of networks which are highly swollen could be due to the effect of the diluent on the firmness with which the junctions are embedded, while those of a network prepared in solution[61] could be due to the solvent partially disentangling the chains prior to their incorporation into the network structure.

Many of the above statements are still somewhat conjectural, and much experimental and theoretical work is currently being carried out in an attempt to evaluate and extend these concepts. In any case, the configurations of the chains are obviously of central importance with regard to rubberlike elasticity, as it is with regard to the other unique properties of polymeric materials.

It is a pleasure to acknowledge that much of the work on chain configurations carried out by the author has been supported by the National Science Foundation (Polymers Program, Division of Materials Research).

The Ligand Polarization Model and the Spectra of Metal Complexes. A Complementation of the Crystal Field

STEPHEN F. MASON

Chemistry Department, King's College, London WC2R 2LS, England

Received January 9, 1978

It is now generally accepted that any formally correct treatment of the electronic states of transition-metal and lanthanide complexes requires an explicit consideration of the electron exchange between the ligands and the metal ion and that independent-systems models which neglect the overlap of the charge distributions of the metal ion and the ligands are necessarily incomplete. In its applications, however, the main independent-systems model, crystal-field theory, has provided a range of qualitatively novel and testable expectations, despite all the limitations of that theory, whereas MO treatments of metal complexes incorporating metal–ligand overlap are more notable for the ex post facto rationalization of known quantities, often with the aid of a more or less extensive set of adjustable parameters.

Not all of the limitations of crystal-field theory are rooted in the neglect of metal–ligand electron exchange. A first-order independent-systems treatment of one-electron quantities, energies or charge distributions, rests upon one of two mutually exclusive limiting assumptions. Either the ligands perturb the metal ion, or the metal ion perturbs the ligands. 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 crystal-field theory, or alternatively a particular charge distribution of the metal ion, usually a given d-electron or f-electron transitional distribution, perturbs all of the electronic states of the ligands. The latter course is adopted in the ligand-polarization model which is complementary, within the first-order independent systems scheme, to crystal-field theory.

Stephen Mason was born in England in 1923 and educated at Oxford University, where subsequently he taught chemistry and the history of science. After research in medical chemistry at the Australian National University, he became lecturer and then reader in chemical spectroscopy at Exeter University, and professor of chemistry first at the University of East Anglia and then at King's College, London. His principal research interests are directed to chiral structures and to molecular spectroscopy, particularly to the two subjects taken in conjunction with one another and with the history of scientific ideas.

The Transition-Probability Anomalies of Crystal-Field Theory

Crystal-field theory has been rather more successful in the treatment of the transition energies than the transition probabilities of d-electron and f-electron excitations in metal complexes. The theory originated during the late 1920s and the following decade from physicists more concerned with frequency relationships in the line spectra of the atoms and gaseous ions than with the line strengths, although spectral intensities were not neglected. In the study of the corresponding condensed-phase cases, attention was naturally directed to linelike spectra, notably those of the lanthanide(III) complexes in the solid state. The well-known Stark effect of the splitting of an atomic line in an electrostatic field provided a straightforward mechanism to account for the appearance of each gaseous Ln(III) line as a multiplet in the corresponding crystal spectrum. The number of components observed was related group-theoretically by Bethe (1929) to the symmetry of the electrostatic field due to the charged ligands and to the particular spectroscopic terms of the gaseous Ln(III) ion connected by the electronic transition.[1]

In extensions of the theory to the electronic transition probabilities of coordination compounds the basic model of the perturbation of the metal ion states by the static crystal field of the ground-state charge distribution in the ligands was retained. Laporte (1924) had shown that electric dipole transitions between two gerade or between two ungerade states are forbidden,[2] and in a pioneer study Van Vleck (1937) distinguished three mechanisms to accound for the nonzero f–f transition probabilities of lanthanide complexes.[3] These invoked either the leading allowed moments of the electronic transition, an electric quadrupole or a magnetic dipole, or an enforced electric-dipole transition

---

(1) H. A. Bethe, *Ann. Phys.*, [5] 3, 133 (1929).
(2) O. Laporte, *Z. Phys.*, 51, 512 (1924).
(3) J. H. Van Vleck, *J. Phys. Chem.*, 41, 67 (1937).

moment. The forced electric dipole arises from the perturbation of the metal ion states either by a static noncentrosymmetric crystal field or, if the complex has inversion symmetry, by a dynamic field resulting from the non-totally symmetric vibrational modes. Subsequently the forced electric dipole mechanism was shown to be the most important of the three for the f–f transitions of lanthanide complexes[4] and the d–d excitations of transition-metal complexes.[5]

The forced electric-dipole mechanism in crystal-field theory was placed upon a quantitative basis for both the transition metal[6,7] and the lanthanide complexes,[8,9] and in each series a class of anomalous cases became evident. The oscillator strengths of the d–d excitations in octahedral transition metal complexes are accommodated by the crystal-field model,[6] whereas those of the corresponding electronic transitions in analogous tetrahedral complexes have calculated values which are as much as two orders of magnitude too small.[7] The crystal-field treatment indicates that analogous O_h and T_d complexes are expected to have comparable d-electron absorption intensities, but the observed T_d extinction coefficients are substantially the larger (Figure 1). Similarly a class of hypersensitive f–f transitions in lanthanide complexes has been identified,[10] with oscillator strengths ranging up to two orders of magnitude larger than the values calculated from the forced dipole mechanism in the crystal-field model. These f–f transitions generally have an allowed electric quadrupole moment, like that of Nd(III) near 600 nm which has an intensity compatible with the crystal-field treatment for the aquo ion, but not for a range of other Nd(III) complexes, particularly the halides NdX_3 in the vapor phase[11] (Figure 2).

Further anomalies became apparent from studies of the temperature dependence of the d–d absorption intensities in a series of tetrahedral transition-metal complexes, where a marked fall in the oscillator strength with increasing temperature is invariably observed.[12] The d-electron oscillator strengths of octahedral transition-metal complexes are found to increase as the temperature is raised, as expected from the vibronic forced electric dipole mechanism in the crystal-field model. In the case of the crystal, $NiSO_4{\cdot}7H_2O$, an intensity increase of some 40% between liquid-nitrogen and ambient temperature is observed.[13] The intensity enhancement is due to the larger excursions from O_h symmetry with increasing temperature, on account of the increasing population of the higher vibrational levels of the non-totally symmetric modes in the electronic ground state of the complex.[13] Similar behavior is expected for tetrahedral complexes, but the contrary trend is observed. The visible absorption band of $[CoCl_4]^{2-}$, for example, has an oscillator strength at 1000 °C little more than one-half of the corresponding ambient-temperature value.[12]

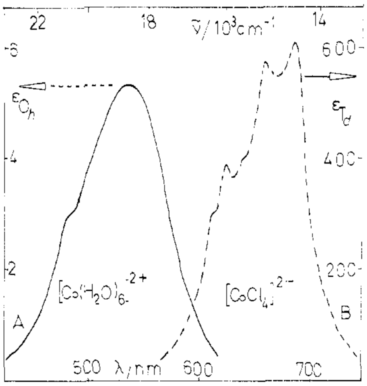


Figure 1. Electronic spectra over the visible region of (A) octahedral $[Co(H_2O)_6]^{2+}$ and (B) tetrahedral $[CoCl_4]^{2-}$.

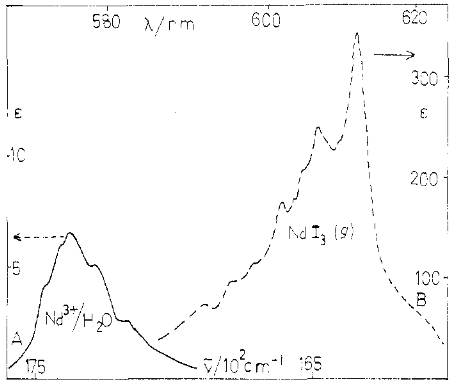


Figure 2. Absorption spectrum of the Nd(III) transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ for (A) the aquo ion and (B) NdI_3 in the vapor phase. The latter spectrum is adapted from ref 11.

An additional transition-probability anomaly in the crystal-field theory of tetrahedral complexes emerged from recent studies of the magnetically induced optical activity of the cobalt(II) tetrahalides.[14–16] An experimentally determined d–d transition moment ratio is of opposite sign to that required either by crystal-field or MO theory.[14–16]

Even more profound and of longer standing are the problems of crystal-field theory in the treatment of the natural optical activity of chiral six-coordinate complexes containing an octahedral chromophore, e.g., the $[Co^{III}N_6]$ cluster of the tris(diammine)cobalt(III) complexes. Sugano,[17] in a critique of the pioneer work of Moffitt,[18] showed that a ligand field with pseudoscalar symmetry, transforming under the A_{1u} representation in the O_h group, is required to confer a finite first-order rotational strength upon a d–d excitation in chiral complexes of this type. The simplest potential with A_{1u} symmetry in the O_h group has a ninth power dependancy upon the electronic coordinates. Such a potential mixes the d orbitals ($l = 2$) only with other metal ion orbitals of large angular momentum ($l = 7$, 9, 11) and high energy, precluding any effective first-order rotational strength.

Second-order treatments[19,20] of the d-electron optical activity in chiral six-coordinate complexes involve

---

(4) L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, *Physica*, **11**, 231 (1945).

(5) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753 and 766 (1954).

(6) A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957).

(7) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectrosc.*, **2**, 342 (1958); **4**, 190 (1960).

(8) B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

(9) G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).

(10) C. K. Jorgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).

(11) D. M. Gruen and C. W. De Kock, *J. Chem. Phys.*, **45**, 455 (1966).

(12) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

(13) O. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(14) P. J. Stephens, *J. Chem. Phys.*, **43**, 4444 (1965).

(15) R. G. Denning, *J. Chem. Phys.*, **45**, 1307 (1966).

(16) R. G. Denning and J. A. Spencer, *Symp. Faraday Soc.*, **3**, 84 (1969).

(17) S. Sugano, *J. Chem. Phys.*, **33**, 1883 (1960).

(18) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

(19) M. Shinada, *J. Phys. Soc. Jpn.*, **19**, 1607 (1964).

(20) G. Hilmes and F. S. Richardson, *Inorg. Chem.*, **15**, 2582 (1976), and references therein.

concurrent T_{2u} and T_{2g} crystal field potentials, the required A_{1u} perturbation appearing as a resultant. However, a finite T_{2g} potential breaks the degeneracy of T_1 and T_2 octahedral d-electron states, so that second-order crystal-field optical activity is ruled out in chiral complexes of *O* symmetry and in complexes of lower symmetry where the component d-electron states with a common T_1 or T_2 octahedral parentage are accidentally degenerate.

Finally, on carrying the crystal-field treatment of the T_{2u} and T_{2g} potentials to all orders of perturbation theory, it has been found,[20] for a wide range of parameter sets, that the computed rotational strengths conflict qualitatively with the corresponding experimental values measured from the CD band areas. In particular, the rotational strengths of the d-electron transitions to the D_3 cobalt(III) states, $^1A_2$ and ^1E with a common $^1T_{1g}$ octahedral parentage, have the theoretical ratio[20] $|R(E)|/|R(A_2)| < 1$, whereas experimentally this ratio is generally greater than unity for the tris(1,2-diammine) and tris(oxalato) complexes of Co(III), Rh(III), and Cr(III), e.g., the two CD bands of Λ-(+)-$[Co(en)_3]^{3+}$ in the 400–500-nm region (Figure 3).

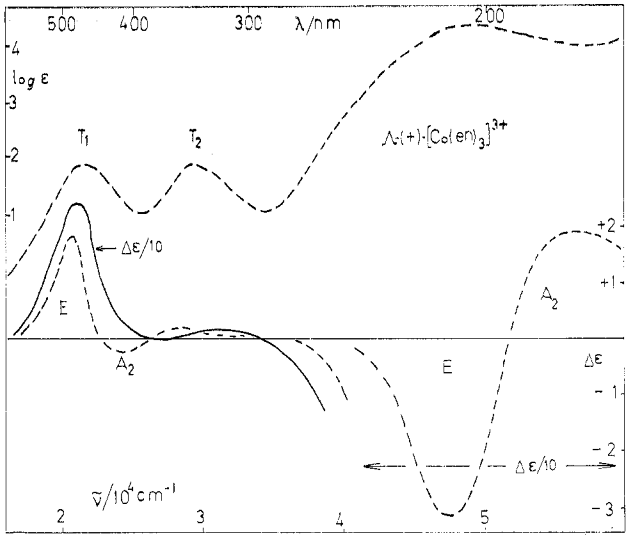


Figure 3. Axial single-crystal circular dichroism spectrum (Δε/10) of Λ-(+)-$Co(en)_3Cl_3]_2$·NaCl·$6H_2O$ (solid curve) and the absorption and CD spectrum of Λ-(+)-$[Co(en)_3](ClO_4)_3$ in water (upper and lower broken curve, respectively). The axial crystal CD spectrum characterizes electronic transitions of the complex ion to upper states of ^1E symmetry, polarized perpendicular to the threefold rotation axis of the ion.

The Ligand-Polarization Model

The anomalies indicated in the crystal-field theory of d–d and f–f transition probabilities in metal complexes are resolved within the independent-systems scheme by a complementary model which allows for the perturbation of the ligand atoms or groups by a potential originating from the central metal ion of a coordination compound.[21-26] With the common neglect of electron exchange between the metal ion and the ligands, the electronic states of the complex are represented in both the crystal field and the ligand-polarization model by a simple product of the metal ion $|M_a)$ and the single-ligand $|L_l)$ functions. In both models the sole perturbation is taken to be the Coulombic potential between the charge distribution of the metal ion and that of each ligand.

$$V = \sum_{i(\mathrm{M})} \sum_{j(\mathrm{L})} e_i e_j / r_{ij} \tag{1}$$

The zero-order product functions, $|M_0L_0)$ for the ground state and $|M_aL_0)$ for the excited electronic state of the metal ion in the complex, require an augmentation with other functions of the set for correction to first order. These are taken as the functions of higher excited metal ion states $|M_kL_0)$ in crystal-field theory. In the ligand-polarization model these are taken as excited-state ligand functions, $|M_0L_l)$ for the correction of the ground state of the complex or as $|M_aL_l)$ for the correction of the excited d-electron or f-electron metal ion state. The two procedures are mutually exclusive to the first order, on account of the one-electron character of the transition moment operators.

The first-order electric dipole moment μ_{0a}^{α} of a d–d or f–f transition $|M_0) \rightarrow |M_a)$ in a metal complex is acquired, according to the ligand-polarization model, from the set of electric-dipole-allowed excitations of the ligands, $|L_0) \rightarrow |L_l)$

$$\mu_{0a}^{\alpha} = \sum_{l \neq 0} (E_a - E_l)^{-1} (M_0L_l|V|M_aL_0)(L_0|\mu^{\alpha}|L_l) + \sum_{l \neq 0} (-E_a - E_l)^{-1} (M_0L_0|V|M_aL_l)(L_l|\mu^{\alpha}|L_0) \tag{2}$$

where $\alpha = x$, y, or z represents the particular dipole component, and energies are measured relative to that of the ground-state E_0 as zero. The ligand-polarization equation (eq 2) indicates that the first-order electric dipole moment of a d–d or f–f transition in a metal complex is located wholly in the ligands, with a value proportional to matrix elements of the form $(M_0L_0|\cdot V|M_aL_l)$. These elements represent the Coulombic potential between the nonoverlapping charge distributions of the transitions $|M_0) \rightarrow |M_a)$ and $|L_0) \rightarrow |L_l)$.

An approximation to the potential is afforded by a multipole expansion of each of these charge distributions, centered upon their respective coordinate origins, and the truncation of each series after the leading term. The term retained for the ligand group charge distribution is the electric dipole, μ_{0l}. The allowed electric charge distributions of an $l \rightarrow l$ metal ion transition are the even electric multipole moments, the 2^n-poles, with $n = 2, 4, \cdots 2l$, each having $(2n + 1)$ components. The components are conventionally and conveniently distinguished by Greek suffixes, denoting Cartesian components, e.g., $\theta_{\alpha\beta}$ symbolizes the *xy*, *yz*, or *zx*, etc., component of a quadrupole, the 2^2-pole, and $H_{\alpha\beta\gamma\delta}$ a given component of a hexadecapole, the 2^4-pole. These two charge distributions, the quadrupole and the hexadecapole, are allowed for d–d transition, while a 2^6-pole electric moment is permitted additionally for f–f excitations.

The point multipole expansion of the Coulombic matrix element governing the first-order electric dipole transition moment in eq 2 gives the selection rules of

---

(21) S. F. Mason, R. D. Peacock, and B. Stewart, *Chem. Phys. Lett.*, **29**, 149 (1974); *Mol. Phys.*, **30**, 1829 (1975).

(22) R. Gale, R. E. Godfrey, S. F. Mason, R. D. Peacock, and B. Stewart, *J. Chem. Soc., Chem. Commun.*, 329 (1975).

(23) R. Gale, R. E. Godfrey, and S. F. Mason, *Chem. Phys. Lett.*, **38**, 441 (1976).

(24) R. Gale, R. E. Godfrey, and S. F. Mason, *Chem. Phys. Lett.*, **38**, 446 (1976).

(25) S. F. Mason and R. H. Seal, *J. Chem. Soc., Chem. Commun.*, 331 (1975); *Mol. Phys.*, **31**, 755 (1976).

(26) J. A. Hearson, S. F. Mason, and R. H. Seal, *J. Chem. Soc., Dalton Trans.*, 1026 (1977).

the ligand polarization model through eq 3 where $M_{0\mathrm{a}}^{\beta\cdots\omega}$

$$(M_0L_0|V|M_\mathrm{a}L_l) = \sum_L \mu_{0l}^{\alpha} M_{0\mathrm{a}}^{\beta\cdots\omega} \mathbf{G}_{\alpha,(\beta\cdots\omega)}^{L} \qquad (3)$$

is a given component of the leading multipole moment of the metal ion transition $|M_0) \rightarrow |M_\mathrm{a})$, dependent upon the particular orbitals connected, and μ_{0l}^{α} is a component of the transient electric dipole induced in a ligand atom or group by the radiation field. In eq 3 the geometric tensor $\mathbf{G}_{\alpha,(\beta\cdots\omega)}^{L}$ represents the radial and angular factors governing the Coulombic potential between the multipole component $M_{0\mathrm{a}}^{\beta\cdots\omega}$ centered on the metal ion and the dipole component μ_{0l}^{α} located in a particular ligand atom or group, the sum being taken over all ligand groups L.

The general condition for a nonzero first-order electric-dipole transition moment in the ligand polarization model requires that the multipole component $M_{0\mathrm{a}}^{\beta\cdots\omega}$ of the metal ion excitation and the dipole component μ_{0l}^{α} of the ligand groups transform under the same irreducible representation, or under the same row of a degenerate representation, in the point group to which the coordination compound belongs.[21] If the condition is satisfied the Coulombic field of the multipole component of the metal ion aligns and correlates constructively the dipoles induced in the several ligand groups, giving a nonvanishing resultant electric dipole transition moment with α polarization.

The general selection rule indicates that a static ligand-polarization mechanism is forbidden in centrosymmetric coordination compounds, since all even multipole components are gerade and the dipole components are ungerade. In these cases the ligand polarization mechanism is dependent upon the dynamic loss of inversion symmetry through the non-totally symmetric vibrational modes, as in crystal-field theory.

Where the metal ion transition is electric quadrupole allowed, the ligand polarization mechanism is effective at the equilibrium nuclear configuration in complexes belonging to the dihedral groups D_p and the C_{pv} groups, with p unrestricted, and to the groups T_d, D_{3h}, C_{3h}, and their subgroups. If the leading multipole moment of the metal ion transition is a hexadecapole component, the mechanism is allowed over a similar range of point group symmetries, with the notable exception of T_d, although permitted for the isomorphous group O. Thus the three dipole components transform under T_2 in T_d, like the three off-diagonal components of a quadrupole, whereas the dipole components are spanned by T_1 in O, as are three hexadecapole components.

Ligand-Polarization Intensities

The ligand-polarization mechanism is developed by substituting eq 3 into eq 2 and summing over the set of ligand excitations $|L_0) \rightarrow |L_l)$. The sum affords an expression containing the components of the polarizability tensor of the ligand atom or group at the frequency of the metal ion transition $\nu_{0\mathrm{a}}$. Each of these components is equated to $\bar{\alpha}(L)$, the corresponding mean polarizability of the ligand at $\nu_{0\mathrm{a}}$, and eq 2 becomes, for an electric quadrupole allowed transition of the metal ion.

$$\mu_{0\mathrm{a}}^{\alpha} = -\sum_L \sum_{\beta\gamma} \theta_{0\mathrm{a}}^{\beta\gamma} \bar{\alpha}(L) \mathbf{G}_{\alpha\beta\gamma}^{L} \qquad (4)$$

The square of the first-order electric dipole moment (eq 4) represents the dipole strength of the metal ion transition in the complex, $D_{0\mathrm{a}}$, and $(D_{0\mathrm{a}}\nu_{0\mathrm{a}})$ is related through universal constants to the corresponding oscillator strength, $f_{0\mathrm{a}}$.

Equation 4 accounts satisfactorily for the observed oscillator-strength values of the hypersensitive f-electron transitions of lanthanide complexes, which are generally electric quadrupole allowed, and of the quadrupolar d-electron excitations in tetrahedral transition-metal complexes.[21,22] The environmentally sensitive f–f transition of Nd(III) near 600 nm, for example, has an oscillator strength ($10^6 f$) of 5.6 for $\mathrm{NdF_3}$ in the $\mathrm{LaF_3}$ lattice, where the metal ion has C_2 site symmetry, compared with the value of 530 for $\mathrm{NdI_3}$ in the vapor phase, where the molecule is trigonal planar (Figure 2). These oscillator strengths and those of other hypersensitive f-electron transitions are satisfactorily reproduced by the ligand-polarization mechanism,[21] while the larger values remain anomalous in the crystal-field treatment.[10,27]

An attempt to accommodate the anomalous hypersensitive f–f intensities by adding first-order spherical harmonics Y_{1m} to the crystal field potential[27] fails conspicuously for the trigonal-planar lanthanide trihalides, as the Y_{1m} are forbidden in D_{3h}. In contrast, the ligand-polarization selection rule indicates that the xy component of the quadrupole transition moment at the metal ion in trigonal-planar complexes correlates constructively the x component of the dipole located in each ligand atom, while the $(x^2 - y^2)$-quadrupole component correspondingly aligns the y components of the ligand dipoles (Figure 4).

The ligand-polarization mechanism accounts not only for the observed d–d oscillator strengths of tetrahedral transition-metal complexes but also for the unusual decline of those strengths with increasing temperature.[22,23] In the cobalt(II) tetrahalides quadrupolar d-electron transitions take place from the $^4\mathrm{A}_2$ ground state to each of the excited states $^4\mathrm{T}_1(\mathrm{F})$, observed in the near-infrared, and $^4\mathrm{T}_1(\mathrm{P})$, found in the visible region. The $\mathrm{d}_{z^2} \rightarrow d_{xy}$ excitation with the quadrupole component θ_{xy} as its leading moment contributes to one of the three components of each of these two transitions. In a tetrahedral complex the potential of the electric quadrupole transition moment θ_{xy} of the metal ion correlates constructively the z component of the electric dipole induced in each of the four ligands (Figure 5). The other two ligand-dipole components are analogously aligned by the field of the corresponding excitation quadrupole components θ_{yz} and θ_{zx}. The resultant first-order electric-dipole moments of the three components of a given $[\mathrm{CoX_4}]^{2-}$ d-electron transition differ only in polarization direction and have the same magnitude, being dependent upon a common geometric tensor (eq 4) of radial and angular factors,

$$\sum_L \mathbf{G}_{\alpha\beta\gamma}^{L} = -15\sum_L (XYZ)_L R^{-7} = -(15/2)\sum_L (\cos\Theta \sin^2\Theta \sin 20)_L R^{-4} \qquad (5)$$

where R is the metal–ligand bond length and $(XYZ)_L$ expresses the product of the Cartesian coordinates of the ligand atom L in the tetrahedral coordinate frame

---

(27) B. R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).

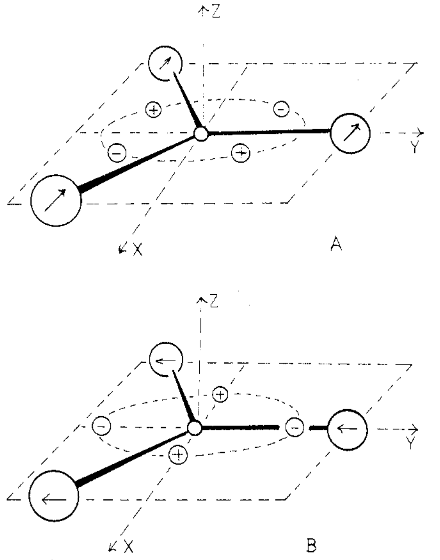


Figure 4. Coulombic correlations between a metal ion quadrupole moment, θ, and the ligand dipole moments μ in a trigonal planar lanthanide trihalide: (a) correlation of μ_x by θ_{xy}; (b) correlation of μ_y by $\theta_{x^2-y^2}$.

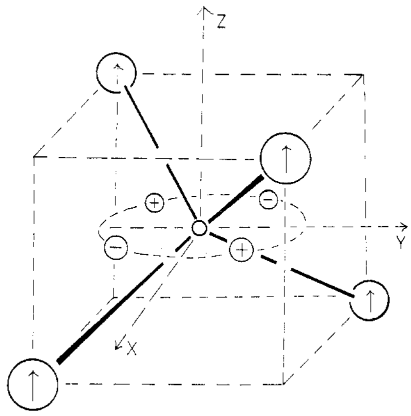


Figure 5. Coulombic correlation of the z component of the transient dipoles induced in each of the ligands by the xy component of the quadrupole moment of a metal ion d–d transition in a tetrahedral metal complex.

(Figure 5), with R, θ_L, ϕ_L representing the equivalent spherical polar coordinates.

For a given metal–ligand bond length R the geometric tensor (eq 5) has an optimum value for tetrahedral symmetry. All departures of the angles θ_L and ϕ_L from the tetrahedral values reduce the magnitude of the tensor, which goes to zero, for example, in the limit of square-planar symmetry. The unusual decrease in the intensity of quadrupolar d–d transitions in tetrahedral complexes with an increase in temperature is thus a consequence of the progressive population of the higher levels of the tetrahedral bond stretching, $\nu_1(a_1)$ and $\nu_3(t_2)$, and angle bending, $\nu_2(e)$ and $\nu_4(t_2)$, vibrational modes as the temperature is raised.[23] The anharmonicity of the stretching modes results in a progressively longer mean metal–ligand bond length with increasing temperature, which entails additionally progressively larger angular excursions of the ligands from their tetrahedral equilibrium nuclear configuration through the bending modes. The loss of intensity with increasing temperature is accounted for by a calculation of the mean-square amplitudes of vibration in the electronic ground state of the complex as a function of temperature for the four tetrahedral modes.[23]

The form of eq 4 indicates that a relationship observed between the first-order electric dipole moments of two d–d transitions in a given tetrahedral complex reflects a corresponding relationship between the allowed zero-order quadrupole moments of those transitions. The magnetically induced CD spectra of the d–d transitions from the $^4A_2$ ground state to the $^4T_1(F)$ and $^4T_1(P)$ excited state of the cobalt(II) tetrahalides afford the reduced dipole moment ratio, q,

$$q = \langle t_2 \| \mu \| t_2 \rangle / \langle e \| \mu \| t_2 \rangle \quad (6)$$

where t_2 and e refer to the d-orbital subsets in T_d complexes. The crystal-field model requires that $q = +2$, and MO theory indicates that the ratio q has a positive value.[14] Measurements of the MCD spectra of the cobalt(II) tetrahalides show[16,24] that the ratio is negative with a value close to that expected, according to the ligand-polarization model, from the corresponding ratio of the reduced zero-order quadrupole moments:[24]

$$\langle t_2 \| \Theta \| t_2 \rangle / \langle e \| \Theta \| t_2 \rangle = -(3/2)^{1/2} \quad (7)$$

Ligand-Polarization Optical Activity

The most widely investigated chiral metal complexes are the diammine chelates of cobalt(III), containing the octahedral $[\mathrm{Co^{III}N_6}]$ chromophore. The principal d–d transition of interest for the optical activity of these chiral complexes is the $^1A_1 \rightarrow {}^1T_1$ octahedral excitation near 465 nm, made up of the three single-orbital promotions, $d_{xy} \rightarrow d_{x^2-y^2}$, and the analogues obtained by the cyclic permutation of the electronic coordinates.

The leading moments of the transition, $d_{xy} \rightarrow d_{x^2-y^2}$, are the z component of a magnetic dipole and the $[xy(x^2 - y^2)]$ component of an electric hexadecapole. The potential of the electric hexadecapole component, $H_{xy(x^2-y^2)}$, constructively correlates the z component of the induced electric dipole moment in each ligand group which does not lie in an octahedral symmetry plane of the $[\mathrm{Co^{III}N_6}]$ chromophore (Figure 6). The resultant first-order electric-dipole transition moment is collinear with the zero-order magnetic dipole moment of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, and the scalar product of these two moments affords the z component of the rotational strength, R^z_{0a}. The other two components, R^x_{0a} and R^y_{0a}, are obtained analogously, and the sum gives the net rotational strength, $R(T_1)$, of the transition $^1A_1 \rightarrow {}^1T_1$ in O symmetry.

The components are oppositely signed and the sum vanishes if the distance between the metal ion and the ligand groups is large compared to the extension of the hexadecapole moment, i.e., if the point-multipole approximation is valid. The radial extension of the hexadecapole moment lies in the range from 0.96 to 0.68 Å for neutral and tripositively charged cobalt, respectively, and neither value is negligible in relation to the Co–N bond length (2.0 Å) or the metal–carbon distance (3.0 Å) in $[\mathrm{Co(en)_3}]^{3+}$.

With an allowance for the finite radial–radial extension of the 2^4-pole moments, the net $R(T_1)$ is nonvanishing. The dominant component has its transitional charge distribution in the mean plane of the chelate ring considered, e.g., the $d_{xy} \rightarrow d_{x^2-y^2}$ component

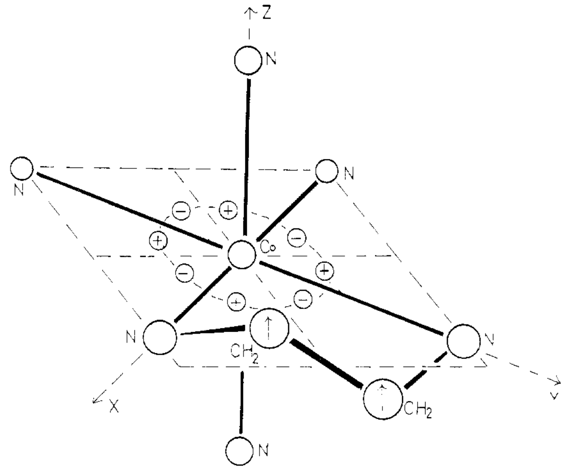


Figure 6. Correlation between the electric hexadecapole moment of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition of the $[\mathrm{Co^{III}N_6}]$ chromophore and the transient electric dipole induced in each ligand group of a 1,2-diamine chelate ring puckered in the δ conformation. The d–d transition depicted corresponds to a clockwise rotation of electronic charge viewed from the $+Z$ direction, producing a magnetic dipole antiparallel to the correlated electric dipoles of the ligand groups, and thence a negative rotational strength.

for a ring spanning the X and Y axes (Figure 6). The sign of the net rotational strength, $R(\mathrm{T_1})$, due to a 1,2-diammine chelate ring is governed by the ring chirality, being positive and negative for the λ and the δ conformations, respectively, and $R(\mathrm{T_1})$ is additive over the number of chelate rings with the same chirality. Thus a hypothetical complex with all octahedral edges of the $[\mathrm{Co^{III}N_6}]$ chromophore spanned by equivalent rings with a common chirality, having true O symmetry, is expected to display a nonvanishing first-order net rotational strength, $R(\mathrm{T_1})$, according to the ligand-polarization model,[25] in contrast to the corresponding crystal-field treatments.[17-20]

In the dihedral tris(diammine) complexes of cobalt(III) the upper state of the octahedral $^1\mathrm{A_1} \rightarrow {}^1\mathrm{T_1}$ d-electron transition is broken down into components with $^1\mathrm{A_2}$ and $^1\mathrm{E}$ symmetry in D_3. The sum of the rotational strengths of the two components, the net resultant $R(\mathrm{T_1})$, has long been known for the prototype case of Λ-(+)-$[\mathrm{Co(en)_3}]^{3+}$ from the CD spectrum of the randomly oriented complex ion in solution. The rotational strengths of the individual components, $R(\mathrm{A_2})$ and $R(\mathrm{E})$, have been determined recently from ortho-axial single-crystal CD measurements,[28] following earlier axial single-crystal CD studies, which afford $R(\mathrm{E})$ alone (Figure 3).

The rotational strengths $R(\mathrm{A_2})$ and $R(\mathrm{E})$, and their more precisely measured sum, $R(\mathrm{T_1})$, of Λ-(+)-$[\mathrm{Co(en)_3}]^{3+}$ are accounted for quantitatively, to within limits comparable to the experimental uncertainties, by extending the ligand-polarization treatment to second order.[25] While the crystal-field and the ligand-polarization model are mutually exclusive to first order, the two treatments may be employed in conjunction to higher orders. The particular second-order treatment adopted considers the mixing of different electronic transitions of the $[\mathrm{Co^{III}N_6}]$ chromophore through the Coulombic field of the induced electric dipoles in the individual ligand groups.[25,26]

The vacuum-UV absorption and CD spectrum of Λ-(+)-$[\mathrm{Co(en)_3}]^{3+}$, including the high wavenumber tail of the single-crystal CD spectrum, characterize two strong electric-dipole transitions in the UV region, the first to a $^1\mathrm{E}$ state and the second, at higher energy, to a $^1\mathrm{A_2}$ state (Figure 3). These two UV transitions provide the main source from which electric-dipole strength is borrowed within the $[\mathrm{Co^{III}N_6}]$ chromophore by the d–d excitations in the visible region. In the second-order model, the induced electric dipoles in the individual ligand groups, themselves aligned by the electric hexadecapole moment of a given D_3 component of the $^1\mathrm{A_1} \rightarrow {}^1\mathrm{T_1}$ d–d transition in the visible region, Coulombically correlate in turn the corresponding D_3 component of the high-intensity UV transition in the $[\mathrm{Co^{III}N_6}]$ chromophore.

Computations based on the second-order model account satisfactorily for the d–d rotational strengths, and the dipole strength enhancement relative to $[\mathrm{Co(NH_3)_6}]^{3+}$, of the tris(diammine)cobalt(III) complexes for which an X-ray crystal structure is available, covering some ten cases in all.[25]

Conclusion

The ligand-polarization treatment and crystal-field theory are complementary not only in methodology, within the independent systems scheme, but also in their principal application to transition probabilities and to transition energies, respectively, in the electronic spectroscopy of metal complexes. The ligand polarization approach has not a great deal to offer on the question of transition frequencies. The model specifies, however, that the ligand transitions in the far-ultraviolet region and the d-electron or f-electron transitions of the metal ion in the visible or infrared region repel one another on the frequency scale. Thus the d–d or f–f transitions are subject to a general ligand polarization red shift, proportional to the oscillator strength of the metal ion transition, which is superimposed upon the basic crystal-field transition energy.[21]

The neglect of electron exchange between the ligands and the metal ions is an evident limitation of both the crystal-field and the ligand-polarization model. In calculations of the energies of d–d and f–f transitions, weak covalency in a largely ionic metal–ligand bond is accommodated by the angular overlap model.[29] A similar development of the ligand polarization treatment, employing antisymmetrized rather than simple product metal–ligand functions, shows that the main terms for the corresponding transition probabilities considered here (eq 2) are augmented by contributions, proportional to the overlap, from metal–ligand charge-transfer transition moments.

The relative importance of the charge-transfer and the ligand-polarization contributions to the intensities of the hypersensitive f–f transitions has been investigated recently[30] by means of correlations, across the lanthanide series, of the hypersensitive oscillator strengths measured for each Ln(III) ion as a guest in the $\mathrm{Y_2O_3}$ lattice with, firstly, the corresponding quadrupole transition moments and, secondly, the corresponding charge-transfer transition energies. The oscillator strengths correlate well with the quadrupole

(28) H. P. Jensen and F. Galsbøl, *Inorg. Chem.*, **16**, 1294 (1977).

(29) C. E. Schäffer and C. K. Jorgensen, *Mol. Phys.*, **9**, 401 (1965); C. E. Schäffer, *Struct. Bonding*, **5**, 68 (1968); 14, 69 (1973).

(30) R. D. Peacock, *Mol. Phys.*, **33**, 1239 (1977).

transition moments but show no systematic relation to the charge-transfer energies, suggesting that the ligand polarization contributions to the hypersensitive intensities are predominant. Charge-transfer bands are prominent in the spectra of lanthanide and transition-metal complexes, and the relative inefficacy of the charge-transfer contributions in the f–f absorption process and their putative role for d–d transition probabilities are problems for future investigation.

It is a pleasure to thank all of my co-workers, cited in references 21-26, on the ligand polarization projects. Our investigations are supported by the U.K. Science Research Council.

Organic Syntheses via the Polybromo Ketone–Iron Carbonyl Reaction

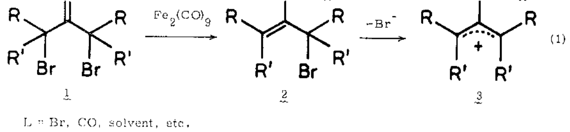
RYOJI NOYORI

Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan

Received May 24, 1978

The chemistry of transition-metal carbonyls has a long history dating from the discovery by Mond in 1890 of the first metal carbonyls. These complexes have been used widely as both synthetic reagents in laboratories and catalysts of certain industrial processes, and development of significant synthetic methods via such complexes is still continuing.[1] This Account describes a new synthetic methodology using iron carbonyls which has been developed in our laboratories. Here, iron carbonyls, perhaps the most economical metal carbonyls, serve as efficient stoichiometric reducing agents.[2] These reagents are essentially neutral, and a variety of functional groups including carbonyl, ester, amide, cyano, ether linkage, etc., are tolerated under the reaction conditions.

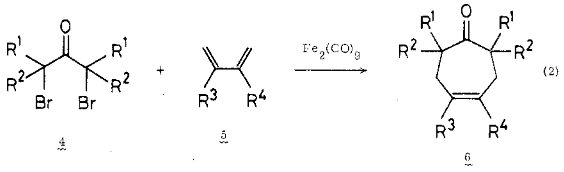
Because there exist no general ways for preparing carbocyclic frameworks by use of bifunctional three-carbon building blocks, this work was started in hopes of generating a reactive three-carbon unit that is capable of undergoing cycloaddition across various unsaturated compounds. First, we employed a system combining α,α'-dibromo ketones and iron carbonyls, and this choice worked well.[3-5] Both mononuclear $Fe(CO)_5$ and dinuclear $Fe_2(CO)_9$ may be used, but the latter complex has stronger reducing ability. The reactive intermediates generated were found to be the enolate 2 and the oxyallyl species 3 as shown in eq 1.



L = Br, CO, solvent, etc.

Evidence for the generation of the cationic 2-oxyallyl species 3 from 1 as the product-determining intermediate was provided by nucleophilic trapping and several skeletal rearrangements.[3,4] Certain oxyallyl species suffer deprotonation, particularly in basic media such as THF or DMF, yielding α,β-unsaturated ketones. In a nonbasic or weakly nucleophilic environment, the allylic cation 3 reacts with a variety of carbon nucleophiles. It is worthwhile to point out that the presence of the central oxygen group in 3 allows the allyl cation to act as both a uni- and a bifunctional electrophile.

The 3 + 4 → 7 Cyclocoupling Reaction between Polybromo Ketones and 1,3-Dienes. Trapping of the oxyallyliron(II) species with 1,3-dienes produces seven-membered ketones directly. Thus, the reaction of the dibromo ketone 4 and an open-chain 1,3-diene, 5, with the aid of $Fe_2(CO)_9$ in benzene at 60–70 °C gave the corresponding 4-cycloheptenone 6 in moderate to high yield (eq 2).[7,8] Both secondary (R^1 = alkyl; R^2 =



R^1 = alkyl; R^2–R^4 = alkyl or H

Ryoji Noyori was born in Japan in 1938. He joined the faculty at Kyoto University as an instructor, after obtaining his bachelor's and master's degrees there, and continued on to the Ph.D. at Kyoto with Hitosi Nozaki. In 1968, he moved to Nagoya University, where he is a Professor. He spent a postdoctoral year at Harvard University with E. J. Corey. His research interests are in the development of new methodologies in organic chemistry and their application to organic synthesis.

(1) Reviews: "Organic Synthesis via Metal Carbonyl", Vol. 1 and 2, I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968 and 1977; R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974; J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes", Springer-Verlag, Berlin and New York, 1975; J. Falbe, "Carbon Monoxide in Organic Synthesis", Springer-Verlag, Berlin and New York, 1970; M. F. Semmelhack, *Org. React.*, **19**, 115 (1972); R. Baker, *Chem. Rev.*, **73**, 487 (1973); C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967; M. Ryang, *Organometal. Chem. Rev., Sect. A*, **5**, 67 (1970); M. Ryang and M. Tsutsumi, *Synthesis*, 55 (1971); R. Noyori, "Transition Metal Organometallics in Organic Synthesis", Vol. 1, H. Alper, Ed., Academic Press, New York, N.Y., 1976, Chapter 2.

(2) Recent accounts on synthetic utility of iron carbonyl complexes: R. Pettit, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **17**, 227 (1973); M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974); J. P. Collman, *ibid.*, **8**, 342 (1975); E. Weisberger and P. Laszlo, *ibid.*, **9**, 209 (1976); A. J. Birch and I. D. Jenkins, "Transition Metal Organometallics in Organic Synthesis", Vol. 1, H. Alper, Ed., Academic Press, New York, N.Y., 1976, Chapter 1.

(3) R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Am. Chem. Soc.*, **94**, 7202 (1972).

(4) R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi, and N. Sonoda, *J. Am. Chem. Soc.*, **100**, 1759 (1978).

(5) Some of the reactions described herein have been achieved by dehalogenation agents other than iron carbonyls.[4] Particularly use of Zn/Cu couple and NaI has been extensively studied by Cookson and Hoffmann.[6]

(6) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 819 (1973).

(7) R. Noyori, S. Makino, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 1272 (1971).

(8) H. Takaya, S. Makino, Y. Hayakawa, and R. Noyori, *J. Am. Chem. Soc.*, **100**, 1765 (1978).

0001-4842/79/0112-0061$01.00/0