Rotational Strengths of Metal-complex $d \rightarrow d$ Transitions

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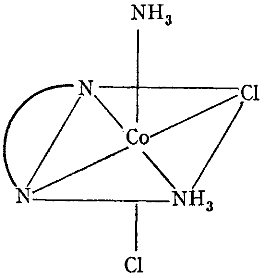
CONSIDERABLE work has been published on the rotational strengths of the $d \rightarrow d$ transitions of metal complexes that are dissymmetric because of either the distribution of chelate rings about the central metal ion[1] or the conformations of the chelate rings.[2] However, little is known about the order of magnitude of the rotational strengths for complexes that derive their dissymmetry solely from the distribution of unidentate ligands, such as *cis*-dichloro-*cis*-diamminemono(ethylenediamine)-cobalt(III) (I), one of the optical isomers of which has been obtained from optically pure *cis*-$[\mathrm{Co\,en}(\mathrm{NH_3})_2\mathrm{CO_3}]^+$ ($[\alpha]_D = +750°$) by reaction with methanolic HCl. The circular dichroism (c.d.) and absorption spectra are given in Figures 1 and 2 for the dichloro- and carbonato-complexes, respectively.



By comparing the dichloro-compound with unresolved *cis**-$[\mathrm{Co}(-)\text{-pn}(\mathrm{NH_3})_2{}^*\mathrm{Cl_2}{}^*]^+$ (Figure 1) and optically pure *cis*-$[\mathrm{Co\,en_2Cl_2}]^+$,[3] it is possible to compare the rotational strengths arising from the above three sources of dissymmetry. Such a comparison seems reasonable as the absorption

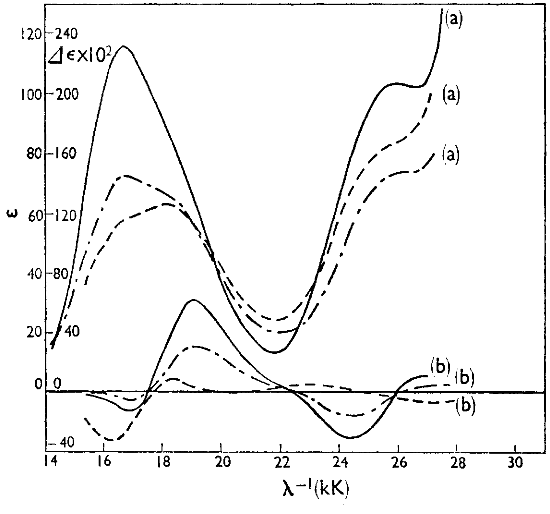


FIGURE 1. *Absorption (a) and circular dichroism (b) spectra of* trans*-$[\mathrm{Co}(-)\text{-pn}(\mathrm{NH_3})_2{}^*\mathrm{Cl_2}]\mathrm{Cl}\cdot\mathrm{H_2O}$ (- - - -), *cis**-$[\mathrm{Co}(-)\text{-pn}(\mathrm{NH_3})_2{}^*\mathrm{Cl_2}{}^*]\mathrm{Cl}$ (—·—·—), *cis**-$[\mathrm{Co\,en}(\overset{*}{\mathrm{N}}\mathrm{H_3})_2\overset{*}{\mathrm{Cl}}_2]\mathrm{Cl}$ (———) *in dimethyl sulphoxide,*

spectra of the three compounds, and thus the order of their *d*→*d* transitions, the energy differences between these transitions, and the degree of cancelling out of their c.d. bands, are very similar. Further, each compound gains its optical activity from mainly one source. Calculations of the energy differences between the two enantiomeric puckered conformations of ethylenediamine in (I) suggests that there is no significant stabilisation of one conformation due to the distribution of the unidentates. The preferred conformation of (*R*)-(−)-propylenediamine in unresolved *cis*-[Co-(−)-pn$(NH_3)_2CO_3]^+$ does not lead to any significant energy difference between the four diastereoisomers of this compound which possess an equatorial methyl group, and hence there is no partial resolution of the compound due to stereoselective effects of (*R*)-propylenediamine and therefore, no preference for any diastereoisomer of *cis**-[Co (−)-pn$(NH_3)_2{}^*(Cl)_2{}^*]^+$. Any vicinal effect from the presence of the asymmetric ligand itself is thought to be unimportant in the propylenediamine complex. Finally, although the distribution of chelate rings in *cis*-[Co en$_2$Cl$_2$]$^+$ does impart some preference to the possible conformations of the ethylenediamine chelate-rings and thus there would be some contribution to the optical activity from the conformation, this contribution will be a minor one relative to that from the distribution of chelates.

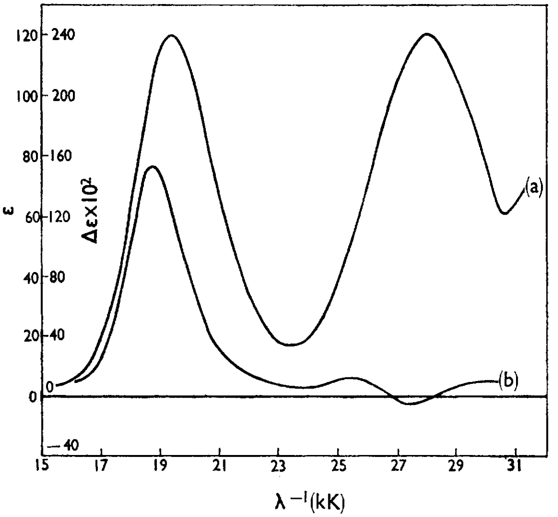


FIGURE 2. *Absorption (a) and circular dichroism (b) spectra of cis*-[Co en$(NH_3)_2CO_3]ClO_4$ *in water.*

It is apparent that, although *cis*-[Co en$_2$Cl$_2$]$^+$ has the largest residual rotational strength for the transitions under consideration,[3] the rotational strengths of the three compounds are of the same order of magnitude. The major difference in their c.d. spectra is the relative heights of the two c.d. bands under the first ligand-field absorption band. It is also of interest to compare these compounds with *trans**-[Co (−)-pn$(NH_3)_2{}^*Cl_2]^+$ (Figure 1) and *trans**-[Co (−)-pn$(NH_3)_2Cl_2{}^*]$,[2] which are also dissymmetric because of the conformation of the chelate ring. The former has a relatively large extinction coefficient for the first ligand field band and this probably accounts for the relatively large value for Δε.

The various theoretical models for calculating the rotational strengths of *d*→*d* transitions of complexes with a chiral arrangement of chelate rings have been based on either the displacement of donor atoms from the regular octahedral positions[4] or the bending of the donor atom orbitals from their normal positions to allow for chelation.[5] Such models need not be invoked for the enantiomers of *cis**-[Co en$(NH_3)_2{}^*Cl_2{}^*]^+$. The central metal chromophore is inherently asymmetric and, therefore, optically active.

From a comparison of the c.d. spectra of D(+)-*cis*-[Co en$_2$CO$_3$]$^+$,[3] and (+)-*cis*-[Co en$(NH_3)_2$-$CO_3]^+$, and of D(+)-*cis*-[Co en$_2$Cl$_2$]$^+$,[3] and (+)-*cis**-[Co en$(NH_3)_2{}^*Cl_2{}^*]^+$, it is obvious that the configurations† of these complexes are related and thus the dichloro-compound is formed with retention of configuration.

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† It is proposed that *R* and *S* are used according to the rules of Cahn, Ingold, and Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385, to define the absolute configurations of complexes that are dissymmetric because of the distribution of unidentate ligands. (+)-[Co en$(NH_3)_2Cl_2]^+$, (I) has thus been assigned the symbol *R*.

[1] See, *e.g.* A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 1965, 2883.

[2] See, *e.g.* C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, 1965, **19**, 1915.

[3] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 1965, 5094.

[4] T. S. Piper and A. G. Karipides, *Mol. Phys.*, 1962, **5**, 475; A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, 1964, **40**, 674; M. Shinada, *J. Phys. Soc. Japan*, 1964, **19**, 1607; C. E. Schäffer, *Proc. Roy. Soc.*, 1967, *A*, **297**, 96.

[5] A. D. Liehr, *J. Phys. Chem.*, 1964, **68**, 665, 3629.