A Hexadecadal Rule for Relating the Configuration and Optical Activity of Dissymmetric Tetragonal Cobalt(III) Complexes

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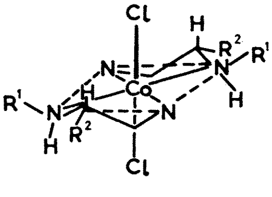
Summary The absolute configuration and c.d. of *trans*-bisdiamine cobalt(III) complexes indicate that optical activity associated with the components of the $A_{1g} \rightarrow T_{1g}(O_h)$ transition is governed by a hexadecadal rule which has the symmetry properties of a pseudo-scalar potential in the group D_{4h}.

IN a recent X-ray diffraction study[1] it has been shown that the $(-)_D$-*trans,trans*-dichlorobis-(N-methylethylenediamine)cobalt(III) ion, $[Co(Meen)_2Cl_2]^+$, has the absolute configuration (I), which is analogous to that of the $(+)_{546}$-*trans*-dichloro-bis{(+)-propylenediamine}-cobalt(III) ion, $[Co(+pn)_2Cl_2]^+$, known to be (II) from an X-ray diffraction investigation of the enantiomeric complex[2] and by conformational analysis.[3] However, the c.d. spectra of the complexes (I)[4] and (II)[5] are virtually enantiomorphous in the region of the $A_{1g} \rightarrow T_{1g}(O_h)$ cobalt(III) absorption (Figure



(I); $R^1 = Me$, $R^2 = H$
(II); $R^1 = H$, $R^2 = Me$
(III); $R^1 = R^2 = Me$

1). Further the c.d., recently reported,[6] of the *trans*-dichlorobis-{N_1-methyl-(+)-propylenediamine}cobalt(III) ion, which on conformational grounds[3] has the structure (III), is also enantiomorphous with that of the complex (II) (Figure 1).

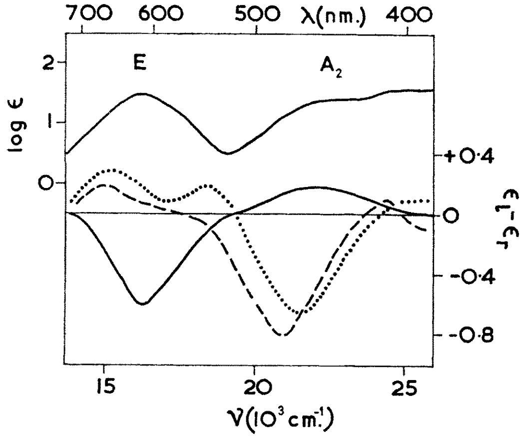


FIGURE 1. *The absorption (upper curve) and c.d. (lower curve) of* $(+)_{546}$-*trans*-dichlorobis-{(+)-propylenediamine}cobalt(II) chloride (————) and the c.d. of $(-)_D$-*trans,trans*-dichlorobis-(N-methylethylenediamine)cobalt(III) chloride (········) *and of* *trans*-dichlorobis-{N_1-methyl-(+)-propylenediamine}cobalt(III) perchlorate (— — — —).

These observations suggest that the dissymmetric perturbation due to the N-methyl groups of the chelate ligands in a *trans*-bisdiaminecobalt(III) complex is of an opposite sign to that due to the CH_2 or $CH{\cdot}CH_3$ groups of the diamine chain, and that the dissymmetric potential due to the substituent groups which lower the tetragonal (D_{4h}) symmetry of the *trans*-CoN_4Cl_2 chromophore is nodal in the three planes containing four metal–ligand bonds. The octant sign rule[7] relating the configuration and optical activity of the $d \rightarrow d$ transitions of cobalt(III) complexes implies a dissymmetric potential due to the ligand substituents of the form $z(x^2 - y^2)$, the Cartesian axes being directed along the metal–ligand bonds. The c.d. (Figure 1) and absolute configuration, (I), (II), and (III), of the complexes considered indicate that this dissymmetric potential must be augmented for tetragonal complexes to $xyz(x^2 - y^2)$, which is the simplest pseudo-scalar function[8] of the group D_{4h} to which the *trans*-CoN_4Cl_2 chromophore belongs. Schellman[8] has shown that a potential function producing optical rotation in a chromophore must have the symmetry properties of a pseudo-scalar in the point group of the unperturbed chromophore. The dependency of the sign of the pseudo-scalar potential upon the co-ordinates then provides regional rules relating the position of a substituent to the sign of the Cotton effect produced by the perturbation due to that substituent.[8]

The regional sign dependency of the D_{4h} pseudo-scalar function, $xyz(x^2 - y^2)$, is illustrated in Figure 2, which gives the sign of the Cotton effect induced by alkyl substituents in the $+z$ hemisphere in the region of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component of the octahedral $A_{1g} \rightarrow T_{1g}$ cobalt(III) absorption. In the case of the *trans*-CoN_4Cl_2 chromophore this component, due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, lies close to the frequency of the $A_{1g} \rightarrow T_{1g}$ transition of the CoN_6 chromophore (21,500 cm.$^{-1}$). For alkyl substituents in the $-z$ hemisphere the signs depicted (Figure 2) hold for the $A_{1g} \rightarrow E_g(D_{4h})$ component of the $A_{1g} \rightarrow T_{1g}$ octahedral cobalt(III) transition, lying near to 16,000 cm.$^{-1}$ for the *trans*-CoN_4Cl_2 chromophore. The signs given (Figure 2) are reversed for substituents in the $-z$ hemisphere in the case of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component and for groups in the $+z$ hemisphere in the case of the $A_{1g} \rightarrow E_g(D_4h)$ component. The double degeneracy of the $A_{1g} \rightarrow E_g(D_4h)$ transition is split in the c.d. spectrum of the complex (I) (Figure 1) and also in those of the $(+)_D$-*trans*-dichlorotriethylenetetraminecobalt(III) ion[5] and its (−)-3,8-dimethyl triethylenetetramine analogue,[9] and in such cases the sign of the Cotton effect of this transition is taken to be that of the major of the two c.d. bands observed when these differ in sign.

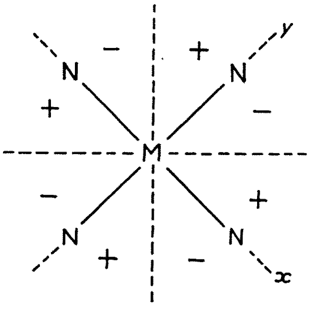


FIGURE 2. *The sign of the Cotton effect induced in the trans-*CoN_4X_2 *chromophore by substituents in the* $+z$ *hemisphere for the* $A_{1g} \rightarrow A_{2g}(D_{4h})$ *component, or the* $-z$ *hemisphere for the* $A_{1g} \rightarrow E_g(D_{4h})$ *component, of the octahedral* $A_{1g} \rightarrow T_{1g}$ *ligand-field* cobalt(III) *transition.*

For the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition near to 21,500 cm.$^{-1}$ it is observed that the CH_2 and $CH{\cdot}CH_3$ groups of the diamine chelate rings in the complexes (I), (II), and (III) lie in positive sectors (Figure 2) whereas the N-CH_3 groups of (I) and (III) lie in negative sectors. The structure analyses of the complexes (I) and (II) indicate that the magnitude of the z-co-ordinate is larger for the carbon atom of the N-CH_3 group than for that of the CH_2 group of the diamine chain, whilst the methyl carbon atom of the $CH{\cdot}CH_3$ group lies close to the xy-plane. Accordingly the dissymmetric potential, $xyz(x^2 - y^2)$, has a larger absolute value for the N-CH_3 group than for the CH_2 and $CH{\cdot}CH_3$ groups of the diamine rings, and the Cotton effect induced by the latter groups in (II), which is positive for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition, is reversed in sign by N-methyl substitution as in (III) or by this substitution accompanied by the replacement of the $CH{\cdot}CH_3$ by CH_2 groups as in (I) (Figure 1).

The hexadecadal sector rule for the Cotton effect associated with the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition (Figure 2) applies to the dissymmetric *trans*-dichlorotriethylenetetraminecobalt(III) ions[5,9] and to the *trans*-diacido-bis-{(−)-propylenediamine}-[10] or -bis-{(−)-*trans*-1,2-cyclohexanediamine}cobalt(III)[11] ions provided, in the latter two cases, that the groups X in the chromophore *trans*-CoN_4X_2 have cylindrical symmetry about the metal–ligand bond direction, and that the chromophore is at least approximately tetragonal and not of effectively higher or lower symmetry. When

$X = NH_3$ the chromophore CoN_4X_2 is effectively octahedral and the tetragonal components, $A_{1g} \rightarrow A_{2g}, E_g(D_{4h})$, cannot be identified unambiguously. Where $X = NO_2^-$ in the chromophore *trans*-CoN_4X_2 the position of the oxygen atoms of the NO_2 groups in the hexadecadal sectors (Figure 2) cannot be specified as yet, and if we ignore these oxygen atoms the c.d. of the (+)D-*trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ ion[4] has a sign contrary to the present rule.

A similar double-octant rule has been proposed[12] for the tripeptide complexes of copper(II) and nickel(II) containing the planar MN_3O chromophore. The $d \rightarrow d$ absorption bands at 560 and 480 nm. for the Cu^{II} and Ni^{II} complexes, respectively, are associated with a negative dichroism if the tripeptides are derived from the L-amino-acids.[12] The signs of the double-octant rule[12] are the same as those suggested (Figure 2) for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition ($d_{xy} \rightarrow d_{x^2-y^2}$) of the *trans*-$CoN_4X_2$ chromophore. In the planar Cu^{II} and Ni^{II} complexes the $d_{x^2-y^2}$ orbital is the only half-vacant or unoccupied *d*-orbital, and transitions to this orbital from d_{xy}, d_{xz}, d_{yz}, and d_{z^2} have magnetic moments of $2\beta_M$ (Bohr magnetons), $1\beta_M$, $1\beta_M$, and zero, respectively. Other factors being equal, the major $d \rightarrow d$ c.d. band of planar Cu^{II} and Ni^{II} complexes is thus due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, which is expected to be susceptible to the same dissymmetric perturbations as the corresponding transition of cobalt(III). For a given tripeptide ligand the c.d. of the Ni^{II} complex is larger by a factor of two than that of the corresponding Cu^{II} complex.[12] In the case of planar complexes the $d_{x^2-y^2}$ orbital is unoccupied in the case of Ni^{II} and half-occupied in the corresponding Cu^{II} complex, so that the intrinsic magnetic moment and the borrowed electric moment of transitions to this orbital from lower levels, notably the d_{xy} orbital, are larger in the former than the latter complex by a factor of $\sqrt{2}$. The rotational strength, governing the area of the corresponding c.d. band, depends upon the scalar product of the magnetic and electric transition moments, and this product is expected to be twice as large for planar Ni^{II} as for the corresponding Cu^{II} complexes.

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