Origins of the Optical Activity of Co-ordination Compounds

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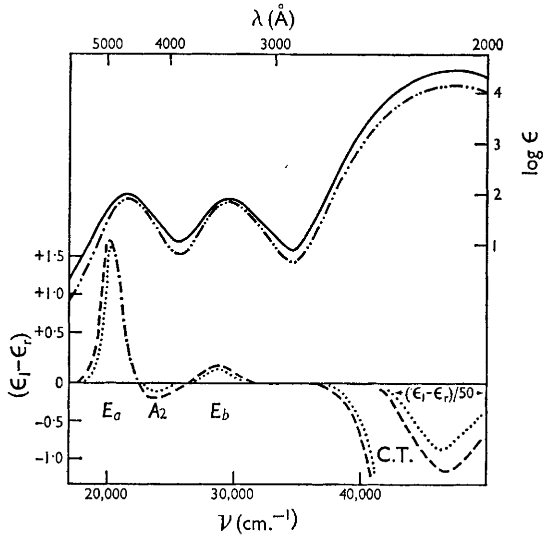
THE origin of the optical activity exhibited by the visible absorption bands of transition-metal complexes is ascribed in a number of current theories solely to distortions of the ligand atoms,[1,2] or their orbitals,[3] or their charges,[1,4] from the octahedral disposition. The atoms of the complex which are not directly bonded to the central metal ion, such as the carbon and hydrogen atoms of ethylenediamine in M(en)$_3^{3+}$ complexes, are considered to be electronically inert and serve only to produce mechanically the required distortions.

According to such theories isotopic substitutions, particularly of atoms not directly bonded to the metal ion, should leave the dipole and rotational strengths invariant, but it is now found that the replacement of N-H by N-D bonds in (+)-Co(en)$_3^{3+}$ produces a reduction in the absorption intensity and in the circular dichroism, the decrease being more pronounced for the A_2 and the charge transfer (C.T.) bands than for the *Ea* and the *Eb* bands (Figure). These reductions, especially the differential decreases, suggest that the electronic wave functions of the states connected by the electronic transitions responsible for the optical activity and the unpolarized absorption extend to the N-H or N-D bonds of the complex.

The isotopic substitution studied reduces both the width and the height of the absorption and the dichroism bands (Figure). These two effects may be related respectively to the smaller quanta and to the smaller amplitudes of the N-D than of the N-H vibrational modes active in the electronic transitions. A progression in a given mode should occupy a smaller frequency interval, giving a smaller band width, for the N-D than for the N-H vibration, and the larger zero-point amplitude of the N-H vibration should afford the larger overlap between the vibrational wave functions of the ground and the excited electronic state if inter-nuclear distances, particularly the N—H bond length, are increased in the latter state. The broadness of the absorption bands (Figure) suggests that inter-nuclear distances are substantially changed in the excited electronic states.



The electronic absorption spectrum of Co(en)$_3^{3+}$ ——— *in* H$_2$O, *and* —··—·· *in* D$_2$O. *The circular dichroism spectrum of* (+)-Co(en)$_3^{3+}$ – – – – *in* H$_2$O, *and*·········· *in* D$_2$O.

Further objections to current theories[1-4] of the electronic properties of trigonal complexes derive from the observation that on chelation the ligand

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field parameter, *Dq*, increases and the electron repulsion parameter, *B*, decreases. For $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, for example, 10*Dq* is 21,000 and 21,350 cm.$^{-1}$, respectively, and 16*B* is 8300 and 8100 cm.$^{-1}$, respectively. Distortion of the ligand atoms from the octahedral position would reduce the overlap of the ligand σ-orbitals with the metal *eg* orbitals and give a non-zero overlap between the ligand σ-orbitals and the metal t_{2g} orbitals. Thereby the energies of the t_{2g} and *eg* orbitals would be raised and lowered, respectively, producing a reduction in *Dq*, contrary to observation. Similarly the partial transfer of the cloud-expanding effect of the ligand σ-orbitals from the *eg* to the t_{2g} metal orbitals should leave the electron repulsion parameter, *B*, unchanged.

Finally, the several[5–7] *X*-ray diffraction studies of $Co(en)_3^{3+}$ salts show that the displacement of the nitrogen atoms from the octahedral position is insignificant. It is concluded that in $Co(en)_3^{3+}$ the *d*-orbital wave functions extend to the carbon and hydrogen as well as the nitrogen atoms of the chelate rings. In particular the t_{2g} electrons are stabilised by partial delocalisation into antibonding σ-orbitals covering all atoms of the ethylenediamine rings, producing an increase in *Dq* and a reduction in *B*. The optical activity of trigonal complexes, due to the mixing of $d \rightarrow d$ with charge-transfer transitions, requires no distortion of the ligand atoms from the octahedral positions in our model, but the activity is sensitive to the particular conformation of the chelate rings, as is observed.[8]

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[8] S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 1964, 339.