate static and vibrational intensities. A corollary is a predicted shift in the c.d. maximum relative to the absorption maximum. Our results indicate that these predictions must be treated with caution in cases resembling this one. An extension of the theory, by Weigang,[1] includes a term, in which both magnetic and electric moments are borrowed, analogous in form to the vibronic mechanism in absorption. This mechanism must, however, be rejected on three grounds:

(i) Weigang predicts an upper limit for borrowed dichroism of 1 l. mol.$^{-1}$ cm.$^{-1}$; we observe $\Delta\epsilon_{\max} \simeq 25$ l. mol.$^{-1}$ cm.$^{-1}$; (ii) if the bulk of the dichroism arises from vibronic borrowing, the c.d. of the magnetically forbidden E_b band should be similar to that of the magnetically allowed E_a band. Actually the latter exceeds the former by a factor[8] of 25; (iii) it may be shown that the anisotropy factor,[12] in the present case, should be much larger for totally symmetric modes than for those in which the dichroism is borrowed.

Weigang's work relies on the orthogonality of ground- and excited-state vibrational wavefunctions, a tenet which requires identical equilibrium nuclear symmetries in both states. We suggest that the first excited state of the $Co(en)_3^{3+}$ ion is Jahn–Teller distorted. In this case the symmetry arguments used above must be discarded and we can expect static magnetic moment contributions in non-totally symmetric modes.

The manifestations of a dynamic Jahn–Teller distortion have been predicted by Ham.[13] Both the orbital angular momentum and the trigonal field splitting of an orbital triplet will be quenched. The latter has been observed experimentally in an excited state of vanadium(III) by Sturge.[14] We have measured the excited-state magnetic moment in the E_a band by magnetic circular dichroism (m.c.d.). We find an orbital reduction factor <0·05. Taken with the remarkably small trigonal splitting[6] (we find $K = +3{\cdot}5$ cm.$^{-1}$) this provides strong support for a Jahn–Teller distortion of the $^1T_{1g}(O_h)$ band.

The implications of these observations on the natural c.d. of the (+)-$Co(en)_3^{3+}$ ion and the intensity mechanism are being explored further in this laboratory. In particular we anticipate that the two c.d. components of the ${}^1T_{1g}(O_h)$ band in solution and in the solid[15] arise not from the trigonal components of the band, as assumed hitherto, but from Jahn–Teller components.

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