Solid-state Absorption and Circular-dichroism Spectra of Five-co-ordinate Trigonal Copper(II) Complexes: Anisotropic Contributions to the *d–d* Transition Probabilities

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The *d–d* dipole strengths of trigonal five-co-ordinated copper(II) complexes in microcrystalline form have been determined, together with the corresponding rotational strengths of the tris(2-aminoethyl)amine (tren) complexes [Cu(tren)(NCS)][SCN], and, as a single crystal, [Cu(tren)(NH_3)][ClO_4]$_2$. The results are compared with the corresponding theoretical transition probabilities based upon the dynamic ligand-polarization mechanism. A consideration of the polarizability anisotropy of the chelate-ring bonds is required to account for the optical activity, and an overall negative *d–d* circular dichroism is found to characterize the δ conformation of the chelate rings in five-co-ordinate (tren) complexes of copper(II).

A NUMBER of five-co-ordinate transition-metal complexes derived from the quadridentate ligand tris(2-aminoethyl)amine (tren), and its hexamethyl derivative tris(2-dimethylaminoethyl)amine (Me_6tren), crystallize in enantiomorphous space groups. These complexes are optically labile in solution, but the racemic mixture is spontaneously optically resolved on crystallization, and all of the complex ions in a given single crystal have a common chirality. Stereochemically, the chirality is based upon the common λ or δ conformation of the three chelate rings in a given complex ion. The salt [Cu(tren)(NCS)][SCN] (1) crystallizes [1] in the chiral orthorhombic space group $P2_12_12_1$, while its analogue [2] [Cu(tren)(NH_3)][ClO_4]$_2$ (2) and each member of the series [3] [M^{II}(Me_6tren)Br]Br, where the metal M is Mn, Fe, Co, Ni, Cu, or Zn, crystallize in the enantiomorphous cubic space group $P2_13$.

The present work reports the determination of the electronic *d–d* absorption and circular-dichroism (c.d.) spectrum of a single crystal of [Cu(tren)(NH_3)][ClO_4]$_2$ and the corresponding spectra of a powdered single crystal of [Cu(tren)(NCS)][SCN] incorporated into a potassium halide matrix. The crystal of the latter salt is biaxial and, although the measurement of the c.d. spectrum of a linearly birefringent crystal is feasible,[4] the corrections required for the linear dichroism and birefringence introduce large uncertainties. The use of a powdered single crystal in a potassium halide matrix ensures an enantiomeric purity and a determinate concentration, which are required for the evaluation of the rotational strengths of the complex ion randomly orientated in an isotropic medium, equivalent to a solution c.d. measurement.

The object of the investigation is an extension of the dynamic ligand-polarization mechanism for *d–d* transition probabilities,[5] including optical activity, to trigonal-bipyramidal five-co-ordination. The mechanism has been employed to analyse the *d–d* optical activity of chiral octahedral six-co-ordinate complexes of cobalt(III), both tris chelate [6] and hexakis unidentate,[7] and that of chiral quasi-tetrahedral four-co-ordinate complexes [8] of cobalt(II). In addition the mechanism accounts for a major part of the *d–d* absorption intensity of the tetrahedral transition-metal tetrahalides,[9] and for the unusual decrease in that intensity with increasing temperature.[10]

In order to apply the mechanism to the *d–d* dipole strengths of trigonal-bipyramidal complexes with penta-unidentate co-ordination, the *d–d* absorption intensities of the [$CuCl_5$]$^{3-}$ and [$CuBr_5$]$^{3-}$ complexes have been determined. The corresponding *d–d* absorption frequencies have been previously determined and analysed.[11–15] The *X*-ray diffraction crystal structures of the salts [Cr(NH_3)$_6$][CuX_5], where the ligand X is chloride [16,17] or bromide,[18] show that the [CuX_5]$^{3-}$ ion has a regular trigonal-bipyramidal structure at ambient temperature. At liquid-nitrogen temperature, the e.s.r. spectrum of the [$CuCl_5$]$^{3-}$ complex as a guest ion in the [Co(NH_3)$_6$][$CdCl_5$] host lattice gives three distinct *g* values, indicating that the guest complex ion loses trigonal symmetry at low temperature, and differential scanning calorimetry shows that, near −10 °C, the mixed crystal and the corresponding individual copper(II) or cadmium(II) crystal undergo a lattice transition.[19] The detailed structure of the low-temperature phase remains undetermined as yet, and the present work is restricted to the *d–d* absorption intensities of the ambient-temperature crystals with a known structure.

EXPERIMENTAL

Materials and Methods.—The salts [Rh(NH_3)$_6$][$CuCl_5$] and [Rh(NH_3)$_6$][$CuBr_5$] were prepared by the method of Mori.[20] In each case, the dried microcrystalline salt was ground in an agate mortar and mixed with a powder of the corresponding potassium halide in a determined weight ratio. The mixture was reground and pressed in an evacuated die to a transparent disc. Reference discs for absorbance measurements were prepared from powdered [Rh(NH_3)$_6$]X_3 and KX mixtures in the same mole ratio, where X is chloride or bromide.

The [tris(2-aminoethyl)amine]copper(II) salt, [Cu(tren)(NCS)][SCN] (1), was prepared by the procedure of Raymond and Basolo,[21] and the analogue [Cu(tren)(NH_3)][ClO_4]$_2$ (2) was obtained by the method of Duggan *et al.*[2] Seed crystals of the latter complex salt were kindly provided by Professor B. Hathaway.[2] Crystals up to 5 mm on edge of each complex salt were grown from aqueous solution, (1) appearing with a facetted parallelepiped morphology and (2) in a tetrahedral pyramid form. The larger individual crystals of (1) were separable by hand sorting into two sets, distinguished by their enantiomorphous facets, but the crystals of (2) appeared to lack any macroscopic enantiomorphous features.

A single crystal of the complex salt (1) from one of the two enantiomorphous crystal sets when powdered and incorporated at a known concentration into a potassium bromide matrix gave a c.d. spectrum over the 0.5—1.0 μm wavelength region which is the mirror image, across the baseline zero, of the corresponding c.d. spectrum afforded by a similarly treated single crystal of (1) from the second morphological set. The c.d. spectra of the two enantiomers of the complex ion (1) were reported in a preliminary account of the present work.[22] The possible exchange of the co-ordinated thiocyanate ion in the complex ion (1) with the bromide ion of the matrix [23] was checked by running the absorption and c.d. spectrum of a powdered single crystal from each of the enantiomorphous sets in a paraffin mull over the 0.5—1.5 μm range. The c.d. spectra of the two enantiomers of complex (1) in the mull were found to be again mirror image in form with c.d. maxima and minima at the same frequencies as the corresponding c.d. extrema observed for (1) in a potassium bromide disc, indicating a negligible anion ligand exchange in the latter case.

As the complex salt (2) crystallizes in a cubic space group [2] the c.d. spectrum of a single crystal is directly accessible, the crystal being optically isotropic. The single-crystal c.d. spectrum of complex (2) over the 0.5—1.0 μm wavelength range, measured by previously described methods,[24,25] was invariant with respect to the rotation of the crystal about the light-propagation direction. Additional absorption and c.d. measurements were carried out with a powdered single crystal of the complex salt (2) in a paraffin mull and in a potassium bromide matrix. The frequencies of the c.d. extrema and the dissymmetry ratio of the c.d. differential absorbance, ΔA, to the total isotropic absorbance, A, while in substantial agreement for the single-crystal and the mull measurements, were lower for the potassium bromide disc measurements, suggesting an appreciable ligand exchange for bromide ion in the preparation of the disc.

TABLE 1

Observed frequency, $\tilde{\nu}$ (10^3 cm^{-1}), dipole strength, D (10^{-60} C^2 m^2), and rotation strength, R (10^{-55} C m J T^{-1}), of five-co-ordinate trigonal-bipyramidal copper(II) complex ions in the solid state and the corresponding ligand-polarization dipole and rotational strengths calculated * from equations (8)—(12). The calculated rotational strengths refer to the δ conformation of each chelate ring in the complex ions (1) and (2)

Complex salt	$\tilde{\nu}_{abs.}$	$D_{obs.}$	$D_{calc.}$	$\tilde{\nu}_{c.d.}$	$R_{obs.}$	$R_{calc.}$
[Cu(tren)(NCS)][SCN]	11.8	8.2	1.91	12.4	+0.40	
	(15)		0.01	15.1	−1.12	−1.86
[Cu(tren)(NH$_3$)][ClO$_4$]$_2$	12.2	13.3	1.91	13.5	+0.27	
	(15.5)		0.04	16.3	−4.90	−1.86
[Rh(NH$_3$)$_6$][CuCl$_5$]	8.3	5.9	1.89			
[Rh(NH$_3$)$_6$][CuBr$_5$]	8.6	7.1	3.01			

* Calculated from the expectation value of $\langle r^2 \rangle$ for the dipositively charged copper ion (0.297 Å^2). The equatorial bond in the copper(II) pentahalide complex ions has lengths of 2.3912 and 2.5291 Å for the chloride (ref. 17) and the bromide (ref. 18) respectively, and the halide polarizabilities are 3.6 and 5.0 Å^3 respectively (ref. 36). The structural factors and polarizability values for the chelated complex ions (1) and (2) are listed in Table 2.

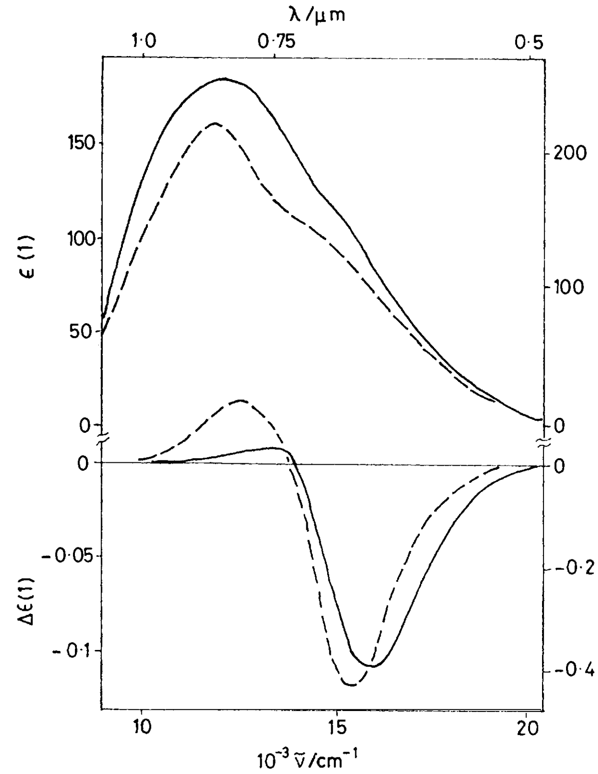

FIGURE 1 Absorption spectrum (upper curves) and the circular dichroism (lower curves) of a powdered single crystal of [Cu(tren)(NCS)][SCN] (1) (— — —) in a potassium bromide matrix and of a single crystal of [Cu(tren)(NH$_3$)][ClO$_4$]$_2$ (2) (——)

The spectra recorded (Table 1, Figure 1) were measured with a Cary 17 (absorption) and a Jasco J 40 CS (circular-dichroism) spectrophotometer. Additional measurements were carried out over the 1.0—5.0 μm range with a laboratory-constructed instrument, recording both absorption and circular dichroism,[26] in order to investigate any lower-energy *d–d* electronic transitions of the complex salts (1) and (2). Only weak, sharp, vibrational c.d. bands were detected, due to C–H and N–H stretching vibration modes over the 2 800—3 300 cm^{-1} range. The strongest, due to a hydrogen-bonded N–H stretching mode near 3 300 cm^{-1}, has a dissymmetry ratio, $\Delta A/A \approx 10^{-4}$, with a negative sign for the enantiomers which give negative electronic c.d. absorption over the 500—700 nm region (Figure 1).

The *d–d* electronic absorption and c.d. band areas were converted into the corresponding transition probabilities recorded, the dipole strength, D, and the rotational strength, R respectively (Table 1) through the relations, given previously with the universal constants evaluated in the c.g.s. unit system,[27] expressed in the S.I. system by equations (1) and (2) where $\Delta\varepsilon$ refers to the decadic molar absorption

$$D/\mathrm{C^2\,m^2} = 1.0218 \times 10^{-61} \int (\varepsilon/\nu)\mathrm{d}\nu \qquad (1)$$

$$R/\mathrm{C\,m\,J\,T^{-1}} = 7.658 \times 10^{-54} \int (\Delta\varepsilon/\nu)\mathrm{d}\nu \qquad (2)$$

coefficient for left and right circular radiation, ($\varepsilon_L - \varepsilon_R$).

RESULTS AND DISCUSSION

Ligand-polarization Intensity Mechanism.—The dynamic ligand-polarization mechanism, like crystal-field theory, is based upon the independent-systems model in which overlap between the charge distributions of the metal ion and of the ligands in a co-ordination compound is neglected. Crystal-field theory has been notably successful in the treatment of the transition energies of *d–d* or *f–f* transitions in open-shell metal complexes, but it has a more limited application to the corresponding transition probabilities, and the limitations do not necessarily arise from the neglect of metal–ligand electron exchange. A first-order perturbation treatment of one-electron properties based upon the independent-systems model takes one of two limiting forms. In the case of open-shell metal co-ordination compounds, either a particular charge distribution of the ligands, generally taken to be that of the ground electronic state, perturbs all of the electronic states of the metal ion, as in the crystal-field theory, or alternatively a particular charge distribution of the metal ion, usually a given *d*- or *f*-electron transitional distribution, perturbs all of the electronic states of the ligands. The latter course is adopted in the ligand-polarization mechanism for *d–d* and *f–f* transition probabilities in metal complexes, which does not preclude additional first-order contributions from the crystal-field mechanism, nor mixed contributions to higher order.[5]

On the independent-systems basis, the zero-order states of an open-shell metal complex are described in terms of simple products of metal-ion $|M_m)$ and single-ligand $|L_l)$ wavefunctions. The initial product functions, $|M_0L_0)$ for the ground state and $|M_mL_0)$ for the excited electronic state of the metal ion in the complex, are corrected to the first order of perturbation theory by means of the complete set of excited ligand functions. The Laporte-forbidden *d–d* or *f–f* transition of the open-shell metal ion, $|M_0)\rightarrow|M_m)$, thence aquires a first-order electric dipole moment, $\mu_{0m}{}^{\alpha}$, which is given by relation (3) where α, denoting *x*, *y*, or *z*, refers to the particular polarization direction of the transition dipole, and the state energies are measured relative to that of the ground state, E_0, as zero.

$$\mu_{0m}{}^{\alpha} = \sum_{\mathrm{L}}\sum_{l=0}[(E_m - E_l)^{-1}(M_0L_l|V|M_mL_0)(L_0|\mu^{\alpha}|L_l) - (E_m + E_l)^{-1}(M_0L_0|V|M_mL_l)(L_l|\mu^{\alpha}|L_0)] \quad (3)$$

The transition dipole of equation (3) is located wholly in the ligands of the co-ordination cluster, representing the resultant of dipoles induced in each ligand atom or group by the Coulombic field of the transitional charge distribution, $(M_0|M_m)$, centred on the metal ion. The Coulomb potential, V, between the transitional charge distribution of the metal ion and that, $(L_0|L_l)$, of a ligand is approximated by expanding each of the charge distributions in a multipole series centred upon the respective co-ordinate origin. Only the leading term of each expansion series is retained, namely, an electric dipole, $\mu_{0l}{}^{\delta}$, for the ligand and an electric quadrupole, $\theta_{0m}{}^{\beta\gamma}$, or a higher even multipole in the range bounded by the $2l$ pole for a $l\rightarrow l$ transition of the metal ion. The Greek suffixes β, γ, δ, denote Cartesian components, *x*, *y*, or *z*, in the co-ordinate frame of the complex centred upon the metal ion (Figure 2).

The more significant of the allowed multipole moments of a *d–d* or a *f–f* transition is the electric quadrupole, on account of the longer range of its Coulomb potential. Following the multipole expansion, the Coulombic matrix elements of equation (3) become, for the quadrupolar transition case, those of equation (4) where the geometric tensor $G_{\beta\gamma\delta}{}^{\mathrm{L}}$ represents the radial and the angular factors governing the potential between the transition quadrupole component, $\theta_{0m}{}^{\beta\gamma}$, centred on the metal ion and the transition dipole component, $\mu_{0l}{}^{\delta}$, located in the ligand, L.[28] Combination of equations (3) and (4) gives equation (5), for the first-order electric dipole moment of a quadrupolar metal-ion transition.

$$(M_0L_0|V|M_mL_l) = \theta_{0m}{}^{\beta\gamma}G_{\beta\gamma\delta}{}^{\mathrm{L}}\mu_{0l}{}^{\delta} \quad (4)$$

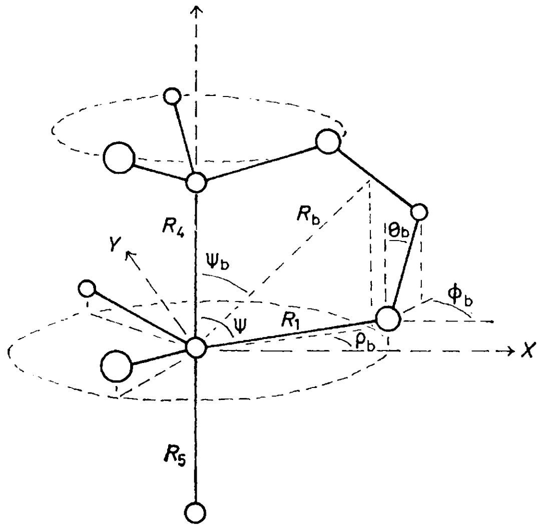

FIGURE 2 Co-ordinate frame of a trigonal five-co-ordinate metal complex with three equatorial bonds, of length R_1, at the polar angle, ψ, to the $C_3(Z)$ axis, and bonds to the axial ligands with lengths R_4 and R_5. A chelate-ring bond is orientated at the polar, θ_b, and azimuthal angle, ϕ_b, in the frame of the co-ordination cluster, and the bond-centre has the radial, R_b, and angular, ψ_b, ρ_b, location in the frame

$$\mu_{0m}{}^{\alpha} = -\sum_{\mathrm{L}}\sum_{l=0}\theta_{0m}{}^{\beta\gamma}G_{\beta\gamma\delta}{}^{\mathrm{L}}(\mu_{0l}{}^{\delta}\mu_{l0}{}^{\alpha})[2E_l/(E_l{}^2 - E_m{}^2)] \quad (5)$$

The ligand dipole components in equation (5), $\mu_{l0}{}^{\alpha}$, and $\mu_{0l}{}^{\delta}$, refer to local co-ordinate axes parallel to those of the co-ordination cluster with the metal ion at the origin. For isotropic ligands, such as the halide ions, only the dipole-component products in equation (5), $\mu_{0l}{}^{\delta}\mu_{l0}{}^{\alpha}$, for which $\alpha = \delta$ survive in the summation over the ligand excitations, $|L_0)\rightarrow|L_l)$. The summation affords the mean polarizability of the ligand at the metal-ion transition frequency, $\bar{\alpha}_{\mathrm{L}}(\nu_{0m})$, for monoatomic ligands or in the approximation where only the mean polarizability of the ligand group is taken into account, and equation (5) becomes equation (6).

$$\mu_{0m}{}^{\alpha} = -\sum_{\mathrm{L}}\theta_{0m}{}^{\beta\gamma}G_{\alpha\beta\gamma}{}^{\mathrm{L}}\bar{\alpha}_{\mathrm{L}}(\nu_{0m}) \quad (6)$$

For an anisotropic but cylindrically symmetric ligand group, such as the C–N or C–C bonds in the complex ions (1) and (2), the orientation of the principal axis of the ligand group (z') is specified by the polar and the azimuthal Eulerian angles,[29] θ and ϕ, respectively, relating the z' axis to the X, Y, Z frame of the metal-centred co-ordination cluster (Figure 2). The angular transformation of each ligand dipole component from the frame orientated parallel to the co-ordinate system of the metal complex to the directions parallel (z') and perpendicular (x', y') to the cylinder axis of the ligand group converts the ligand dipole products, $\mu_{0l}{}^{\delta}\mu_{l0}{}^{\alpha}$, of equation (5) into the corresponding products of components referring to the local x', y', z' ligand frame. The principal components of the polarizability tensor of the ligand group at the metal-ion transition frequency are extracted from the transformed component-dipole products through the summation [28] of equation (7) and the analogous

$$\alpha_{\|} = \alpha_{z'z'} = \sum_{l=0} 2E_l(E_l{}^2 - E_m{}^2)^{-1}|\mu_{0l}{}^{z'}|^2 \qquad (7)$$

summation for the degenerate perpendicular component, $\alpha_{\perp} = \alpha_{x'x'} = \alpha_{y'y'}$. The mean polarizability, $\bar{\alpha}$, corresponds to the average, $(\alpha_{\|} + 2\alpha_{\perp})/3$, and the anisotropy of the ligand-group polarizability is represented by $\beta\bar{\alpha} = (\alpha_{\|} - \alpha_{\perp})$.

Trigonal-bipyramid Co-ordination.—The ligand-field energies of the *d* electrons of a transition-metal ion in a five-co-ordinate trigonal-bipyramidal complex [30,31] give the D_{3h} halides, $[\mathrm{CuX_5}]^{3-}$, and the C_3 complexes (1) and (2) a $^2A_1{}'$ and a ^2A ground state respectively, corresponding in both cases to a singly occupied d_{z^2} orbital in the otherwise filled 3*d* shell (Figure 3). The two doubly degenerate *d*-electron excitations, corresponding to the hole promotions $a_1{}' \rightarrow e'$, e'', remain pure in D_{3h} symmetry, but are intermixed in the C_3 complexes (Figure 3). The leading moments of the lower-energy transition are the xy and the $x^2 - y^2$ component of an electric quadrupole for the $d_{z^2} \rightarrow d_{xy}$ and the $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation component, respectively. Neither of these components has a magnetic dipole transition moment. Each component of the higher-energy transition has a magnetic moment $m_x = -i\sqrt{3}$ B.M.* (Bohr magneton) for the $d_{z^2} \rightarrow d_{yz}$ excitation and $m_y = +i\sqrt{3}$ B.M. for the $d_{z^2} \rightarrow d_{xz}$ promotion, together with an electric quadrupole moment, θ_{yz} and θ_{xz} respectively.

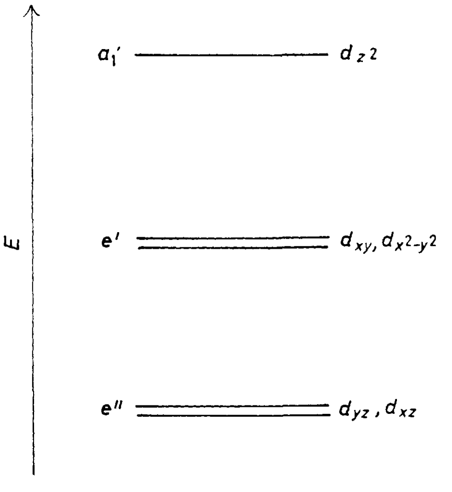

FIGURE 3 Ligand-field energy splitting of the free-ion *d*-orbital degeneracy in a five-co-ordinate trigonal-bipyramidal complex ion with D_{3h} symmetry

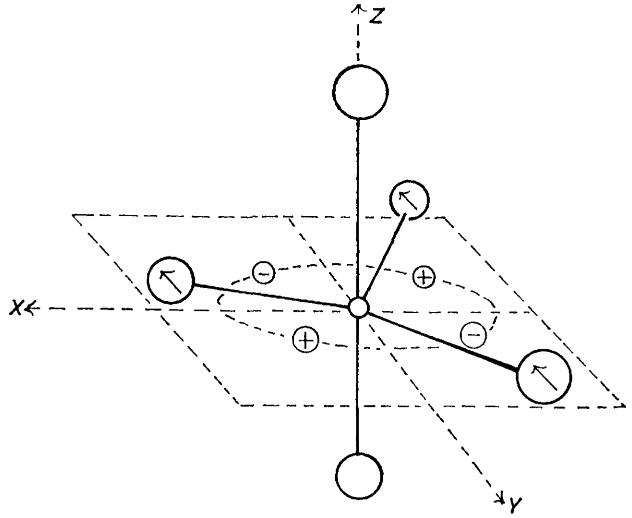

FIGURE 4 Coulombic correlation of the y component of the electric dipole induced in each co-ordinated ligand group by the field of the xy component of the electric quadrupole *d–d* transition moment, centred on the metal ion, in a five-co-ordinate trigonal-bipyramidal complex with C_3 or higher symmetry

At the equilibrium nuclear configuration of a five-co-ordinate D_{3h} complex, only the quadrupole moments of the lower-energy transition give a constructive correlation of the electric dipoles induced in each ligand. The correlation is confined to the dipoles induced in the three equatorial ligands, even if the symmetry of the complex is reduced to C_{3v} by the introduction of inequivalent axial ligands and the distortion of the angle between the axial and the equatorial bonds from $\pi/2$ (Figure 4). The contribution from the axial ligands vanishes because the Coulomb potential between the quadrupole component of the metal ion, θ_{xy}, and the y component of the dipole induced in each ligand [equation (4)] is governed by a geometric tensor,[28] $G_{xy,y}{}^{\mathrm{L}} = 3X_{\mathrm{L}}R_{\mathrm{L}}{}^{-7}(R_{\mathrm{L}}{}^2 - 5Y_{\mathrm{L}}{}^2)$, which goes to zero for an axial ligand but not for an equatorial ligand. The corresponding geometric tensor for the potential between the quadrupole component $\theta_{x^2-y^2}$ of the metal ion and the x component of the dipole induced in each ligand similarly vanishes for an axial ligand. The summation of the non-zero contributions over the three equatorial ligands [equation (6)] gives the relation (8) for the y component of the resultant first-order

$$\mu_{0m}{}^{y} = -(45/4)\theta_{0m}{}^{xy}R_1{}^{-4}\ (\alpha_{\mathrm{eq}})\sin^3\psi \qquad (8)$$

electric dipole moment of the lower-energy *d–d* transition

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

of copper(II) in a five-co-ordinate trigonal complex. The corresponding x component is given by a relation analogous to equation (10) in which the quadrupole component, $+\theta_{0m}^{x^2-y^2}$, replaces $-\theta_{0m}^{xy}$. In equation (8) and its analogue, R_1 refers to the length of the bond between the metal ion and an equatorial ligand, with a mean polarizability, $\bar{\alpha}_{eq}$, and ψ is the angle between each equatorial bond and the $C_3(Z)$ molecular axis (Figure 2).

The higher-energy copper(II) d-electron transition acquires a non-vanishing ligand-polarization electric dipole moment only if the symmetry of the complex is reduced from D_{3h} (Figure 5). With inequivalent axial ligands, or equatorial ligands equivalently displaced from the molecular XY plane (Figure 2), the quadrupole transition moment, θ_{xz}, at the metal ion correlates the x component of the dipole induced in each ligand atom or group through the Coulomb potential governed by the geometric tensor,[28] $G_{xz,x}^{L} = 3Z_LR_L^{-7}(R_L^2 - 5X_L^2)$ (Figure 5). Similarly, the y component of the dipole induced in each ligand group is correlated by the field of the degenerate quadrupole transition moment of the metal ion, θ_{yz}.

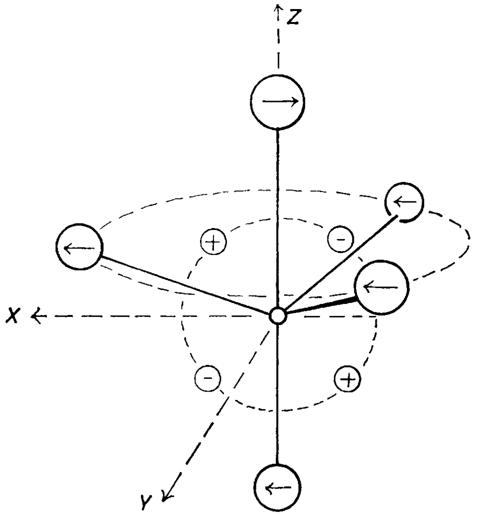


FIGURE 5 Coulombic correlation of the x component of the electric dipole induced in each co-ordinated ligand group by the field of the xz component of the electric quadrupole d–d transition moment, centred on the metal ion, in a five-co-ordinate trigonal-bipyramid complex with C_3 or higher symmetry

The summation of the contributions from the five co-ordinated ligand groups gives the expression (9) for the

$$\mu_{0m}^{x} = 3\theta_{0m}^{xz}[(3/2)R_1^{-4}(3\cos\psi - 5\cos^3\psi)\bar{\alpha}_{eq} - R_4^{-4}\bar{\alpha}_4 + R_5^{-4}\bar{\alpha}_5] \quad (9)$$

x component of the resultant first-order electric dipole moment of the higher-energy copper(II) d–d transition in the mean polarizability approximation [equation (6)]. The corresponding y component is given by the analogue of equation (9) in which θ_{0m}^{yz} replaces θ_{0m}^{xz}. Ligand groups which are not directly co-ordinated to the metal ion, notably the CH_2 groups of the chelate rings in the complex ions (1) and (2), give additional contributions, governed by terms analogous to that for the three co-ordinated equatorial ligand groups in equation (9). An evaluation of the additional contributions due to the CH_2 groups shows that the sum of these is small, as is the sum of the opposed contributions from the two axially co-ordinated groups, L_4 and L_5, with a positive and a negative Z co-ordinate respectively, in the molecular frame of the complex (Figures 2 and 5).

The ligand-polarization mechanism in the mean-polarizability approximation [equation (6)] does not account for the observed d-electron optical activity of the chelated copper(II) complex ions (1) and (2) (Figure 1). While each component of the higher-energy d–d transition has a zero-order magnetic dipole moment and a first-order electric dipole moment, the two moments are orthogonal to one another. Thus, the component $d_{z^2} \rightarrow d_{xz}$ involves a charge rotation about the Y axis, giving rise to the y component of a magnetic dipole, but the corresponding first-order electric dipole moment has x polarization [equation (9)]. Collinear moments are required for a non-vanishing rotational strength [equation (10)] where Im denotes that the imaginary part is

$$R_{0m} = \mathrm{Im}[(\mu_{0m}^{\alpha}m_{m0}^{\beta})\delta_{\alpha\beta}] \quad (10)$$

retained, since the magnetic dipole operator is purely imaginary, and $\delta_{\alpha\beta} = 1$ for $\alpha = \beta$ and zero otherwise.

Each component of the higher-energy copper(II) d-electron transition acquires a first-order electric-dipole moment collinear with the zero-order magnetic moment if the polarizability anisotropy of the C–N and the C–C bonds of the chelate rings in the complex ions (1) and (2) is taken into account. The ligand dipole components of equation (5), each with a polarization referred to the molecular co-ordinate frame, are resolved into components referring to the local directions parallel (z') and perpendicular (x', y') to each C–C or C–N bond through the Eulerian angles, θ_b, ϕ_b, subtended by the bond in the molecular frame (Figure 2). The resolved dipole products for a given bond, summed through equation (7) and its analogues, give the principal components of the bond polarizability, $\alpha_{\parallel}$ and $\alpha_{\perp}$. Additional ligand-polarization contributions to the first-order electric dipole moment of a Laporte-forbidden transition are found to be dependent solely on the bond polarizability anisotropy, $(\beta\bar{\alpha})_b = (\alpha_{\parallel} - \alpha_{\perp})_b$, summed over the individual bonds in the complex.[32]

In the case of the higher-energy copper(II) d–d transition of the chelated complex ions (1) and (2), the additional contributions to the electric dipole moment have the polarization required to give, with the zero-order magnetic moment, a non-vanishing rotational strength [equation (10)]. For the particular component $d_{z^2} \rightarrow d_{xz}$, the bond-anisotropy contribution, with y polarization in contrast to the x polarization of the mean polarizability contribution [equation (9)], is given by expression (11).

$$\mu_{0m}^{y} = -(9/8)\theta_{0m}^{xz}\sum_{b}(\beta\bar{\alpha})_b\sin\psi_b[5\sin2\psi_b\sin^2\theta_b\sin2(\rho_b - \phi_b) + (5\cos\psi_b + 3)\sin2\theta_b\sin(\rho_b - \phi_b)] \quad (11)$$

The degenerate component, $d_{z^2} \rightarrow d_{yz}$, provides a bond-anisotropy contribution with x polarization, given by the analogue of equation (11) with $-\theta_{0m}{}^{xz}$ replaced by $+\theta_{0m}{}^{yz}$. The contributions of bonds equivalent under the C_3 rotational operation in the complex ions (1) and (2) are combined in equation (11), where the sum is taken over the inequivalent bond sets, each set being specified by a generator bond, N(1)–C(1), C(1)–C(2), or C(2)–N(4). Each set is characterized by the common bond-polarizability anisotropy, $(\beta\bar{\alpha})_b$, and by the distance of the metal ion from the centre of the generator bond, R_b, together with the polar and azimuthal angles specifying the bond-centre position, ψ_b and ρ_b, and the bond orientation θ_b and ϕ_b, in the molecular co-ordinate frame (Figure 2, Table 2).

TABLE 2

Radial and angular structural factors (Figure 2) for the chelated complex ions (1) and (2) entered into equations (8), (9), and (11), together with the mean polarizability, $\bar{\alpha}$, of the ligand groups and the polarizability anisotropy, $\beta\bar{\alpha}$, of the chelate-ring bonds. The structural factors refer to the heavy atom of a group or to the centre of a bond. With the exceptions noted, the structural factors are based upon the X-ray molecular structure determination of (1) (ref. 1), and the polarizability data are taken from ref. 36

Bond	N(1)–C(1)	C(1)–C(2)	C(2)–N(4)
R/Å	2.418	2.785	2.373
ψ/°	67.90	42.56	17.31
ρ/°	−4.07	+0.27	+13.75
θ/°	18.55	53.73	108.29
ϕ/°	−43.11	−32.34	+13.76
$\beta\bar{\alpha}$/Å^3	+0.35 [a]	+0.79	0.35 [a]

Group	$H_2N(1)$	N(4)	N(5) [b]
R/Å	2.085	2.033	1.059
ψ/°	84.1	0	180
α/Å^3	1.76	1.09	1.09

[a] Ref. 37. [b] For complex (1), where the carbon and sulphur atoms of the thiocyanate ligand lie at R = 3.101 and 4.713 Å respectively, with $\bar{\alpha}$ = 1.0 and 3.2 Å^3 respectively. For complex (2), $\bar{\alpha}(NH_3)$ = 2.22 Å^3, and R = 2.023 Å for Cu–N(5) (ref. 2).

Dipole and Rotational Strengths.—The dipole strength of each copper(II) d–d transition in the complex ions (1) and (2) corresponds to the sum of the strengths of the individual components, equation (12), and the rotational

$$D_{0m} = |\mu_{0m}{}^{x}|^2 + |\mu_{0m}{}^{y}|^2 \qquad (12)$$

strength of the higher-energy transition is made up similarly of two components, $\alpha = x$ and $\alpha = y$ [equation (10)]. Estimates of the transition probabilities require the evaluation of the electric quadrupole moments of each of the copper(II) d–d transitions, in addition to the structural and the polarizability data for the complex ions considered (Table 2). Following the method of Griffith,[33] the moments are evaluated, in units of the electron charge, from equations (13) and (14) where

$$\langle d_{z^2}|\theta_{xy}|d_{xy}\rangle = \langle d_{z^2}|\theta_{x^2-y^2}|d_{x^2-y^2}\rangle = -(2/7\sqrt{3})\langle r^2\rangle \qquad (13)$$

$$\langle d_{z^2}|\theta_{xz}|d_{xz}\rangle = \langle d_{z^2}|\theta_{yz}|d_{yz}\rangle = +\,(1/7\sqrt{3})\langle r^2\rangle \qquad (14)$$

$\langle r^2\rangle$ refers to the radial expectation value, $\langle 3d|r^2|3d\rangle$, for copper(II).

Double-exponent radial $3d$ wavefunctions for copper[34] give $\langle r^2\rangle$ values in the range from 0.297 Å^2 for the dipositively charged ion to 0.440 Å^2 for the neutral atom. For consistency within the general independent-systems model, the $\langle r^2\rangle$ value for the dipositively charged copper ion was employed to calculate the dipole and rotational strengths recorded (Table 1) from equations (8), (9), and (11) and their analogues. The $\langle r^2\rangle$ value adopted is too small, since the charge distribution in the $Cs_2[CuCl_4]$ crystal, measured by X-ray diffraction analysis,[35] gives the copper(II) ion an effective charge of +0.60, and the corresponding charge in the $[CuCl_5]^{3-}$ complex ion is estimated to be +0.23 by molecular-orbital calculations.[13] The use of the $\langle r^2\rangle$ value for the neutral copper atom gives dipole and rotational strengths larger by a factor of 2.2 and 1.5, respectively, than the corresponding values listed (Table 1).

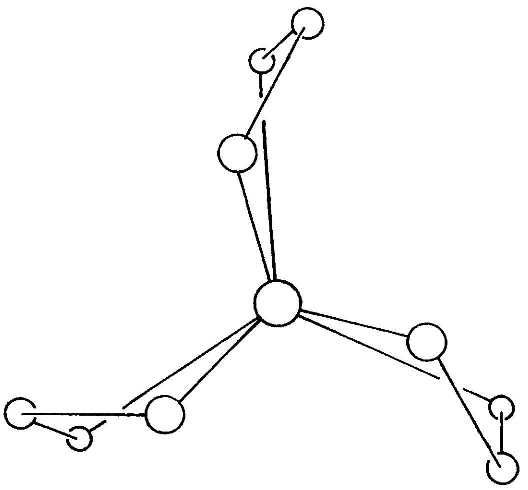
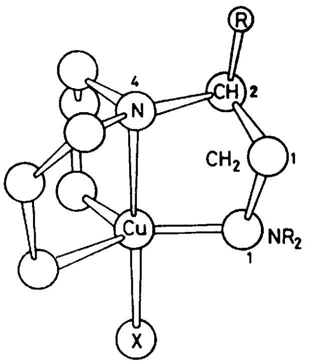


FIGURE 6 Projection on the XY plane from the $+Z$ axis of the molecular structure of the complex ions (1) and (2) with the chelate rings in the δ conformation

The ligand-ion or group mean-polarizability and bond-polarizability anisotropy values[36,37] employed are not corrected to the copper(II) d–d transition frequency, since the corrections involved are small relative to the uncertainties in the appropriate expectation value of $\langle r^2\rangle$, dependent upon the particular charge on the copper(II) atom in the complex ion. The radial and the angular structural and orientation factors for the chelate-ring bonds of the complex ions (1) and (2) (Figure 2, Table 2) refer to values averaged over the three chelate rings to give C_3 symmetry, which is not exact in the molecular structure of (1) determined by X-ray crystallography.[1] The bond-orientation and bond-centre position values recorded (Table 2) refer to the δ conformation of the chelate rings (Figure 6).

The sign of the azimuthal position, ρ, and bond orientation angle, ϕ, is changed for each bond in the enantiomeric λ conformation of the chelate rings. A change in the sign of the azimuthal angles, due to an inversion of the chelate-ring conformation, reverses the direction of the first-order electric dipole moment of the higher-energy copper(II) *d–d* transition for a given phase of the electric quadrupole moment [equation (11)]. The zero-order magnetic dipole and electric quadrupole moment of each component of the higher-energy *d–d* transition are phase-locked, so that an inversion of the chelate-ring conformation changes the sign of the rotational strength [equation (10)] from negative for the δ conformation (Table 1) to positive for the λ conformation.

The theoretical assignment of a negative rotational strength to the higher-energy copper(II) *d–d* transition in the complex ions (1) and (2) with the chelate rings in the δ conformation[22] is supported by the recent isolation, and characterization by c.d. spectroscopy, of the analogous five-co-ordinate copper(II) complex ions (3) and (4), containing a chiral derivative of Me_6tren, (*S*)-2,4,8-trimethyl-5-(2-methyl-2-azabutyl)-2,5,8-triazanonane, abbreviated as *S*-tan.[38] The (*S*) configuration at the carbon atom of the chelate ring substituted by the exocyclic methyl group in the complex ions (3) and (4) is determined by the synthesis of the *S*-tan ligand from (+)-alanine.[38] For the (*S*) configuration, the equatorial preference of the exocyclic methyl group gives the chelate ring into which it is substituted a preferred δ conformation, and the energy of the two other chelate rings in a given complex ion (3) or (4) is lowered by the adoption of the same δ conformation. The c.d. spectra of the complex ions (1)—(4) have the common form of a minor positive band at lower frequency and a major negative band at higher energy[38] (Figure 1). The similarities between the c.d. spectra of the more-directly comparable complex ions (2) and (3) are close in respect of both the c.d. band frequencies and rotational strength.



(1) R = H, X = NCS
(2) R = H, X = NH_3
(3) R = CH_3, X = NH_3
(4) R = CH_3, X = Br

The excited states of both of the copper(II) *d–d* transitions in the C_3 complex ions (1)—(4) have a common ^2E symmetry and are mixed. The mixing process in itself is expected to give rotational strengths of equal magnitude and opposite sign, giving a vanishing sum over the frequency range of the *d–d* manifold. While the *d–d* excited-state mixing accounts for the weak positive c.d. absorption associated with the lower-energy transition, which is devoid of a zero-order magnetic moment, it does not accommodate the major negative c.d. absorption due to the higher-energy transition (Figure 1). The net negative rotational strength observed over the *d–d* manifold as a whole of the complex ions (1)—(4) provides a measure of the intrinsic rotational strength of the higher-frequency transition, due to the coupling of the zero-order magnetic dipole moment with the first-order electric dipole moment [equation (11)] arising from the polarizability anisotropy of the bonds composing the chelate rings with a common δ conformation. On this basis the calculated rotational strength is in satisfactory accord with the corresponding observed values (Table 1).

The calculated dipole strengths are generally too small (Table 1). The adoption of the $\langle r^2 \rangle$ expectation value for an uncharged copper atom accounts for the major part of the dipole strength observed for the pentahalide copper(II) complex ions through equation (8) and its analogue for the second component of the lower-energy *d–d* transition, with $\psi = \pi/2$ for D_{3h} symmetry, where the higher-energy transition remains forbidden. At ambient temperature a low-intensity shoulder is observed on the high-frequency side of the *d–d* absorption band.[11–14] The shoulder is ascribed to the correlation of the dipoles induced in each halide ligand by the quadrupole moment of the components of the higher-energy *d–d* transition at the turning points of the non-totally symmetric vibrational modes in the copper(II) pentahalide ions. The mechanism becomes particularly effective at the C_{3v} turning points of the $\nu_4(a_2'')$ out-of-plane bending mode of the equatorial CuX_3 group, where $\psi \neq \pi/2$ (Figure 5), and at the C_{2v} turning points of the $\nu_1(e')$ bending mode of the axial CuX_2 group in the $[CuX_5]^{3-}$ pentahalide complex ions. The ν_4 and ν_1 modes have frequencies of 170 and 83 cm^{-1}, respectively, in the trigonal-bipyramidal $[TiCl_5]^-$ ion,[39] and an appreciable population of the higher vibrational levels of the analogous modes in the ground electronic state of the $[CuX_5]^{3-}$ ions is expected at ambient temperature.

The calculated *d–d* dipole strength of the chelated complex ions (1) and (2) (Table 1) derives primarily from the correlation of the dipoles induced in the equatorial NH_2 groups by the quadrupole moment of the two components of the lower-energy transition [equation (8), Figure 3], and secondarily from the corresponding correlation by the quadrupole moment of the higher-energy transition components [equation (9), Figure 5]. The contribution to the dipole strength from the axial ligands is minor and non-zero only for the higher-energy transition, while the corresponding contributions from the CH_2 groups of the chelate rings are small for both transitions. The additional contribution to the first-order electric dipole moment of the higher-energy transition dependent upon the polarizability anisotropy of the bonds forming the chelate rings [equation (11)], while accounting for the rotational strength, does not appreciably augment the theoretical dipole strength. It is concluded that the ligand polarization mechanisms considered account for only a minor fraction of the *d–d* dipole strength of the chelated trigonal copper(II) complex ions (1) and (2), and that other mechanisms are additionally operative.

The additional dipole-strength mechanism is the more significant for the chelated complex ions (1)—(4) than for the copper(II) pentahalides (Table 1), and for copper(II) than for other transition-metal ions in chelated five-co-ordinate complexes. In the trigonal-bipyramidal series $[M^{II}(Me_6tren)Br]^+$, the dipole strength over the *d–d* manifold has the value of 14.7 and 3.2 in units of 10^{-60} C^2 m^2 for the copper(II)[40] and the chromium(II) complex,[41] respectively. The *d–d* transitions considered are directly comparable for the two complexes, and equations (8), (9), and (12) hold for the chromium(II) complex additionally. The expectation value of $\langle r^2 \rangle$ is larger (0.536 Å^2) for dipositively charged chromium than for the corresponding charge state of copper, but the chromium–ligand bonds are probably longer. The adoption of the metal–ligand bond lengths reported[3] for the $[Mn(Me_6tren)Br]Br$ structure gives the corresponding chromium(II) complex a calculated ligand-polarization dipole strength of 2.8×10^{-60} C^2 m^2 over the *d–d* manifold.

The intensity data for the $[Fe(Me_6tren)Br]^+$ complex, while incomplete, are sufficient to show that the lower-energy *d–d* transition has a dipole strength larger than that of the higher-energy transition, by an approximate factor of 3 ± 1, and that the total *d–d* dipole strength is small compared to that of the corresponding chromium(II) complex.[42] The higher-energy *d–d* transition in the iron(II) complex, $e'' \rightarrow a_1'$, is the analogue of the corresponding transition in the copper(II) or chromium(II) complex, but the lower-energy transition, $e'' \rightarrow e'$ (Figure 3), differs in kind. The leading moments of the components of the $e'' \rightarrow e'$ transition are either the yz component of an electric quadrupole accompanied by the x component of a magnetic dipole, or an xz quadrupole component accompanied by a y magnetic dipole component, as in the case of the higher-energy $e'' \rightarrow a_1'$ transition. The magnitude of the quadrupole moment of a given component of the $e'' \rightarrow e'$ transition is larger by a factor of $\sqrt{3}$ than that of the corresponding component of the $e'' \rightarrow a_1'$ transition, while the magnetic moment is smaller by a factor of $1/\sqrt{3}$, and the phase relationship between the quadrupole and magnetic moment is changed in sign.

These relationships give the expectation, on the basis of the ligand-polarization mechanism, that in a five-co-ordinate trigonal-bipyramidal $[Fe^{II}(tren)X]^+$ complex the lower-energy $e'' \rightarrow e'$ transition has a dipole strength three times larger than that of the higher-energy $e'' \rightarrow a_1'$ transition, and a rotational strength of equal magnitude but opposite sign to that of the latter transition. For the δ conformation of the chelate rings in a $[Fe^{II}(tren)X]^+$ complex, the rotational strength is expected to be positive for the lower-energy $e'' \rightarrow e'$ transition and negative for the higher-energy $e'' \rightarrow a_1'$ transition, with a magnitude similar to that of the higher-frequency rotational strength of the copper(II) analogues (1)—(4).

We thank Mr. J. M. Gould for a preparation of complex (2), Dr. A. F. Drake for the measurement of the i.r. absorption and c.d. spectra, and the S.R.C. for support.

[1/732 *Received, 8th May*, 1981]

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