Complementation of the Crystal Field for Dihedral Optical Activity

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Summary The *d*-electron optical activity of the tris-diamine complexes of cobalt(III), whether randomly oriented or with a fixed orientation in a single crystal, is quantitatively rationalised by a model in which the transient-induced electric dipole moments in the ligand groups are correlated collinear to the magnetic dipole moment of the metal-ion transition by the leading electric multipole moment of that transition, a hexadecapole.

In octahedral and other centrosymmetric transition metal complexes the intensity mechanism for *d*-electron transitions discussed in the preceding communication[1] is forbidden, although the corresponding vibronic mechanism, dependent upon the *ungerade* nuclear modes, remains operative. On reducing the symmetry of a 6-co-ordinate complex from O_h to O the mechanism becomes allowed, but not for the quadrupolar *d*-electron transitions which are the effective excitations in the complexes belonging to the isomorphous T_d group. For a complex of O symmetry only the charge distribution of the hexadecapolar *d*-electron transitions constructively correlate transient induced electric dipole moments in the ligands (Figure). In contrast to the T_d case, the $xy(x^2 - y^2)$, $yz(y^2 - z^2)$, and $xz(z^2 - x^2)$ components of a hexadecapole transform under the same row of the T_1 representation in O as, respectively, the z, x, and y component of an electric and a magnetic dipole moment.

The *d*-electron transitions $|A_0) \rightarrow |A_a)$ with an electric hexadecapole moment, H_{0a}, are generally magnetic-dipole allowed, the moment $|m_{a0}|$ being,[2] *e.g.*, $2\sqrt{2}$ Bohr magneton for each of the three components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $[Co(NH_3)_6]^{3+}$ at 21 kK.† In non-centrosymmetric complexes containing the $[CoN_6]^{3+}$ chromophore the induced electric dipole moments μ_{0b} in the ligands (B) are correlated by H_{0a} to give a resultant electric dipole transition moment with the z-component (equation 1). Equation (1) is the

$$\mu^z_{0a} = -\sum_B \bar{\alpha}(B) H^{xy(x^2-y^2)}_{0a} G^B_{xy(x^2-y^2),z} \tag{1}$$

analogue of equation (6) in the preceding communication and has a similar basis. The individual groups B of the ligands have the mean polarisability $\bar{\alpha}(B)$ at the frequency ν_{0a}, and the potential between the induced moment μ^z_{0b} in such a group and the 2^4-pole $H^{xy(x^2-y^2)}_{0a}$ has the angular and radial geometric factor given by equation (2), where

$$Gxy(x^2 - y^2),z = 315\, XYZ(Y^2 - X^2)/2R^{11} \tag{2}$$

X,Y,Z refer to the co-ordinates of B in the octahedral frame.

The component of the $^1A_1 \rightarrow {}^1T_1$ transition of the $[CoN_6]^{3+}$ chromophore with O symmetry giving the 2^4-pole $H^{xy(x^2-y^2)}_{0a}$ is the excitation $d_{xy} \rightarrow d_{x^2-y^2}$ which results in the configuration $\chi^{x^2-y^2}_{xy}$. This component has a z-polarised magnetic moment m^z_{a0}, collinear with μ^z_{0a} (equation 1), producing the rotational strength R^z_{0a}. However, the summation of R_{0a} over all three components of the $^1A_1 \rightarrow {}^1T_1$ transition gives a zero resultant using equation (1), since the cyclic permutation of X,Y,Z in equation (2) gives a set of three G-factors with a vanishing sum for O symmetry.

Equations (1) and (2) are based on the point multipole approximation, which is inadequate for the present purpose. The radial factor for the 2^4-pole moment of a $3d$-electron transition is dependent upon $\langle 3d|r^4|3d\rangle$, and double-exponent $3d$-wave functions[3] give $[\langle r^4\rangle]^{\frac{1}{4}}$ the values of

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† $1 kK = 10^3 cm^{-1}$.

0·684 and 0·956 Å for Co^{3+} and neutral cobalt, respectively. These distances are not negligible relative to the Co—N bond length[4] (2 Å) or the metal–carbon distance (3 Å) in $[Co(en)_3]^{3+}$. Accordingly each 2^4-pole moment of the $^1A_1 \rightarrow {}^1T_1$ transition was taken for computational purposes in the present work to consist of eight charges $\pm\sqrt{2}\ e/4$ disposed according to the particular component angular distribution, *e.g.* $[xy(x^2\text{-}y^2)/r^4]$ (Figure), at a distance r = 0·837 Å from the metal ion, corresponding to $[<r^4>]^{\frac{1}{4}}$ for cobalt with +1·3 charge.

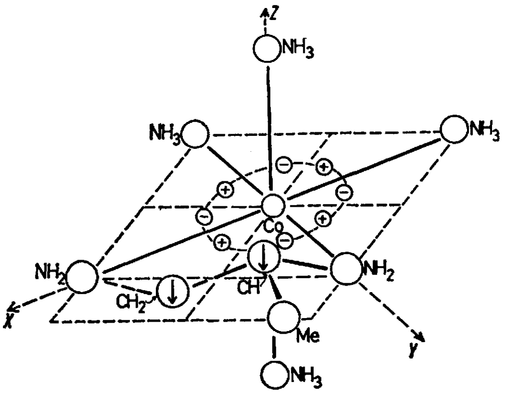

FIGURE. The correlation of the induced electric dipole moment in the CH_2 group below the xy plane and in the CH group above that plane in the λ-puckered *R*-(−)-propylene-diamine chelate ring produced by the electric hexadecapole moment of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition of the $[CoN_6]^{3+}$ chromophore. The *d*-electron transition corresponds to a clockwise rotation of charge viewed from the $+Z$ direction, producing a *z*-polarised magnetic dipole moment parallel to the correlated induced electric dipole moments in the ligand groups, and so resulting in a positive rotational strength.

With the extended multipole model, the product of the 2^4-pole moment and *g*-factor in equation (1) becomes a sum over the transition monopolar charges, $q^j_{oa} = \pm\sqrt{2}\ e/4$ [Figure; equation (3)], where $\boldsymbol{R}_{jB}$, with the components

$$-H^{xy(x^2-y^2)}_{oa}G^{B}_{xy(x^2-y^2),z} \equiv S^{B}_{z} = \sum_{j=1}^{8} q^{j}_{oa}Z_{jB}\boldsymbol{R}_{jB}{}^{-3} \tag{3}$$

X_{jB}, Y_{jB}, Z_{jB}, is the position vector of the point induced dipole μ^z_{ob} in the ligand group B with respect to the monopole q^j_{oa}. Equations (1) and (3) give the *z*-component of the $^1A_1 \rightarrow {}^1T_1$ transition in a $[CoN_6]^{3+}$ complex with *O* symmetry the first-order rotational strength given by equation (4). The corresponding R^x_{oa} and R^y_{oa} components

$$R^z_{oa} = -\,im^z_{ao}\sum_{B}\bar{\alpha}(\mathrm{B})S^B_z \tag{4}$$

arising respectively from the excitations to the configurations $\chi^{y^2-z^2}_{yz}$ and $\chi^{z^2-x^2}_{xz}$, follow from equation (4) by cyclic permutation of *x*, *y*, and *z*. A model complex of *O* symmetry was considered, consisting of the O_h chromophore $[CoN_6]^{3+}$ with each octahedral edge spanned by a $-CH_2-CH_2-$ grouping with the λ-puckered conformation and bond distances and angles measured in the *X*-ray crystal structure analyses[4] of R-(−)-pn complexes of cobalt(III). From the model it is found, employing[5] $\bar{\alpha}(CH_2)$ = 1·84 Å^3, that the three $^1A_1 \rightarrow {}^1T_1$ components have an equal positive rotational strength, the sum *R*(*O*) having the value + 0·40 per chelate ring in units of 10^{-40} c.g.s. The effect is additive over the number of rings, as is the approximate experimental counterpart, the conformational rotational strength, which has the value[6] of +0·6 per λ-ring in the same units for *R*-(−)-pn complexes of cobalt(III).

In the D_3 complexes, $[Co(diamine)_3]^{3+}$, the three O_h components of the $^1T_{1g}$ state are no longer necessarily degenerate, and appropriate linear combinations transforming as A_2 and E in D_3 are required, *e.g.*, equation (5).

$$\psi(A_2) = \frac{1}{\sqrt{3}}(\chi^{x^2-y^2}_{xy} + \chi^{y^2-z^2}_{yz} + \chi^{z^2-x^2}_{xz}) \tag{5}$$

The induced electric dipoles in the ligands correlated by one O_h component now form a non-zero scalar product with the magnetic dipole moment of the other components, resulting in relatively large first-order rotational strengths for the D_3 components, $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$, of the parent $^1A_1 \rightarrow {}^1T_1$ transition. The first-order values for the *E*-component, *R*(*E*), are found to be in tolerable agreement with the corresponding experimental values obtained from axial single-crystal c.d. measurements,[7,8] but the calculated first-order sum, $R(T_1) = R(A_2) + R(E)$, which corresponds to the measured c.d. for the randomly-oriented complex ion, is found to be too small.

TABLE

The calculated and the observed rotational strengths, *R* (10^{-40} c.g.s.), and increase in dipole strength relative to $[Co(NH_3)_6]^{3+}$, Δ*D* (10^{-38} c.g.s.), for the $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition and its *E* component near 21 kK in the tris-diamine complexes cobalt(III) complexes. Calculated values are based on the absolute configuration and molecular structure determined by *X*-ray diffraction methods with the NH_2 groups ($\bar{\alpha}$ = 1·44 Å^3)[a] and CH_n groups [$\bar{\alpha}$(CH) = 1·435; $\bar{\alpha}(CH_2)$ = 1·84; and $\bar{\alpha}$(Me) = 2·24 Å^3][a] placed at the corresponding heavy-atom position.

Complex[b] and configuration		$R(E)$[c]	$R(T_1)$	$R(O)$[d]	$\Delta D(T_1)$[e]
(+)-$[Co(en)_3]Cl_3 \cdot H_2O$	calc.	+64	+4·0	−1·0	4·0
Δ(δδδ) *lel*[f]	obs.	+53[k]	+4·4		3·5
(−)-$[Co(R\text{-}pn)_3]Br_3$	calc.	−65·1	−3·8	+1·0	4·4
Δ(λλλ) *lel*[g]	obs.	−41·5[l]	−4·2	+1·9	4·5
(+)-$[Co(R\text{-}pn)_3]^{3+}$	calc.	+63	+5·9	+0·7	3·6
Δ(λλλ) *ob*[h]	obs		+8·0	+1·9	4·5
(−)-$[Co(S,S\text{-}cptn)_3]$-$Cl_3 \cdot 4H_2O$	calc.	+69·2	+3·9	−1·0	4·8
Δ(δδδ) *lel*[i]	obs	+43·4[m]	+4[n]		2·0
(−)-$[Co(tn)_3]Cl_3 \cdot H_2O$	calc.	−10·2	−0·20	0	0·2
Δ(tris-chair)[j]	obs.	−10·5[l]	−1·36[p]	0	1·0

[a] From ref. 5 with $\bar{\alpha}$ (NH_2) reduced from the free amine value (1·76 Å^3) to allow for co-ordination by the lone-pair, based on the reduction between NH_3 ($\bar{\alpha}$ = 2·23 Å) and NH_4^+ ($\bar{\alpha}$ = 1·71 Å^3). [b] Abbreviations: en = ethylenediamine; *R*-pn = R-(−)-1,2-propylenediamine; *SS*-cptn = *trans*-SS-1,2-diaminocyclopentane; tn = trimethylenediamine. [c] Where uncorrected (refs. 7 and 8), the observed *R*(*E*) reported are corrected by the factor 2/3 to allow for the fixed orientation of the complex ion in the crystal. [d] The calculated *R*(O) refer to the contributions (equation 4) summed over the three *O* components and three chelate rings. The observed *R*(O) refer to the conformational effect of three λ-puckered *R*-(−)-pn rings (ref. 6). [e] $\Delta D = \Sigma|\mu_{0a}|^2$ from equation (1), the sum being taken over the three components of $^1A_1 \rightarrow {}^1T_1$. [f] M. Iwata, K. Nakatsu, and Y. Saito, *Acta Cryst.*, 1969, **B25**, 2562. [g] H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, 1966, **39**, 92. [h] From the crystal structure of Δ-(+)-$[Co(R\text{-}pn)_3][Co(CN)_6] \cdot 2H_2O$; R. Kuroda and Y. Saito, *Acta Cryst.*, 1974, **B30**, 2126. [i] Ref. 12. [j] R. Nagao, F. Marumo, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 2438. [k] Ref. 7. [l] Ref. 8. [m] Ref. 9. [n] KBr matrix value; $R(T_1)$ = − 5·4 for aqueous solution (ref. 9). [p] KBr matrix value for Δ-(−)-$[Co(tn)_3]Br_3 \cdot H_2O$; $R(T_1)$ = − 0·23 for aqueous solution (ref. 6).

This deficiency is rectified on proceeding to second-order (Table) where the induced electric dipoles in the ligand groups correlated by the 2^4-pole moment of the *d*-electron transition (Figure) themselves correlate a component of the electric dipole moment of the u.v. ligand–metal charge-transfer transition. The combination of single-crystal and vacuum u.v. c.d. spectroscopy places[10] the *E* and the A_2 component of the charge-transfer transition in (+)-[Co(en)$_3$]Cl$_3$ at 48 and 58 kK, respectively, while the band-origins of the corresponding components of the $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition near 21 kK are virtually degenerate.[11] As the energy-interval between the two *E* components is the smaller, the second-order *d*-electron $R(E)$ is the larger in (+)-[Co(en)$_3$]Cl$_3$ and, by analogy, in other tris-diamine cobalt(III) complexes.

The sums of the calculated first- and second-order rotational strengths are found to be in satisfactory agreement with experiment (Table) provided that the experimental data refer to the particular crystals on the *X*-ray structural data[4] for which the calculations were based. The experimental $R(T_1)$ for $\Delta(\lambda\lambda\lambda)$-(+)[Co(*R*,*R*-cptn)$_3$]Cl$_3$ is negative in a KBr matrix but positive in aqueous solution,[9] and our calculation based on the *X*-ray crystal structure analysis of the enantiomer[12] is in agreement with the KBr matrix c.d. measurement (Table). The calculations have been extended[13] from the cases recorded (Table) to all tris-diamine cobalt(III) complexes for which c.d. data[6,14] and *X*-ray crystal structure analyses[4,15] are at present available.

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