Chemical Significance of Ligand-field Parameters in Chromium(III) Complexes of Quadrate Symmetry

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Electronic spectra of some complexes of the chromium(III) ion of general formula $[CrX_4Z_2]$ have been interpreted using the crystal-field and angular-overlap models (X_4 = a tetra-amine, two diamines, or four monoamines; Z = F, Cl, Br, I, dmf, or $MeCO_2$). Values of the various ligand-field parameters have been obtained and are discussed in terms of their chemical utility and their relation to ligand-field strength. A spectrochemical series in *Cp*, the second-order crystal-field parameter, has been derived and shown to reflect trends in the chromium–ligand interactions which are not apparent from the conventional spectrochemical series in *Dq*.

LIGAND-FIELD theories have been remarkably successful in rationalising a vast amount of experimental data by the use of empirical or semiempirical parameters.[1-3] Basic to this success is the symmetry of the ligand field and the symmetry alone will establish the number of parameters necessary to describe the one-electron orbital or many-electron term splittings. Thus $\Delta_{oct.}$ is, by symmetry, the only parameter needed to describe the e_g–t_{2g} orbital separation in an octahedral complex and values of this parameter may be obtained by recourse to experiment. However, as the symmetry of the complex becomes lower than cubic the number of symmetry parameters increases and there are frequently insufficient experimental data to establish values for all of them. Under these circumstances semiempirical ligand-field models may be used to reduce the number of parameters and from a chemist's viewpoint these models may be extremely valuable if the parameters employed may be related from one compound to another in a chemically meaningful way.

There are two commonly encountered ligand-field models both of which employ a two-parameter representation of the general metal–ligand interaction. The crystal-field model parameterises the interaction in terms of Cp and Dq,[3] the second- and fourth-order radial integrals, and, although this model cannot be said to provide a reasonable chemical basis for the *d*-orbital splittings,[4] it retains some utility as an operator-equivalent formalism.[5] Alternatively, the angular-overlap model [3,6,7] may be used and the orbital energies described by e_σ' and e_π', where the parameters relate to the σ- and π-antibonding effects arising from a weak covalent metal–ligand interaction.† While the angular-overlap model can be said to be more realistic, it is not yet apparent that its parameters are chemically useful.

This paper is the first of a series devoted to a study of ligand-field parameters for a wide range of transition-metal complexes of distorted symmetries. Such complexes are particularly well suited to these studies because all the fundamental ligand-field parameters may be evaluated, often unambiguously, in carefully chosen systems. Clearly in an octahedral complex only Dq or the quantity $(3e_\sigma' - 4e_\pi')$ may be obtained because one parameter only is experimentally available, $\Delta_{oct.}$. We herein report electronic spectra of some complexes of the chromium(III) ion of the type $[CrX_4Z_2]$ of D_{4h} idealised symmetry, where X_4 represents a tetra-amine, two diamines, or four monoamines. Chromium(III) complexes of this type are easily accessible and several studies of their electronic spectra have been reported recently,[8-13] although previous interpretations have generally been based on the quadrate-symmetry parameters Dq, Ds, and Dt which have somewhat limited chemical usefulness.

EXPERIMENTAL

The *trans*-difluorochromium(III) complexes were prepared as described in the literature;[14] the tetra-amine ligands, 4,8-diazaundecane-1,11-diamine and 5,8-diazadodecane-1,12-diamine, were prepared by the amended methods of Van Alphen [15] as described by Glerup *et al.*[14] The ligand 5,9-diazatridecane-1,13-diamine has not been previously reported; it was prepared analogously from 1,3-dibromopropane and propane-1,3-diamine (pd), being obtained as the fraction distilling between 169 and 172 °C at 9 mmHg. The *trans*-$[Cr(diamine)_2X_2]Y$ complexes [X = Cl, Br, I, *NN*-dimethylformamide (dmf), and acetate] were prepared by literature methods [16] although the pd complexes do not appear to have been prepared previously by this method. Analytical results are shown in Table 1. The electronic spectra were measured as diffuse reflectance using a Beckman DK 2A ratio-recording spectrophotometer with a liquid-nitrogen sample mount.

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† In using the two-parameter version of the angular-overlap model we are assuming that the σ- and π-antibonding effects are measured relative to the δ-antibonding and also that the ligands are linearly ligating.

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TABLE 1

Analysis (%) *

Complex †	C	H	N
$[Cr(en)_2I_2][ClO_4]\cdot H_2O$	8·80 (8·85)	3·40 (3·30)	10·25 (10·3)
$[Cr(pd)_2F_2][ClO_4]$	21·35 (21·35)	4·65 (6·00)	16·45 (16·6)
$[Cr(pd)_2Cl_2][ClO_4]$	19·4 (19·45)	5·40 (5·45)	15·5 (15·1)
$[Cr(pd)_2Br_2]Br\cdot H_2O$	16·2 (16·15)	4·95 (4·90)	12·7 (12·45)
$[Cr(pd)_2I_2][ClO_4]\cdot H_2O$	11·2 (12·5)	3·70 (3·80)	9·90 (9·80)
$[Cr(pd)_2(dmf)_2][ClO_4]_3$	14·0 (13·6)	4·50 (4·50)	10·3 (10·05)
$[Cr(pd)_2(O_2CMe)_2]I\cdot 1{\cdot}5H_2O$	25·55 (25·4)	5·95 (6·15)	12·1 (11·9)
$[Cr(pnd)_2F_2][ClO_4]\cdot H_2O$	20·65 (30·2)	6·05 (6·25)	16·0 (15·85)
$[Cr(chd)_2F_2][ClO_4]\cdot H_2O$	33·2 (33·1)	7·10 (6·95)	13·15 (12·95)
$[Cr(daud)F_2][ClO_4]$	24·05 (24·1)	5·85 (5·80)	16·2 (16·0)
$[Cr(dadd)F_2][ClO_4]$	26·65 (26·5)	6·10 (6·05)	15·8 (15·45)
$[Cr(datd)F_2][ClO_4]$	28·25 (28·6)	6·15 (6·35)	14·35 (14·7)

* Calculated values are given in parentheses. † en = Ethylenediamine, pd = propane-1,3-diamine, pnd = propylene-1,2-diamine, chd = cyclohexane-1,2-diamine, daud = 4,8-diazaundecane-1,11-diamine, dadd = 5,8-diazadodecane-1,12-diamine, and datd = 5,9-diazatridecane-1,13-diamine.

RESULTS

The liquid-nitrogen spectra for the pd complexes, previously unreported, and the various aminefluoride complexes are shown in Table 2. The quadrate-symmetry parameters Dq, Ds, and Dt together with the Racah parameter B also given in this Table were obtained by fitting the observed spectra to the strong-field matrix for the d^3 ion in quadrate symmetry.[17] Although the observed and calculated spectra are in almost perfect agreement (within ± 20 cm^{-1}) for the parameter values given, this does not in itself prove that the band assignments are correct. However, comparison of our results with those available from single-crystal polarised spectral studies together with the consistency in the parameter values here presented indicates that our assignments are substantially correct.

TABLE 2

Electronic spectra (cm^{-1}) at liquid-nitrogen temperature with assignments and quadrate-symmetry parameters

	Assignments				Parameter values			
Complex	$^4B_{1g}\rightarrow{}^4E_g$	$\rightarrow{}^4B_{2g}$	$\rightarrow{}^4E_g$	$\rightarrow{}^4A_{2g}$	Dq	Ds	Dt	B
$[Cr(pd)_2F_2]^+$	19 260	22 030	24 270 (sh)	30 670	2 203	−1 200	260	520
$[Cr(pd)_2Cl_2]^+$	17 570	22 220	25 510		2 220	150	509	590
$[Cr(pd)_2Br_2]^+$	16 490	23 040	26 670	23 800	2 304	535	682	600
$[Cr(pd)_2I_2]^+$ †	14 950				2 100 *	650 *	720 *	600 *
$[Cr(pd)_2(dmf)_2]^{3+}$ (*a*)	19 530	23 360	26 650	29 000 (sh)	2 336	−360	436	625
(*b*)	19 530	23 360	29 000 (sh)	26 650	2 336	445	405	670
$[Cr(pd)_2(O_2CMe)_2]^+$	20 240	22 520	27 930		2 252	250	250	625
$[Cr(en)_2I_2]^+$ †	15 770	20 960 (sh)			2 096	600 *	600	600 *
$[Cr(pnd)_2F_2]^+$	19 690	22 370	25 190	29 940	2 237	−835	292	566
$[Cr(chd)_2F_2]^+$	19 530	22 700	25 380	29 760	2 270	−755	359	595
$[Cr(daud)F_2]^+$	19 800	22 570	25 910	30 450	2 257	−810	307	630
$[Cr(dadd)F_2]^+$	19 690	22 420	25 450	30 300	2 242	−870	296	595
$[Cr(datd)F_2]^+$	19 680	22 320	25 640	30 450	2 232	−875	286	621

sh = Shoulder.

* Assumed parameter values (see text). † Room-temperature spectra.

The band assignments are based on calculations of the energy levels as functions of the quadrate-symmetry parameters together with a knowledge of the likely signs of Ds and Dt which reflect the sign of the distortion. Figure 1 shows the variation of the spin-quartet energy levels of the d^3 ion for different, and fairly typical, values of the symmetry parameters, the energies being plotted relative to the $^4B_{1g}$ ground state. The $^4B_{1g}\rightarrow{}^4B_{2g}$ transition is independent of Ds and Dt, being given exactly by $10Dq(xy)$ where $Dq(xy)$ is the fourth-order parameter for the ligands in the xy plane. This transition thus occurs close in energy to the first transition in the octahedral CrX_6 parent complex and it is largely independent of the axial ligand. The $^4B_{1g}\rightarrow{}^4E_g[^4T_{2g}(t_{2g}{}^2e_g{}^1)]$ transition is separated from the previous one by $\frac{35}{4}$ Dt to first-order and so a knowledge of the sign of Dt or the magnitude of $Dq(xy)$ allows an assignment to be made for the first two transitions. The sign of Dt is fixed by comparing the Dq values for the equatorial and axial ligands since Dt can be written as (1),

$$Dt = 4/7[Dq(xy) - Dq(z)] \qquad (1)$$

if we make the additional assumption that we are dealing with a point-charge crystal-field model where $Dq = ze^2r^4/6a^5$. Thus the sign ‡ and approximate magnitude of Dt is available since the splitting of the $^4T_{2g}(t_{2g}{}^2e_g{}^1)$ octahedral level is virtually unaffected by Ds [Figure 1(*a*)]. The octahedral term $^4T_{1g}(t_{2g}{}^2e_g{}^1)$ is split to first order by $6Ds - \frac{5}{4}Dt$ and so is determined largely by the parameter Ds. The order of the $^4B_{1g}\rightarrow{}^4A_{2g}(^4T_{1g})$ and $^4B_{1g}\rightarrow{}^4E_g(^4T_{1g})$ transitions is then determined by the sign of Ds, Figure 1(*a*). Although the point-charge crystal-field model gives the equation for Ds as (2), it is not possible to use this

$$Ds = [Cp(xy) - Cp(z)] \qquad (2)$$

to predict the likely sign because of the acute lack of knowledge concerning the Cp values ($Cp = 2ze^2r^2/7a^3$) for typical ligands.[3] We have assumed that the sign of Ds will be the same as that observed in the chromium(III) ethylenediamine series where Ds is negative for Z = F^-, H_2O, and OH^- and positive for Cl^- and Br^-. The Racah parameter has little effect on the energy-level splittings but it is important in determining the overall energy spread of the spectrum.

In the majority of the spectra four bands were observed which correspond to transitions to the split components of the octahedral $^4T_{1g}(t_{2g}{}^2e_g{}^1)$ and $^4T_{2g}(t_{2g}{}^2e_g{}^1)$ levels, transitions to the upper $^4T_{1g}(t_{2g}{}^1e_g{}^2)$ components being at too high an energy to be observed. While four bands are sufficient to determine the four parameter values shown in Table 2, the failure to observe the higher-energy bands precludes an experimental check on these values. In a

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‡ Dt and Ds are here defined as positive when $Dq(xy) > Dq(z)$ and $Cp(xy) > Cp(z)$, respectively; this convention may differ from that used elsewhere.

[17] J. R. Perumaredi, *J. Phys. Chem.*, 1967, **71**, 3144.

few cases either the splitting of the $^4T_{1g}$ level was too small to be observed even at liquid-nitrogen temperatures or the transitions to the components of this level were obscured by charge-transfer bands. Thus for $[Cr(pd)_2Cl_2][ClO_4]$ fairly accurate values of *Dq*, *Dt*, and *B* may be obtained whereas the sign and magnitude of *Ds* were assumed to be the same as for $[Cr(en)_2Cl_2][ClO_4]$ (en = ethylenediamine). The spectra of these two chloro-complexes were virtually superimposable with near identical *Dq* and *Dt* values and the diamine ligands are chemically similar so that the assumption is a reasonable one. A similar situation exists regarding the spectrum of $[Cr(pd)_2(O_2CMe)_2]I{\cdot}1{\cdot}5H_2O$, but here we cannot obtain a precise estimate of *Ds* and we assume that this parameter lies in the range -250 to $+250$ cm^{-1} since larger values would almost certainly lead to a measurable splitting of the $^4T_{1g}$ level.

The complex $[Cr(pd)_2(dmf)_2][ClO_4]_3$ exhibited a four-band spectrum at liquid-nitrogen temperature, although at room temperature the splitting of the $^4T_{1g}$ level was not observed. Despite this, however, we obtain two possible assignments which differ in the order of the $^4A_{2g}$ and ^4E_g components of this level, *i.e.* the sign of *Ds* differs for the two assignments. At this stage we assume that both assignments are equally possible. Complexes with iodo-ligands exhibit only two bands as in $[Cr(en)_2I_2][ClO_4]{\cdot}H_2O$ or only one band as in $[Cr(pd)_2I_2][ClO_4]$ because of the low-lying charge-transfer bands. For the en complex, estimates of *Dq* and *Dt* are possible and in comparison with the chloro- and bromo-complexes it is likely that *Ds* is positive and greater than 500 cm^{-1}. Quadrate-symmetry parameters for a series of tetra-amines with axial fluoro-ligands were obtained from the solution spectra of Glerup *et al.*[14] and these are shown in Table 3.

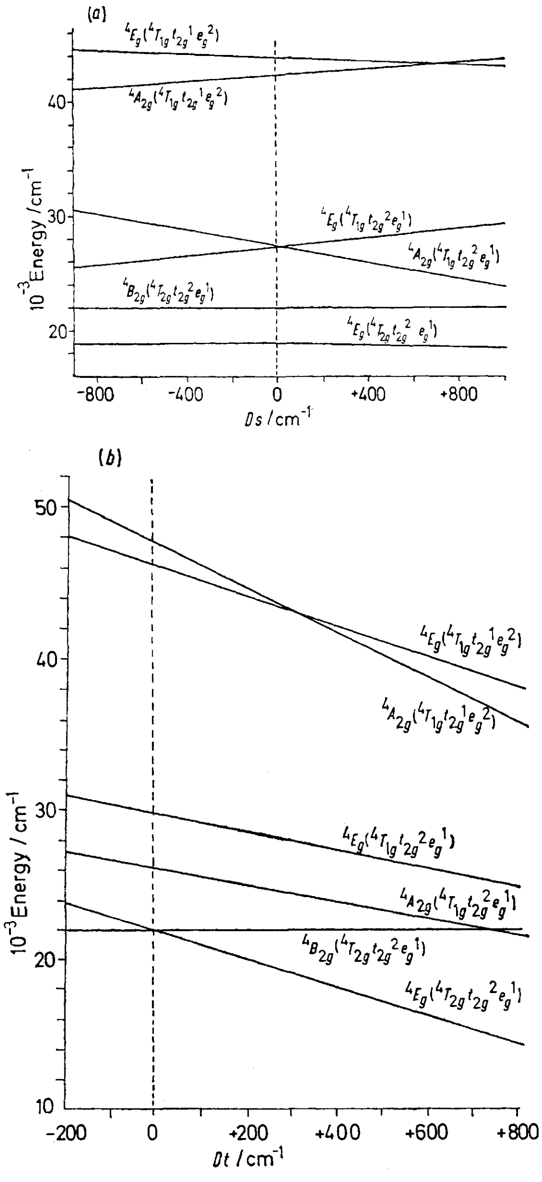

FIGURE 1 (*a*) and (*b*)

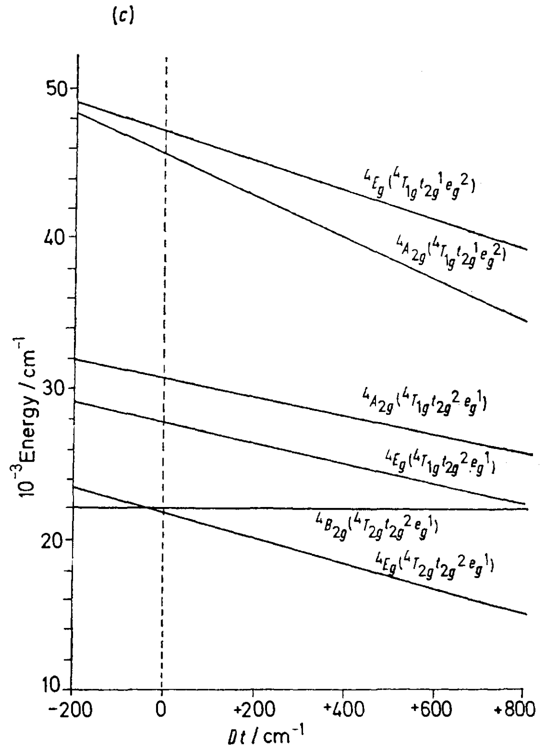

FIGURE 1 Strong-field energy levels relative to the $^4B_{1g}$ ground term for quadrate chromium(III) complexes: (*a*) against *Ds* for $B = 700$, $Dq = 2\,200$, and $Dt = +350$ cm^{-1}; (*b*) against *Dt* for $B = 600$, $Dq = 2\,200$, and $Ds = +600$ cm^{-1}; and (*c*) against *Dt* for $B = 600$, $Dq = 2\,200$, and $Ds = -600$ cm^{-1}

TABLE 3

Parameter values (cm^{-1}) of monoamine complexes $[Cr(amine)_4F_2]^+$

	Parameter values			
Amine	*Dq*	*Ds*	*Dt*	*B*
NH_3	2 090	−640	317	667
$MeNH_2$	2 022	−675	244	683
$EtNH_2$	2 022	−675	244	683
$PrNH_2$	1 992	−745	205	660
$C_3H_5NH_2$	1 965	−840	165	660

DISCUSSION

The parameters *Ds* and *Dt* express differences between the metal–ligand interactions in the axial and equatorial directions. These parameters have been extensively used within the crystal-field formalism and their relation to the second- and fourth-order radial integrals Cp and Dq have been shown in equations (1) and (2). Similar equations showing the relation between Dq, Ds, and Dt and the angular-overlap parameters may be easily derived and these are given in equations (3)—(5).

$$Dq = 3e_\sigma'(xy) - 4e_\pi'(xy) \qquad (3)$$

$$Ds = \frac{2}{7}[e_\sigma'(xy) + e_\pi'(xy) - e_\sigma'(z) - e_\pi'(z)] \qquad (4)$$

$$Dt = \frac{7}{35}[3e_\sigma'(xy) - 4e_\pi'(xy) - 3e_\sigma'(z) + 4e_\pi'(z)] \qquad (5)$$

While the symmetry parameters themselves are of limited chemical use in relation to the interactions between the chromium ion and the individual ligands, certain trends are apparent. As expected from the position of the axial ligands in the spectrochemical series[18] compared with the equatorial diamines, we find that Dt is always positive and, further, from the magnitudes of Dt, the ligand-field strengths of the axial ligands are in the order (6), again consistent with the

$$OH^- > F^- \sim H_2O \sim MeCO_2^- > dmf > Cl^- > Br^- > I^- \qquad (6)$$

relative spectrochemical Dq values for these ligands. According to the sign of Dt we would define the axial ligands as producing a weaker field than the equatorial ones. However, the parameter Ds may be positive or negative depending on the axial ligand and, as Ds expresses the difference in ligand-field strength as measured by Cp values, it is clear that high values of Cp do not necessarily equate with high values of Dq. Alternatively, equations (4) and (5) show how the different e_σ' and e_π' bonding parameters contribute to the symmetry parameters and from these equations it can be seen that different signs for Ds and Dt will be related to the relative importance of the e_π' parameters for the axial and equatorial ligands. In order to investigate the trends underlying the values of the symmetry parameters and to determine the significance and usefulness of the various parameters in relation to ligand-field strength in distorted complexes, we must derive values for the angular-overlap and crystal-field parameters.

TABLE 4

Crystal-field and angular-overlap parameters (cm^{-1}) for $[Cr(amine)_nZ_2]$ complexes

		Crystal-field parameters					Angular-overlap parameters			
Complex	Ref.	$Dq(xy)$	$Cp(xy)$	$Dq(z)$	$Cp(z)$	$Cp(z):Dq(z)$	$e_\sigma'(xy)$	$e_\pi'(xy)$	$e_\sigma'(z)$	$e_\pi'(z)$
$[Cr(en)_2F_2]^+$	11	2 170	2 067	1 610	2 867	1·78	7 233	0	8 033	2 000
$[Cr(en)_2Cl_2]^+$	12	2 250	2 143	1 341	1 971	1·47	7 500	0	5 857	1 040
$[Cr(en)_2Br_2]^+$	12	2 250	2 143	1 236	1 677	1 37	7 500	0	5 120	750
$[Cr(en)_2I_2]^+$		2 096	1 996	1 050	1 396	1·32	6 987	0	4 292	594
$[Cr(en)_2(OH_2)_2]^{3+}$	12	2 350	2 238	1 685	2 545	1·51	7 833	0	7 497	1 410
$[Cr(en)_2(OH)_2]^+$	13	1 992	1 897	1 710	2 565	1·50	6 640	0	7 473	1 405
$[Cr(en)_2(dmso)_2]^{3+}$	21	2 260	2 152	1 367	2 404	1·76	7 534	0	6 769	1 653
$[Cr(pd)_2F_2]^+$		2 203	2 098	1 748	3 298	1·89	7 343	0	9 093	2 450
$[Cr(pd)_2Cl_2]^+$		2 220	2 117	1 329	1 967	1·48	7 400	0	5 832	1 052
$[Cr(pd)_2Br_2]^+$		2 304	2 194	1 110	1 659	1·47	7 680	0	5 417	903
$[Cr(pd)_2I_2]^+$		2 100	2 000	900	1 350	1·50	7 000	0	3 986	739
$[Cr(pd)_2(dmf)_2]^{3+}$ (*a*)		2 336	2 225	1 573	2 585	1·64	7 787	0	7 418	1 630
(*b*)		2 336	2 225	1 626	1 780	1·09	7 787	0	5 833	347
$[Cr(pd)_2(O_2CMe)_2]^+$		2 252	2 145	1 815	1 895—2 395	1·04—1·32	7 507	0	6 382—7 382	250—1 000
$[Cr(pnd)_2F_2]^+$		2 237	2 131	1 726	2 966	1·72	7 457	0	8 394	1 933
$[Cr(chd)_2F_2]^+$		2 270	2 162	1 742	2 917	1·78	7 567	0	8 180	2 030
$[Cr(daud)F_2]^+$		2 257	2 151	1 720	2 961	1·72	7 523	0	8 382	1 981
$[Cr(dadd)F_2]^+$		2 242	2 135	1 724	3 005	1·74	7 473	0	8 472	2 045
$[Cr(datd)F_2]^+$		2 232	2 126	1 732	3 001	1·73	7 440	0	8 476	2 027
$[Cr(NH_3)_4F_2]^+$	14	2 090	1 991	1 535	2 631	1·71	6 976	0	7 453	1 753
$[Cr(H_2NMe)_4F_2]^+$	14	2 022	1 926	1 595	2 601	1·63	6 740	0	7 479	1 622
$[Cr(H_2NEt)_4F_2]^+$	14	2 022	1 926	1 595	2 601	1·63	6 740	0	7 479	1 622
$[Cr(H_2NPr)_4F_2]^+$	14	1 992	1 897	1 633	2 642	1·62	6 640	0	7 617	1 630

Angular-overlap Bonding Parameters.—The one-electron orbital splittings in quadrate symmetry are completely defined by the three parameters Dq, Dt, and Ds, whereas the angular-overlap model requires four parameters to describe these splittings. The problem of extracting four parameters from the three experimentally determined ones is made tractable by the choice of amines as the equatorial ligands since the nitrogen-donor atoms have no orbitals available for π-bonding to the chromium ion. Thus $e_\pi'(xy)$ may be set equal to zero and all the required parameters are evaluated using equations (3)—(5). The angular-overlap parameters calculated in this way are given in Table 4 together with the parameter values obtained similarly from the single-crystal polarised-light spectra of some bis(ethylenediamine)chromium(III) complexes. The parameters for these complexes have been reported previously[3] but not fully discussed.

For the complex $[Cr(pd)_2(dmf)_2][ClO_4]_3$, where two assignments are possible, the parameters derived from both are included in the Table. The positive Ds value, assignment (*b*), requires a very large $e_\sigma'(z):e_\pi'(z)$ ratio implying strong σ- and weak π-bonding. Comparison with the other oxygen-donor axial ligands suggests that the lower $e_\sigma'(z):e_\pi'(z)$ ratio of 4·55 : 1 may be more

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[18] Ref. 2, p. 107.

likely. For this reason assignment (*a*) is preferred and so *Ds* is negative for this complex and probably also for the en analogue, although this was previously reported to have a positive *Ds* value based on a two-band spectrum.[19] Similarly, for $[Cr(pd)_2(O_2CMe)_2]^+$ it may be expected that the ratio of $e_\sigma'(z) : e_\pi'(z)$ would be in the range 4—8 : 1 and certainly not above 10 : 1 as required by negative values of *Ds*; accordingly the range of *Ds* values may be narrowed to 150—250 cm^{-1}. The series of *trans*-difluoro-complexes with a variety of amine ligands exhibit only small changes in the parameter values and so identifiable trends are hard to find. However, for the monoamine complexes it appears that as the degree of nitrogen substitution increases so does $e_\sigma'(z)$ and $e_\pi'(z)$ whilst $e_\sigma'(xy)$ decreases. The decrease in the metal–ligand equatorial interaction can be correlated with steric repulsions in the equatorial plane and with the inductive effects of the alkyl substituents. The fact that the propylene-1,2-diamine complex has a lower $e_\sigma'(xy)$ than the propylamine one may indicate that the latter effect is more important. It appears that a decrease in the equatorial metal–ligand interaction is balanced by an increase in the axial interaction and that steric repulsions between the monoamines and the fluoride are negligible. In the case of the di- and tetra-aminedifluoro-complexes the differences in parameter values are too small to be considered significant.

Our main concern is with the trends in parameter values as a function of ligand since it is the relative rather than the absolute magnitudes of the parameter values that are amenable to chemical comparisons. Also, small variations in parameter values that arise from the differing sources of the data will be minimised. The variations of e_σ' and e_π' for the ligands here studied are given in (7) and (8), using the values from the en and pd series. The variations in e_σ' and e_π' are in

$$F^- > OH^- > en \sim pd > H_2O \sim dmf > dmso > MeCO_2^- > Cl^- > Br^- > I^- \quad (7)$$

$$F^- > dmso \sim dmf > OH^- > H_2O > Cl^- > MeCO_2^- > Br^- > I^- \gg en = pd \quad (8)$$

substantial agreement with an empirical rule suggested by Schäffer's study[7] of some $[Cr(NH_3)_4X_2]$ complexes in that ligands with high e_σ' values also have high e_π' values. Although there is some small variation for ligands such as dmf and dmso, it is seen that ligands bonding to the chromium ion through fluorine or oxygen atoms are high in both series. Such a result is consistent with the known affinity of the chromium(III) ion for hard bases such as F^- or *O*-bonding ligands. Thus chromium(III) amines form *O*-bonded nitrito-complexes in preference to *N*-bonded nitro-ones,[20] and rupture of the chromium–nitrogen bond occurs in aquation of a variety of bis(ethylenediamine) complexes,[21] although clearly kinetic as well as thermodynamic factors are important in these reactions. The affinity for fluoride and oxygen-donor ligands as compared with nitrogen donors or the heavier halides is rationalised in terms of Chatt's π-bonding theory for hard and soft acid–base behaviour[22] in that the hard ligands form strong π-bonds to the partially filled d_{xz},d_{yz} orbitals of the hard chromium ion. Although this is a rather simplistic model, it appears that π-bonding effects are important in discussing the chemical and electronic properties of chromium(III) complexes and there is some indication that the e_σ' and e_π' parameters realistically parallel these trends in chemical properties.

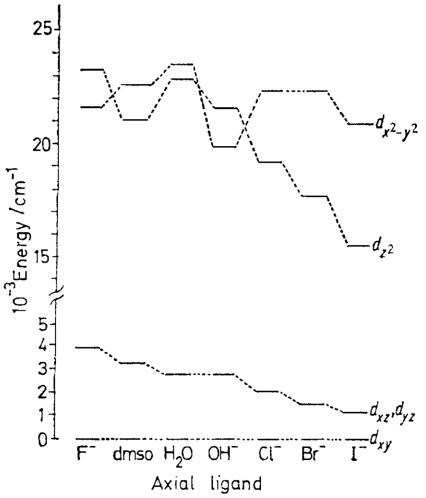

FIGURE 2 One-electron *d*-orbital energy-level sequence for $[Cr(en)_2Z_2]^{n+}$ relative to the d_{xy} orbital

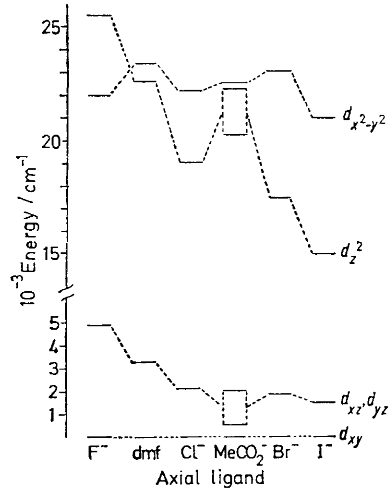

FIGURE 3 One-electron *d*-orbital energy-level sequence for $[Cr(pd)_2Z_2]^{n+}$ relative to the d_{xy} orbital

The relative magnitudes of the e_σ' and e_π' parameters are emphasised in Figures 2 and 3 where we plot the one-electron orbital energies, relative to d_{xy}, for the en and pd series, respectively. These orbital sequences

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[19] W. W. Fee and J. N. MacB. Harrowfield, *Austral. J. Chem.*, 1969, **23**, 1049.

[20] W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, 1967, **6**, 87.

[21] C. S. Garner and D. A. House, *Transition Metal Chem.*, 1970, **6**, 59.

[22] J. Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

together with equations (4) and (5) indicate how positive and negative signs for the quadrate-symmetry parameters are related to the bonding in the axial and equatorial directions. The splitting of the t_{2g} orbital set, $\Delta(t_{2g})$, depends on the differences in the π-bonding capabilities of the equatorial and axial ligands and, since for both series of complexes the axial ligands are π-donors and the diamines non-π-bonding, the sign of $\Delta(t_{2g})$ remains constant with the d_{xy} orbital below the d_{xz},d_{yz} orbitals, the latter pair being destabilised by interaction with the π-orbitals of the axial ligand. The e_g orbital splitting is determined by the difference in the equatorial and axial σ-bonding and the order is $d_{x^2-y^2}$ below d_{z^2} for the axial ligands fluoride and hydroxide while the reverse splitting occurs for the remaining complexes. From equations (7) and (8) we see that the positive value of Dt is to be associated with either axial ligands being weaker σ-donors than the diamines or with the axial ligands which are strong σ- and π-donors. On the other hand ligands which are strong π-donors will tend to produce negative values of Ds provided that their σ-donor strength is comparable with that of the equatorial diamines.

Previous attempts have been made to account for the signs and relative magnitudes of the parameters which define the d-orbital splittings in terms of the relative base strengths of the ligands and the number of lone pairs available for π-bonding.[19,23,24] However, there appears to be no simple correlation between ligand pK_a values and the σ-bonding parameters since it was on such a basis that the complexes $[Cr(en)_2(H_2O)_2]^{3+}$ and $[Cr(en)_2(dmf)_2]^{3+}$ were assigned positive Ds values [19] whereas the opposite is true for these moderately strong π-bonding axial ligands. Keeton *et al.* discussed [13] the magnitudes of the angular-overlap parameters for some $[Cr(en)_2X_2]$ complexes and they prefer to ascribe the orbital splittings to ionic rather than covalent metal–ligand interactions. This conclusion was based on the premise that high e_σ' and e_π' values for a ligand imply extensive σ- and π-charge donation from the ligand to the metal and that a ligand could not function simultaneously as a strong σ- and π-donor because its effective charge would become too positive. We consider that such an interpretation is invalid for two reasons.

An ionic metal–ligand interaction cannot account for d-orbital splittings because it must inevitably yield ligand-field parameters of the wrong sign due to the various coulomb and exchange interactions between the electrons of the metal and the ligands and the coulomb interaction between the metal electrons and the ligand nucleii.[25,26] While these factors are neglected in naïve crystal-field theory, their inclusion in a realistic ionic model would lead to the t_{2g}-orbital set being placed at higher energy than the e_g set in an octahedral field, contrary to observation. Donation of charge from the ligand to the metal is only one aspect of the covalent metal–ligand interaction and, as shown by Watson and Freeman,[26] it arises as a result of covalent mixing of metal and ligand orbitals. A more important effect is the overlap contribution to the orbital splittings arising from the orthogonalisation of metal and ligand orbitals in the limit of zero covalency. More recent calculations [27] confirm the relative importance of these two contributions, the splitting arising from the non-orthogonality being approximately twice that from the covalency. Insofar as the angular-overlap parameters relate to the total bonding process, it is not possible to equate high parameter values solely with a large ligand to metal charge donation. Intuitively we tend to associate covalency with ligands such as bromide and iodide, whereas these ligands are characterised by low values of e_σ' and e_π'. On the other hand, the overlap effects depend on the magnitude of the metal–ligand overlap integrals and it is reasonable to suggest that the smallest ligands, having relatively large S_σ and S_π values, may well have high bonding parameters for this reason without the necessity to invoke large σ- and π-charge donations. Furthermore, *ab initio* calculations [28] of the electronic structures of $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ support the notion [29] that charge donation from the ligands is small, certainly much less than that anticipated from mutual neutralisation of metal and ligand charges in the Pauling sense. For these reasons we prefer to use e_σ' and e_π' as parameters referring to the total bonding process, covalency effects being augmented by an ionic interaction, and whose magnitudes may be more affected by overlap considerations than by charge donation. Qualitatively, at least, the trend in the e_σ' series, and to a lesser extent in the e_π' series, appears to parallel the variation in the chromium–ligand distance thus suggesting a measure of dependence on the overlap integrals.

Crystal-field Parameters and Ligand-field Strength.—Despite its lack of physical reality, the crystal-field model still enjoys a wide popularity and the formalism of the theory provides a simple means of calculating orbital splittings. Under such circumstances the theory can be legitimately employed as an operator-equivalent method, but then the parameters can only have physical significance through their relation with the equivalent parameters e_σ' and e_π'. The relation between the alternative parameters are given by linear equations (9) and (10) [3,7] and from these equations it is clear that

$$Dq = \frac{1}{10}(3e_\sigma' - 4e_\pi') \qquad (9)$$

$$Cp = \frac{2}{7}(e_\sigma' + e_\pi') \qquad (10)$$

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[23] L. Dubicki and R. L. Martin, *Austral. J. Chem.*, 1969, **22**, 839.

[24] D. A. Rowley, *Inorg. Chem.*, 1971, **10**, 397.

[25] S. Sugano and R. G. Shulman, *Phys. Rev.*, 1963, **130**, 517.

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[29] C. K. Jørgensen, ' Oxidation Numbers and Oxidation States,' Springer–Verlag, Berlin, 1969.

Dq is a measure of the difference in the σ- and π-antibonding strengths of the ligands whereas *Cp* is a measure of the total σ- and π-antibonding. Values of *Cp* and *Dq* are given for the various ligands in Table 4 where we include also the value of $Cp : Dq$, the ratio of the second- and fourth-order radial parameters which has been prominent in discussions of the activation energies for ligand-substitution reactions.[30,31]

In (11) the ligands are ordered according to their *Dq* values whereas (12) lists the ligands as a function

$$\text{pd} \sim \text{en} > \text{MeCO}_2^- > \text{OH}^- > \text{H}_2\text{O} > \text{F}^- > \text{dmf} > \text{dmso} > \text{Cl}^- > \text{Br}^- > \text{I}^- \quad (11)$$

$$\text{F}^- > \text{dmf} > \text{OH}^- \sim \text{H}_2\text{O} > \text{dmso} > \text{pd} \sim \text{en} > \text{MeCO}_2^- > \text{Cl}^- > \text{Br}^- > \text{I}^- \quad (12)$$

of *Cp*. The *Dq* series generally follows the traditional spectrochemical series and the order of the ligands occasions no surprise. The diamine ligands are strong σ-donors and lie higher in the series than ligands which act as σ- and π-donors. From equation (9) it is seen that a ligand's position in the *Dq* series is determined by the difference in σ- and π-antibonding effects so that although e_σ' for fluoride is slightly greater than that for en or pd the relatively large value of e_π' is responsible for the lower position of fluoride in the series. The *Cp* series, for which no comparable data are known, is quite different with fluoride- and oxygen-donor atoms lying higher than the diamines although the heavier halides retain their lowly positions. The magnitude of *Cp* is determined by the sum of the σ- and π-antibonding and in this series the traditionally stronger diamines have low positions because e_π' is zero. Also we see that inclusion of the π-bonding effects places the acetate, dmf, and dmso ligands above the diamines in the *Cp* series despite their lower e_σ' values.

In many crystal-field calculations approximate, and often arbitrary, values have been assumed for the ratio of the second- and fourth-order radial integrals, generally in the range 2—4 : 1. The crystal-field model gives little indication of the likely values of this ratio and, although values greater than five were thought possible in some complexes,[3] it now appears that the ratio is small and certainly less than 2 : 1. Trends in the value of $Cp : Dq$ can be discussed in terms of the π-bonding of the various ligands. It is trivial that for the equatorial ligands, since $e_\pi'(xy) = 0$, the ratio $Cp(xy) : Dq(xy)$ remains constant at 0·95 : 1. The axial ligands, however, are all capable of π-bond formation and the extent of this will affect the $Cp(z) : Dq(z)$ ratio. If $e_\pi'(z)$ is positive, *i.e.* Z is a π-donor ligand, then $Dq(z)$ will be reduced and $Cp(z)$ increased from their values in the absence of π-bonding, tending to give $Cp(z) : Dq(z) > 1 : 1$. Furthermore, a strong π-donor may tend to produce a negative value for *Ds* if $Cp(z)$ is sufficiently increased implying high $Cp(z) : Dq(z)$ but low $e_\sigma'(z) : e_\pi'(z)$ values; positive *Ds* implies the converse. For π-acceptor ligands e_π' will be negative and the ratio $Cp : Dq < 1 : 1$; also *Cp* will be small compared with *Dq* so that $Ds \gg Dt$.

A relation between the various parameters and the so-called ligand-field strength now emerges. Ligand-field strength has previously been equated with *d*-orbital splitting in an octahedral (or tetrahedral) complex and hence with the spectrochemical *Dq* series. Equivalently, we can express the field strength as the difference between the σ- and π-antibonding strengths of the ligand, although e_σ' and e_π' cannot be separately evaluated. In distorted complexes we have more splitting parameters which can be written as functions of *Dq* and *Cp* for each ligand and either of these two parameters could be used to express ligand-field strength. As is apparent from equations (11) and (12), the spectrochemical *Dq* and *Cp* series differ so that ligands to the left of the diamines in the *Cp* series could be said to be stronger and those to the right weaker, whereas in the *Dq* series all ligands are weaker than the diamines. Thus according to the *Cp* series the axial ligand field in $[\text{Cr(en)}_2\text{F}_2]^+$ is greater than the equatorial field, negative *Ds*, while the *Dq* values for these two ligands suggest that the equatorial field strength is the stronger, positive *Dt*. Despite the common acceptance of *Dq* as a measure of ligand-field strength in octahedral complexes, we consider that in these complexes with quadrate symmetry the parameter *Cp* is a more useful measure of this strength because its magnitude is related to a ligand's ability to bond to the metal. Such a definition then allows a correlation between ligand-field strength as the sum of e_σ' and e_π' and the chemical properties of these chromium(III) complexes to be established, as discussed above. It is an accident of symmetry that *Cp* vanishes in cubic complexes so that attention has historically been focused on *Dq* and the spectrochemical series.

Finally we wish to test the utility of the ligand-field parameterisations as regards the transferability of parameter values from one complex to another. Using the *Cp* and *Dq* values for the ligands fluoride and water, then assuming that bond-length changes are negligible, we can predict that for the complex $[\text{Cr(OH}_2)_4\text{F}_2]^+$ the values of *Dq*, *Ds*, and *Dt* will be *ca.* 1 685, −300, and $< \pm 50$ cm^{-1}. The sign of *Dt* is ambiguous depending on the exact value of $Dq(\text{F}^-)$ taken, but it is a small quantity in comparison with *Ds* which is large and negative. Without assuming a value for *B* we cannot predict the spectrum of this complex, but use of the transferred ligand-field parameters alone suggests that the ${}^4B_{1g} \rightarrow {}^4B_{2g}$ transition will occur at 16 850 cm^{-1} and be separated from the ${}^4B_{1g} \rightarrow {}^4E_g$ transition by less than ± 440 cm^{-1} so that the splitting of the octahedral ${}^4T_{2g}$ term will be small and probably not observable at room temperature. The splitting of the ${}^4T_{1g}$ octahedral term will however be large, *ca.* 1 740 cm^{-1}, with the ${}^4E_g$ component below the ${}^4A_{2g}$. The experimental spectrum[32]

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[30] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1958.

[31] S. T. Spees, jun., J. R. Perumaredi, and A. W. Adamson, *J. Phys. Chem.*, 1968, **72**, 1822.

[32] T. Y. Chia and E. L. King, *Discuss. Faraday Soc.*, 1960, **29**, 109.

consists of a single band at 16 300 cm^{-1} and bands at 22 700 and 25 500 cm^{-1}, strongly supporting the relative signs and magnitudes of the transferred ligand-field parameters and confirming the assignment suggested by Dubicki and Martin.[23] Once again, if the traditional spectrochemical series had been used, the axial and equatorial ligand-field strengths would be almost equal notwithstanding the large splitting of the $^4T_{1g}$ term. Use of the Cp series indicates stronger metal–ligand bonding in the axial direction and the sense of the distortion is reflected in the sign of Ds.

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