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A Central Field Interpretation of the Absorption and M.C.D. Spectroscopic Parameters in Arylcyanamocobaltate Complexes

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The electronic (absorption and MCD) spectra of a series of substituted tetrahedral tetrakis*(phenylcyanamo)cobaltate(II) complexes are interpreted to show an interrelationship between the 'crystal field' parameters, DQ, B and λ, which are usually taken to be independently variable. This relationship, satisfied adequately by the present data, is derived from a ligand field adaptation of crystal field formulae obtained* via *an identity transform of conventional LCAO radial wavefunctions which yields an approximate central field radial function dependent on an effective central charge, Z_{eff} and effective quantum number, n_{eff}.*

Since much chemistry has been rationalized by considering trends in DQ, B and λ as independent, the possibility of interrelationship is chemically non-trivial. Although the empirical scope of the approximations needed is not defined by the presently available data, they support the model sufficiently to warrant its careful evaluation.

Introduction

The majority of semiempirical theories of metal complexes focus on LCAO–MO methods. In most cases this allows a poorly integrated treatment of *interelectronic repulsion effects* which are never negligible in experimental spectroscopy. Interelectronic repulsion theory remains firmly rooted *in central field methods.* It seems, therefore, valuable to explore the consequences of a transformation of LCAO–MO wavefunctions to a central field viewpoint. This transformation will lead to a unified treatment of the parameters obtained from experimental molecular spectroscopy, especially such sensitive tools as magnetic circular dichroism (MCD). This amounts to a return to ligand field theories which are usually regarded as 'too mature' for important extensions. However, careful attention to the significance of regarding the central field wavefunctions as transforms of LCAO–MO wavefunctions may support a much more optimistic reading.

At present it is extremely difficult to find suitable sequences of complexes for full experimental tests of the ideas that emerge from renewed effort on central field models. But the tests available – including the series of complexes described here – hint at very interesting results [1, 2]. In particular, the ligand field splitting parameter DQ (and DS, DT, DM or DN in lower symmetry), the interelectronic repulsion parameters, B and C, or Racah, the spin orbit coupling constant, λ, and the metal–ligand difference in optical electronegativity, $\Delta\chi_{opt}$, can be related to each other in terms of two parameters of the central field model. These two are Z_{eff}, the effective orbital charge and n_{eff} the effective orbital principle quantum number [3].

Since DQ trends (spectrochemical series), B, C trends (nephelauxetic series), and $\Delta\chi_{opt}$ trends are usually used *separately* and *independently* to account for many chemical phenomena (either qualitatively or semi-quantitatively), it is chemically non-trivial to explore what relations may tend to exist among them. This paper is intended to provide a sketch of such relationships. The experimental range (which is hard to extend) is so far small enough that there is risk in accepting the approximations required. However, the reward of interconnection is large enough to render the risk, at least tentatively, quite acceptable.

Experimental

The substituted phenylcyanamide ligands were prepared from the substituted anilines via formation of the thiourea and subsequent desulphurization with lead acetate [4]. The desulphurization step was performed satisfactorily in each case at 50 to 55 °C preventing much of the decomposition found using boiling aqueous NaOH.

Silver and thallous salts of the ligand were prepared by precipitation by mixing equimolar amounts of 50% aqueous acetone solutions of silver nitrate or thallous acetate with the neutralized cyanamide in the same solvent. Precipitation was forced to completion in the case of weakly acidic cyanamides by catalytic amounts of aqueous ammonia.

The tetrasubstituted cobaltate(II) anionic complexes were prepared by metathesis at room temperature from tetraphenylarsonium tetrachlorocobaltate(II) and four equivalents of the silver or thallous derivatives of each substituted phenylcyanamide, in dry degassed dichloromethane. In general, the thallous derivatives yielded purer products than the silver salts. In each case, the ligand salt was insoluble but the complex was soluble in dichloromethane and the degree of chloride replacement was monitored by the weight of the undissolved material.

The following ligands (melting point) and complexes (analytical results) were prepared:

Phenylcyanamide (48°)

Tetraphenylarsonium tetrakis(phenylcyanamo)cobaltate(II) (Calc.: C, 70.5; H, 4.6; N, 8.6. Fnd: C, 69.4; H, 4.8; N, 8.5).

3,5-dichlorophenylcyanamide (160–2°)

Tetraphenylarsonium tetrakis-(3,5 dichlorophenylcyanamo)cobaltate(II) (Calc.: C, 58.1; H, 3.3; N, 7.1. Fnd: C, 57.9; H, 3.0; N, 7.1).

2,4-difluorophenylcyanamide (94–5°)

Tetraphenylarsonium tetrakis-(2,4-difluorophenylcyanamo)cobaltate(II) (Calc.: C, 63.4; H, 3.6; N, 7.8. Fnd: C, 62.6; H, 3.7; N, 7.4).

2,4,6-trichlorophenylcyanamide

Tetraphenylarsonium tetrakis(2,4,6-trichlorophenylcyanamo)cobaltate(II) (Calc.: C, 63.8; H, 4.1; N, 10.9; Cl, 41.7. Fnd: C, 63.7; H, 4.0; N, 10.9; Cl, 41.5).

2-chlorophenylcyanamide

Tetraphenylarsonium tetrakis(2-chlorophenylcyanamo)cobaltate(II) (Calc.: C, 43.9; H, 4.0; N, 4.6. Fnd: C, 43.9; H, 4.1; N, 11.6).

2,4,6-trimethylphenylcyanamide (57–8°)

Tetraphenylarsonium tetrakis(2,4,6-trimethylphenylcyanamo)cobaltate(II) was prepared for spectroscopy in solution but was unstable as a solid. The initial reaction yielded the expected amount of AgCl (Calc.: 0.568 g; Fnd: 0.56 g).

Spectra

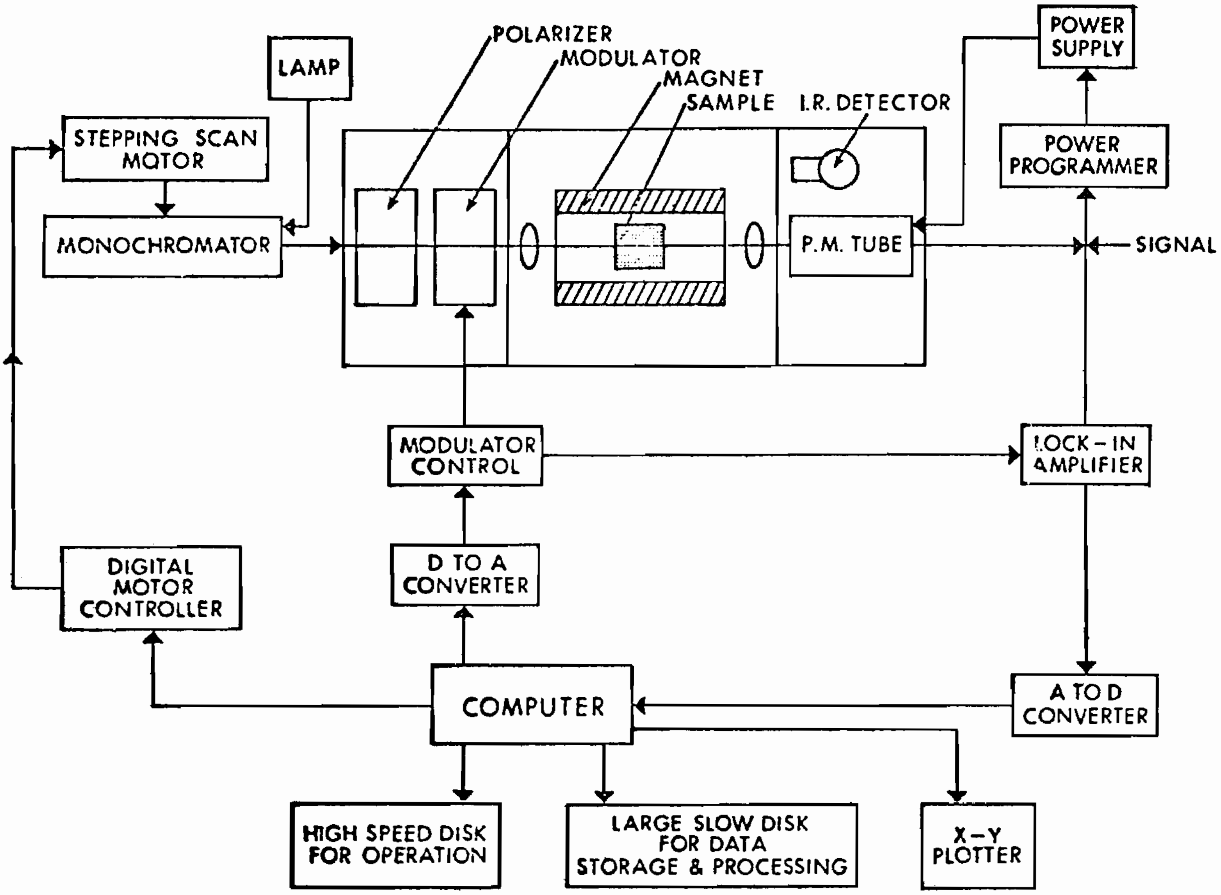
Absorption spectra were obtained on a Cary 14 Spectrophotometer. The instrument used to measure the magnetic circular dichroism spectra was constructed from components. The basis design is similar to recently described systems [5]. Monochromated light from a 150 watt Xenon arc lamp is polarized in a 20 mm Lambrecht calcite polarized at 45° to a Morvue photoelastic modulator. The polarized beam passes through the sample in a 2.5 cm bore of a 4.5 T Oxford horizontal superconducting magnet and is detected using an R.C.A. gallium arsenide photomultiplier. The output of the phototube is maintained at 1.2 volts using a locally constructed power supply control attached to a Kepco Model IX power supply. The C.D. signal is amplified in a Princeton Applied Research Model 124 amplifier locked to the photoelastic modulator frequency. The wavelength and corresponding modulator amplitude are controlled using a NOVA 1220 computer and the spectroscopic amplitude data can be digitized and stored directly by the system control program. The instrument was calibratred for wavelength with rare earth filters to ±0.5 nm. The circular dichroism response was calibrated with standard solution of (α) + camphorsulphonic acid and the M.C.D. response and field strength determined with standard solutions of cobalt sulphate [6]. The sign of the MCD spectra reported is referred to a negative signal at 510 nm for the aqueous cobalt sulphate solution.

Data Processing

The absorption data and those MCD data not directly digitized in the dedicated computer were digitized from chart recorder outputs by the digitizing service of the University of Alberta (Fig. 1). In all cases the energy scale was made linear in energy and the baselines subtracted using the programme NLDIGIT [7]. Spectra characterized by 400 points between 12000 and 20000 cm^{-1} were then plotted using CALXY [7] on a Calcomp 925 plotter. Moments under the absorption and MCD bands in this region were computed from the same spectral data [7] using the conventions of Stephens *et al.* [8].

Results

The spectroscopic data are given in Table I. Band positions were taken as either peaks or distinct shoulders in both the absorption and MCD spectra. Three typical spectra are given in Figs. 2–4, the spectra of the remaining three complexes are similar. In each case the MCD bands are essentially C terms [9], thus the absorption and MCD band heads should



MONITOR	i) Calculates and sets new position of monochromator and modulator control voltage. ii) Reads data at fixed scan position. iii) Calculates data mean and standard deviation. iv) Uses standard deviation to control scan rate in i). v) Outputs data file including comment record and calibration points.
MERGE	i) Subtracts baseline file from data file correcting for both baseline offset and rotation using two locking energies. ii) Permits data smoothing by linear interpolatiou. iii) Permits resetting of calibration points and number of data points in final data file.
PLOT	Plots either raw or merged data files together with axes and calibration points on energy axes.
MCDFIT	Permits a coefficient fitting of Gaussian or Lorentzian bands of chosen energy and width to data files from MERGE.
LFFIT	Permits an intermediate ligand field model fit of band centres from MCDFIT in all d^n configurations for all geometries derived from O_h^* symmetry.

Fig. 1. Schematic of data acquisition and processing.

TABLE I. Spectroscopic Data.

	Compound	Band Position (kK)	E	$[\theta]_M$
1.	$[Co(NCN\phi)_4]^{2-}$	7.55	220	–
		15.38	880	–0.74
		15.57	825	–0.65
		16.25	980	–0.21
		17.24	555	+0.15
		15.58	535	+0.20

(continued overleaf)

TABLE I. *(continued)*

	17.99	450	+0.12
2. $[\mathrm{Co(NCN\phi 3,5Cl_2)_4}]^{2-}$	7.55	225	–
	15.52	1200	–1.64
	15.64	1230	–0.30
	16.32	1250	–0.30
	16.80	880	+0.28
	17.24	770	+0.72
	17.69	550	+0.48
3. $[\mathrm{Co(NCN\phi 2,4F_2)_4}]^{2-}$	7.33	930	–
	15.50	1690	–2.04
	15.98	1690	–1.14
	16.18	1730	–0.62
	16.67	1150	+0.43
	17.19	1000	+0.99
	17.66	630	+0.54
4. $[\mathrm{Co(NCN2,4,6\text{-}Cl_3)_4}]^{2-}$	7.27	160	–
	15.39	970	–1.35
	15.92	980	–0.79
	16.60	680	+0.36
	17.09	570	+0.70
	17.62	325	+0.32
5. $[\mathrm{Co(NCN\phi 2Cl)_4}]^{2-}$	6.80	200	–
	15.18	1180	–1.88
	15.44	1200	–1.61
	15.66	1185	–1.23
	16.74	720	+0.73
	16.98	645	+0.77
	17.52	360	+0.39
6. $[\mathrm{Co(NCN\phi 2,4,6\text{-}Me_3)_4}]^{2-}$	6.45	130	–
	15.60	480	–0.60
	16.44	640	–0.36
	16.72	570	–0.30
	17.72	480	+0.08
	18.58	315	+0.05

TABLE II. Spectroscopic Parameters.

Compound	B (K)	DQ (kK)	'B' $\times 10^3$	D	'B/D' $\times 10^3$	$[(\text{'B/D'})(\mathrm{DQ}/4)]^{1/4}$
$[\mathrm{Co(NCN\phi)_4}]^{2-}$	622	12.32	1.20	1.73	0.692	1.21
$[\mathrm{Co(NCN\phi 3,5Cl_3)_4}]^{2-}$	667	12.10	1.75	1.79	0.979	1.31
$[\mathrm{Co(NCN\phi 2,4F_2)_4}]^{2-}$	671	11.80	2.20	2.13	1.035	1.32
$[\mathrm{Co(NCN\phi 2,4,6Cl_3)_4}]^{2-}$	672	11.65	1.35	1.33	1.018	1.31
$[\mathrm{Co(NCN\phi 2Cl)_4}]^{2-}$	701	10.80	2.61	2.10	1.242	1.35
$[\mathrm{Co(NCN\phi 2,4,6Me_3)_4}]^{2-}$	722	10.10	1.58	1.14	1.388	1.37

coincide for each transition. In some cases such as the tetrakis(2-chlorophenylcyanamo)-cobaltate(II) complex the visible band (Fig. 3) is very compact and the transitions are not separated while in other cases such as the tetrakis(phenylcyanamo)cobaltate(II) ion the transitions are more clearly resolved.

The ligand field parameters derived from these spectra are given in Table II. These data were obtained using the peak of the broad infra-red band and the lowest energy strong peak of the visible band. This latter peak was chosen because the higher energy transitions tend to be strongly mixed with doublet spin [10] states (*vide infra*). The moments under the entire band in both the absorption and M.C.D. are also given in Table II. Since no A term character is observable, the MCD moment is quoted as the resi-

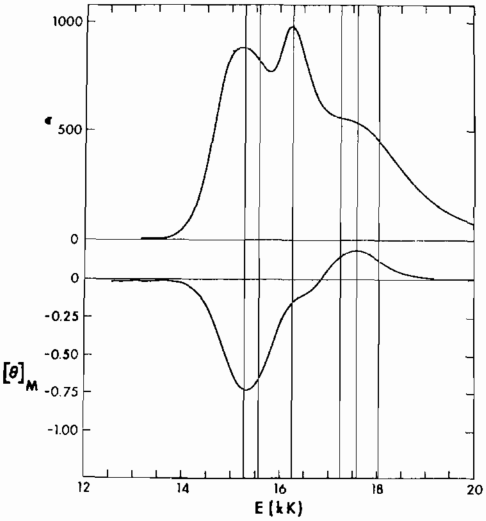


Fig. 2. The absorption and M.C.D. spectra of the visible band of the $[Co(NCN\phi)_4]^{2-}$ ion.

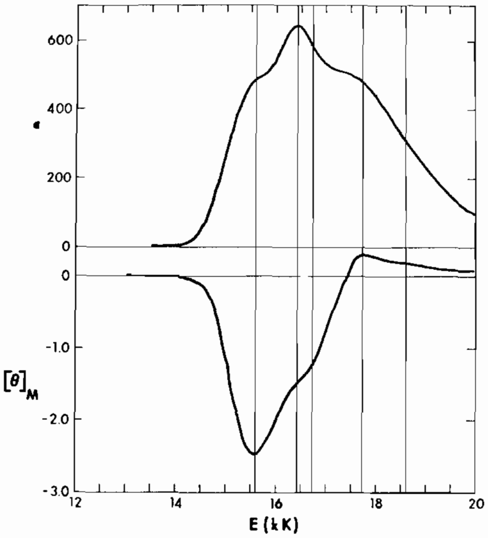


Fig. 3. The absorption and M.C.D. spectra of the $[Co(NCN\phi\text{-}2,4,6(CH_3)_3)_4]^{2-}$ ion.

dual 'B' term including integration across all negative and positive contributions [9, 11]. The ϵ and $[\theta]_M$ data quoted for the tetrakis(2,4,6-trimethylphenylcyanamo)cobaltate(II) complex are approximate since the concentration was estimated from the amounts of starting materials. The precision of the relative 'B/D' ratio however is constant throughout the series.

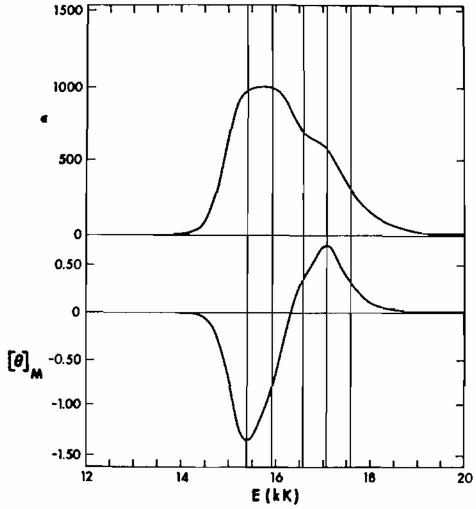


Fig. 4. The absorption and M.C.D. spectra of the $[Co(NCN\phi\text{-}(2,4,6Cl)_3)_4]^{2-}$ ion.

Derivation of Spectroscopic Parameters

Ligand field parameters

A full ligand field calculation of tetrahedral cobaltate(II) species, including doublet free ion terms, shows that at DQ/B = 16.5 [12] ligand field terms from both the ^4P and ^2G free ion terms are nearly degenerate [10]. The assignment of the visible band in the present series of substituted cyanamide complexes is expected to be very similar to that of $CoCl_4^{2-}$ [9]. The reduced resolution of the observed band correlates with the expected reduction in the spin orbit coupling constant since the donor atom is nitrogen rather than chlorine [3]. Even the most resolved spectrum is inadequate for a detailed assignment and estimate of λ. Thus a quantitative estimate of λ is obtained instead from a comparison of MCD and absorption intensities of the visible band.

Moments analysis of the visible band. The ratio of the net integrated area of the M.C.D. band to the area of the absorption can be interpreted as a function of the spin orbit coupling constant of the complex [11]. This net or residual C term, which does not vanish on integration, can be expressed as;

$$C_{11} = \frac{3}{\lambda\Gamma^{1/2}} \sum_{\Gamma_1\to\Gamma_2} c\langle\Gamma_1\gamma_1|\mu|\Gamma_1\gamma_1\rangle[\langle\Gamma_1\gamma_1|m_+|\Gamma_2\gamma_2|\rangle \langle\Gamma_2\gamma_2|m_-|\Gamma_3\gamma_3\rangle\langle\Gamma_3\gamma_3|m_+|\Gamma_2\gamma_2\rangle\langle\Gamma_2\gamma_2|m_-|\Gamma_1\gamma_1\rangle] \quad (1)$$

in which μ and $m_\pm$ are the magnetic and electric dipole operators and the perturbed ground state wave function is:

$$|\Gamma_G\gamma_G\rangle = \left[\frac{1}{\sqrt{2}}|\Gamma_1\gamma_1\rangle + \frac{c}{\sqrt{2}}|\Gamma_3\gamma_3\rangle\right]\frac{1}{\sqrt{1+c^2}} \quad (2)$$

In the present case the $^4A_{2g}(F)$ ground term is perturbed by spin orbit mixing with the $^4T_{2g}(F)$ term and the mixing coefficient is [8]

$$c \propto \frac{4\lambda}{DQ} \tag{3}$$

On expansion in an intermediate field model, the dipole matrix elements of (1) vanish if only states of $(d)^n$ configurations are considered. Following the treatment of octahedral nickel complexes [11] the rotation C_{II} is allowed for transitions preserving spin multiplicity through perturbation of the excited state wave function $|\Gamma_2\gamma_2\rangle$ by states of odd parity from configurations $(d)^{n-1}(p)^1$. This perturbation arises predominantly through odd spherical harmonic contributions to the ligand field Hamiltonian which in turn are permitted either directly if the point group of the complex has no centre of inversion or indirectly through antisymmetric vibrations if an inversion centre exists.

The tetrahedral cobaltates of this work have no centre of inversion and it is not necessary to invoke a vibrational mechanism for introducing states of odd parity. Apart from this difference and a systematic substitution of the representation T_2 in T_d for T_{1u} in O_h, the treatment of the orbital dipole matrix elements in an intermediate field expansion of (1) is identical to that derived for octahedral nickel(II) complexes by Harding *et al.* [11].

For transitions to states of different spin multiplicity, the predominant perturbation permitting the dipole elements of (1) is spin orbit coupling. However, the exact nature of the dipole perturbation is unimportant in defining relative C term intensities within a manifold. Moreover, if as in the present case, states from two different orbital manifolds overlap, the C_{II} contributions are additive. In a series of similar compounds if the perturbation mechanisms remain essentially constant the residual C_{II} magnitude will depend essentially on the mixing coefficient c defined in (2) and (3); a similar expansion of B_{II} terms yields the same conclusion. Therefore the observed spectroscopic moment is derived from a sum of the two residual moment contributions which is usually denoted 'B',

$$\frac{\text{'B'}}{D} \propto \frac{(B_{II} + C_{II}/kT)}{D_o} \cdot \frac{4\lambda}{DQ} \tag{4}$$

or;

$$\lambda \propto \frac{\text{'B'}\cdot DQ}{4D} \tag{5}$$

at a fixed temperature. This result implied that for a series of related complexes the relationship of λ to the zeroth moment of the MCD spectrum is independent of the relative magnitudes of B_{II} and C_{II}/kT.

Discussion

Methodology of Correlation of Spectroscopic Parameters

The complexes were designed to minimize nonelectronic changes in the chemical conditions. The strategy included the following elements.

(i) The ligands were designed to reduce interference from geometric distortions.

(ii) Since the electronic effects observed at the metal ion are initiated many atoms away on the phenyl ring, changes in steric effects between ligands are minimized.

(iii) The vibration frequencies of the metal-ligand bonds were expected to remain essentially constant since the relative changes in ligand mass are small and occur well removed from the ligand donor atom.

(iv) Changing substituents at long range should not significantly affect the metal–ligand σ bond strength, nor consequently the bond length. As we shall see below, the point may be expressed as saying that the effective orbital quantum number at the metal centre is constant.

The primary anticipated effect of changing a substituent on the phenyl ring of the ligand is a change in the π electron properties of the ring which may be transmitted through conjugation with the π system of the donor group to the dπ* orbitals of the metal ion. Since the covalent character of the dσ and dπ orbitals is low, the d–d and low-lying charge transfer spectra can be analysed using Koopmans' Theorem. The observed value of a typical spectroscopic parameter P can then be factored as a degeneracy weighted average of one-electron orbital parameter involved in the transition [3]

$$P_{\Gamma\Gamma'} = \frac{mP_\Gamma + nP_{\Gamma'}}{(m+n)]} \tag{6}$$

in which Γ is the representation of the more stable orbital. If the perturbation reaches a finite limiting value at the free ion limit,

$$\lim P_{\Gamma\Gamma'} = P_J \tag{7}$$

$$\Delta P_{\Gamma\Gamma'} \rightarrow 0$$

in which $\Delta P_{\Gamma\Gamma'} = \pm(mP_\Gamma - nP_{\Gamma'})$ and P_J is the limiting parameter value in the J state of the free ion.

It is often possible to measure the values of two or more parameters of the general type $P_{\Gamma\Gamma'}$ for any given orbital, *e.g.*, $DQ_{\Gamma\Gamma}$, $B_{\Gamma\Gamma}$ and χ_Γ. Using adequately defined perturbation operators and a complete orbital basis set it is formally possible to calculate the magnitude of each parameter using one complete wave function for each orbital. To be useful such calculations should be in the simplest possible form and defined on the ***minimum necessary*** set of parameters. Crystal field theory is a convenient initial model for these calculations but its inadequacy in defining magnitudes of the fitting parameters $P_{\Gamma\Gamma'}$ is well known [13]. If a crystal field value of DQ is calculated from the expression

$$DQ \propto \frac{1}{6}\,\frac{Ze^2\bar{r}^4}{a^5} \qquad (8)$$

by expanding $\bar{r}^4$ with the 3d metal ion radial wave functions, the result is one order of magnitude too small. However, this expansion and those representing the other fitting parameters can be adapted to a ligand field model. The exponents of the radial wave functions used to evaluate each $\bar{r}^n$ can be varied to account for a changing effective central charge with changing ligands.

This adaptation requires care for parameters like DQ, DT and DS which must simultaneously involve the charges Z_L and Z_M of the ligand donor atom and metal ion respectively. In classical crystal field theory the magnitudes of these parameters are defined from the perturbation Hamiltonian and central charge on the d orbitals of the free ion alone. In a ligand field model the same Hamiltonian can operate on more complete wave functions which are linear combinations of metal ion and ligand group orbitals.

This many-centre theory can be transformed into an equivalent single-centre approximation which formally resembles the crystal field formulation but retains the more complete L.C.A.O. ligand field description. If the L.C.A.O. radial wave functions are expanded as either single zeta Slater orbitals or double zeta hydrogenic basis functions, the mixing coefficients and radial exponents can be combined using a series of hyperbolic identities (*Appendix*). In the projected single-centre model the charges on the individual atoms of the complex are not distinguished but instead are replaced by an effective central charge [14, 15] for each molecular orbital. This type of model can be directly compared to the classical single-centre crystal field formulation, [13], but it retains the role played by ligands in M.O. models. It is clear that the only essential difference in a first order approximation is the replacement of the fixed ionic radial exponent by one (Slater orbital) or two (hydrogenic orbitals) variable parameters. Using a hydrogenic basis set and assuming that the parameters n_{eff} remain constant in a series of complexes, the parametric charges become:

$$Z_{eff} \cong (-Z_M + Z_L) \qquad (9)$$

Each perturbing term in the Crystal Field Hamiltonian is characterized by one or more fitting parameters which, like DQ, can be expanded in terms of an average radial integral, $\bar{r}^n$. The value of n represents the principal quantum number of the spherical harmonics required to construct the perturbation operator. Since the perturbation must operate in each case on one-electron d orbitals it is convenient to expand the various $\bar{r}^n$ with hydrogen-like radial wave functions maintaining l = 2. These are then readily adapted to the Ligand Field by substitution of the single-centre effective change for the formal central hydrogen charge Z. This substitution results in the following simplified expansions for the most commonly used d electron parameters [3]

$$DQ_{\Gamma\Gamma'} = \frac{Z_{eff}e^2}{a^5}\langle\bar{r}^4\rangle \propto \frac{n_{eff}^8}{Z_{eff}^3} + \text{lower powers} \qquad (10a)$$

$$DS_{\Gamma\Gamma'} = \frac{Z_{eff}e^2}{a^3}\langle\bar{r}^2\rangle \propto \frac{n_{eff}^4}{Z_{eff}} + \text{lower powers} \qquad (10b)$$

$$\chi_\Gamma = \langle\overline{r^{-1}}\rangle \propto \frac{Z_{eff}}{n_{eff}^3} \qquad (10c)$$

$$\lambda_{\Gamma\Gamma'} = \frac{Z_{eff}e^2t^2}{2\mu^2c^2a^3}\langle\overline{r^{-3}}\rangle \propto \frac{Z_{eff}^4}{15n_{eff}^3} \qquad (10d)$$

and the interelectron repulsion parameter which becomes

$$B_{\Gamma\Gamma'} \propto \frac{Z_{eff}}{n^3}$$

Experimental Correlations with the Model

The validity of these expression can be tested by experiments. Two recent sets of data can be used to test the correlation of $B_{\Gamma\Gamma'}$ with λ_Γ [1, 2] and the present work provides tests of $B_{\Gamma\Gamma'}$ against $\lambda_{\Gamma\Gamma'}$ and DQ_Γ. We take these up in turn.

In a wide range of transition metal hexafluoride complexes a linear correlation was observed between χ_Γ, the optical electron-negativity of the metal and $B_{\Gamma\Gamma}$, the nephelauxetic ratio [1]. Since the ligand is constant, $\Delta\chi_\Gamma$ depends to first order only upon the charge of the isolated metal ion. Substitution into (10b) yields;

$$Z_{eff} \propto Z_M \qquad (11a)$$

In a complementary series of tetrahedral anionic complexes with a fixed metal ion, cobalt(II), and a series of essentially σ bonded ligands a linear relationship between χ_Γ and $\beta_{\Gamma\Gamma'}$ was again observed [2]. In this case, substitution into (10b) implies;

$$Z_{eff} \propto Z_L \qquad (11b)$$

These two observations are both consistent with the first order assumption (9).

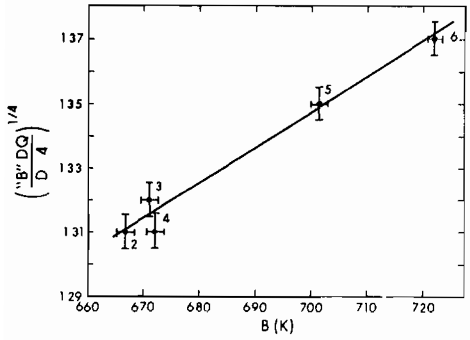


Fig 5 The dependence of $[\text{'B'/D DQ/4}]^{1/4}$ on B for complexes of orthosubstituted ligands The complexes are labelled according to their order in Table I The point (2) for the meta substituted $[\mathrm{Co(NCN\phi 3,5Cl_2)}]^{2-}$ ion is included as is the approximate position (7) for the impure $[\mathrm{Co(NCN2,4\text{-}(Ome)_2)}]^{2-}$ ion

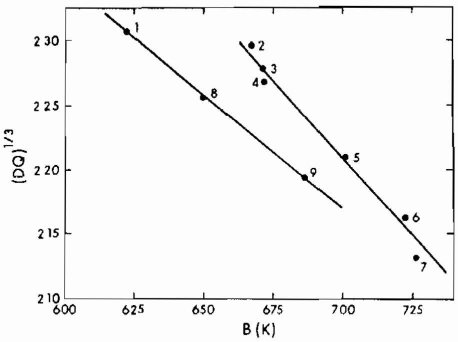


Fig 6 The dependence of $(DQ)^{1/3}$ on B for complexes of orthosubstituted ligands I labelled according to Table I and nonorthosubstituted ligands II These latter complexes include the $[\mathrm{Co(NCH\phi 4Me)_4}]^{2-}$ ion (8) and the $[\mathrm{Co(NCN\phi\text{-}4CN)_4}]^{2-}$ ion (9) prepared only in solution

The ligand field assignment and moments analysis of the absorption and MCD spectra of the present series of complexes provide data for a comparison of $B_{\Gamma\Gamma'}$ and $\lambda_{\Gamma\Gamma'}$ Using the series of complexes with orthosubstituted ligands, a plot of B_{et_2} against the fourth root of 'B'DQ/4D (Fig 5) yields a linear correlation within the experimental error limits This is consistent with the behaviour expected from a comparison of (10c) and (10d)

The ligand field data for both the series of ortho unsubstituted and orthosubstituted complexes can be used to compare the behaviour of DQ_Γ and $B_{\Gamma\Gamma'}$ A plot of B_{et_2} against the cube root of DQ (Fig 6) yields two linear correlations both with negative slopes as is predicted from eqns (10c) and (10a)

Conclusions

Taken together, all these linear correlations of experimental orbital parameter values suggest that the parameters themselves act as manifestations of a global orbital parameter By choosing to expand the single centre radial wave functions as linear combinations of the double zeta hydrogenic radial basis functions, it can be further suggested that the global parameter is the ratio of the two parameters Z_{eff}/n_{eff} In the present series of compounds, which were designed to minimize the dependence of observables on n_{eff}, the trends in orbital parameters quantitatively follow the trends in Z_{eff} predicted by this model within the experimental error

The model itself is very simplistic in attributing the observed variations to one charge parameter However the evidence available does not require greater sophistication Nor indeed is there much prospect of better evidence in other series of complexes In the present example the substitution of the ligand was designed to test both the low and high electronegativity limits of the series and it was quite clear that these limits were reached Attempts to prepare ligands and complexes beyond the range reported resulted either in ligand decomposition or redox reactions with the metal ion Within the available ten percent range of the paratmeter values the error limits preclude finer distinctions than those plotted here and hence preclude the need at present for a more complicated model

Besides suggesting that a rather simple single-centre ligand field model can be used to predict relative magnitude of parameters in a series of similar complexes, the correlations are essentially consistent with a simple L C A O interpretation It is now possible using the connection between these two models to predict the trends in what have been regarded as central metal parameters like $B_{\Gamma\Gamma'}$ and $\lambda_{\Gamma\Gamma'}$ on complex formation from the well established L C A O approach The quantitative aspects of these predictions remain to be developed Success in quantitative application would represent a real increase in the power of simple models The qualitative trends already seem to be clear

As an example of qualitiative uses, the correlations of $B_{\Gamma\Gamma'}$ against $(DQ_\Gamma)^{1/3}$ can be interpreted using this connection The correlation for ligands without ortho substituents lies at lower $B_{\Gamma\Gamma'}$ values than that with ortho groups In the single centre expansion model this implies, using (7) for repulsive potentials, that Z_{eff} is reduced with orthosubstituted ligands, or in an L C A O model that Z_{effL} is reduced The reason for this reduction may be a direct overlap of in-plane filled orbitals on the orthosubstituent with π orbitals of the donor group [16] This would provide additional π release to the metal ion, increasing $B_{\Gamma\Gamma}$ and reducing DQ_Γ since the stability of the e orbital would be reduced Work is continuing to characterize the trends more completely

Appendix

The radial wave functions of the e and t_2 orbitals of a metal complex can be described as linear combinations of metal and ligand group orbitals. A series of identity operations can be applied to these wave functions which converts them into single-centre expansions and demonstrates the dependence of these latter functions on sums or differences of the atomic radial exponents. If the approximate Slater radial wave functions are used, the bonding and antibonding combination for any set of interacting group orbitals may be written;

$$\psi_b = \frac{1}{N_b}(c_1 e^{-V_L} + c_2 e^{-V_M}) \qquad \text{(A1a)}$$

$$\psi_a = \frac{1}{N_a}(-c_2 e^{-V_L} + c_1 e^{-V_M}) \qquad \text{(A1b)}$$

in which N_b and N_a are normalization constants for the bonding and antibonding combinations respectively, c_1 and c_2 are mixing coefficients and V_L and V_M are the radial exponents of the ligand and metal group orbital respectively. The mixing coefficients can be converted to exponential form;

$$c_1 = e^{-u} \qquad \text{(A2a)}$$

$$c_2 = e^{-t} \qquad \text{(A2b)}$$

and the wave functions rewritten;

$$\psi_b = \frac{1}{N_b}(e^{-u-V_L} + e^{-t-V_M}) \qquad \text{(A3a)}$$

$$\psi_a = \frac{1}{N_a}(e-^{-t-V_L} + e^{-u-V_M}) \qquad \text{(A3b)}$$

These forms can be rearranged using standard identities for hyperbolic functions;

$$\psi_b = \frac{1}{N_b} \times$$

$$(\cosh(u + V_L) - \sinh(u + V_L) + \cosh(t + V_M) - \sinh(t + V_M))$$

$$= \frac{2}{N_b}\left[\cosh\left(\frac{u + V_L + t + V_M}{2}\right)\cosh\right] \times \left(\frac{u + V_L - t - V_M}{2}\right) - \sinh\left(\frac{u + V_L + t + V_M}{2}\right) \times \cosh(u + V_L - t - V_M)]$$

$$= \frac{2}{N_b}\left[\frac{1}{2}\, e\left(\frac{u + V_L - t - V_M}{2} + e\,\frac{-u - V_L + t + V_M}{2}\right) \times \left(e\,\frac{-u - V_L - t - V_M}{2}\right)\right] \qquad \text{(A4a)}$$

Similarly;

$$\psi_a = \frac{1}{N_a}(-\cosh(t + V_L) + \sinh(t - V_L) + \cosh(u + V_M) - \sinh(u + V_M))$$

$$= \frac{2}{N_a}\left[-\sinh\left(\frac{t + V_L + u + V_M}{2}\right) \times \sinh\left(\frac{t + V_L - u - V_M}{2}\right) + \cosh\left(\frac{t + V_L + u + V_M}{2}\right) \times \sinh\left(\frac{t + V_L - u - V_M}{2}\right)\right.$$

$$= \frac{2}{N_a}\left[\frac{1}{2}(e^{(t + V_L - u - V_M)/2} - e^{(-t - V_L - u - V_M)/2}) \times (e^{(-t-V_L-u-V_M)/2})\right] \qquad \text{(A4b)}$$

Assuming that the bonding is largely ionic,

$$C_1 \gg C_2 \text{ and } u \ll t \qquad \text{(A5)}$$

After simplification of (A4) terms retaining t are considered negligible so that the expansion (A4) becomes;

$$\psi_b \cong \frac{1}{N_b}(e^{(-2u - 2V_L + V_M - V_M)/2})$$

$$= \frac{1}{N_b}(e^{(-V_L-V_M-u)/2 + (V_M-V_L-u)/2}) \qquad \text{(A6a)}$$

and

$$\psi_a \cong \frac{1}{N_a}(e^{(-2u-2V_M+V_L-V_L)/2})$$

$$= \frac{1}{N_a}(e^{(-V_M+V_L-u)/2 + (-V_L-V_M-u)/2}) \qquad \text{(A6b)}$$

In each case the second bracket of the exponent is an approximately constant term. This can be seen qualitatively in each case. In the bonding orbital, assuming the V_L remains constant for a series of changing metal ions, then V_M and u may vary. If V_M increases then c_2 increases, decreasing c_1 and through (A5) increasing u. The factors V_M and u occur as a difference in (A6a) which remains approximately constant since both factors increase or decrease together. An equivalent argument applies if V_M is constant and V_L varies. In the antibonding orbital a similar argument applies. Assuming V_M is constant, an increase in V_L means an increase in c_1, and a decrease in u from (A5). The factors V_L and u occur as a sum in (A6b) which remains constant if the two factors change equally in opposite directions. For these reasons (A6) can be approximated by;

$$\psi_b \cong \frac{1}{N_b}(e^{(-V_L-(V_M+u))/2}) = c_1 e^{(-V_L-V_M)/2} \tag{A7a}$$

$$\psi_a \cong \frac{1}{N_a}(e^{(-V_M+(V_L-u)/2}) = c_1 e^{(-V_M+V_L)/2} \tag{A7b}$$

These results correlate with the assumptions made in a single centre expansion theory of a complexed ion. In ψ_b the orbital exponent c_1 is clearly increased leading to stabilization while it is decreased in the antibonding orbital ψ_a.

If the Slater type orbitals were replaced by a hydrogenic radial basis set the reformulation remains essentially the same but the parameters V_i can be identified with effective orbital moments;

$$V_i \propto \frac{2Z_{eff}}{n_{eff}a} r \tag{A8}$$

Substitution into (A7) yields the dependence, at this level of approximation of the orbital, on effective charges in the complex. Thus if n is constant;

$$Z_{eff_b} \propto (Z_{eff_L} + Z_{eff_M}) \tag{A9a}$$

and

$$Z_{eff_a} \propto (Z_{eff_M} - Z_{eff_L}) \tag{A9b}$$

The equation (A9b) becomes equation (5).

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