Thermodynamic Properties of Transition-metal Ions as a Consequence of *d*-Orbital Splitting from a Molecular-orbital rather than a Crystal-field Viewpoint

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A simple molecular-orbital (m.o.) method is used to view the stabilisation energies of octahedrally and tetrahedrally co-ordinated transition-metal complexes. Direct comparison with the crystal-field (c.f.) theory shows why the latter approach has had its successes and failures in the past in looking at heats of hydration, tetrahedral *versus* octahedral co-ordination, rates of reaction, *etc.* as a function of *d*-orbital configuration. The m.o approach shows that while *nd* orbital effects are important in determining total (and relative) stabilisation energies, interaction of the ligand σ orbitals with metal $(n+1)s$ and $(n+1)p$ orbitals is generally larger and varies smoothly across the first transition-metal series. It is argued that the wholesale use of *d*-orbital stabilisation energies alone to quantitatively compare the chemistry of different d^n configurations is a dangerous and far from reliable approach.

FOR many years the variations with *d*-orbital population of a range of parameters such as hydration energies, metal–oxygen bond lengths,[1] and metal–chlorine stretching force constants[2] have been correlated with the crystal-field stabilisation energy (c.f.s.e.) afforded by the d^n configuration of a first-row transition-metal complex. A similar approach has been partly successful in viewing the relative stabilisation energies associated with octahedral and tetrahedral co-ordination[3] and in rationalising, at least in part, the occurrence of normal and inverse spinel structures.[1] It has, however, received vigorous criticism [4,5] as a general method with which to determine the relative stabilities of species of different co-ordination number, as a function of electronic configuration. With the more recent popularity of molecular-orbital (m.o.) methods in structural transition-metal chemistry, this paper compares the results of the crystal-field (c.f.) model with that of a simple m.o. approach which we have used to look at other aspects of the subject.[6-8] We shall attempt to define the conditions under which the c.f.s.e. is a valid way of looking at some of these thermodynamic, kinetic, and structural effects.

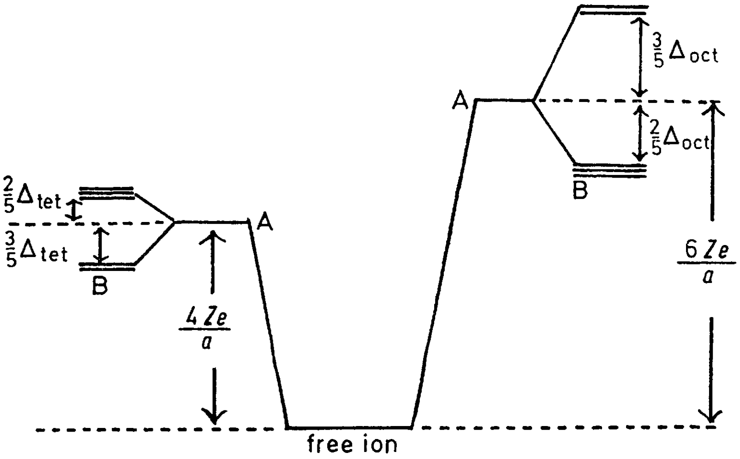

FIGURE 1 Parameters of the crystal-field approach in tetrahedral and octahedral systems. $\Delta_{oct} = \frac{5}{3}\cdot\frac{Ze}{a^5}\cdot\langle r^4\rangle$, $\Delta_{tet} = (4/9)\,\Delta_{oct}$, Z = the charge on the central ion, and a = the central atom–ligand distance

RESULTS AND DISCUSSION

The Crystal-field and Simple Molecular-orbital Models. —The assumptions, premises, and shortcomings of the c.f. model are well known.[1] Figure 1 shows the energy shifts of the *d* orbitals of a transition-metal ion when the free ion is co-ordinated in octahedral and tetrahedral fashion. The c.f.s.e. is the energy change of a given d^n configuration on moving from A to B in Figure 1. Such energy changes are simply calculated in terms of Δ, and for the high-spin (spin-free) d^0—d^{10} configurations are given in the Table.

The simple m.o. method we have chosen to use is based on the angular-overlap model.[6-8] Here it is assumed that the interaction energy of a pair of orbitals (i,j) to form a molecular orbital is given by $\beta S_{ij}{}^2$ where S_{ij} is the overlap integral between the two orbitals and β is a proportionality constant dependent, among other things, inversely on the energy separation of the interacting orbitals i and j (Figure 2). This simple approach may be

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[1] For a general summary of this text-book material see D. S. McClure in 'Some Aspects of Crystal Field Theory,' eds. T. M. Dunn, D. S. McClure, and R. G. Pearson, Harper and Row, New York, 1965.

[2] P. Labonville, J. R. Ferraro, M. C. Wall, and L. J. Basile, *Co-ordination Chem. Rev.*, 1972, **7**, 257.

[3] For example, D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, 1968.

[4] L. I. Katzin, *J. Chem. Phys.*, 1961, **35**, 467.

[5] L. I. Katzin, *J. Chem. Phys.*, 1962, **36**, 3034.

[6] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.

[7] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 931.

[8] J. K. Burdett, *Inorg. Chem.*, 1976, **15**, 212.

readily used to calculate the stabilisation energies of the σ orbitals in octahedral and tetrahedral molecules.[6] Figure 3 shows the result, where S_σ is the overlap integral of d_{z^2} with a ligand σ orbital located along the z axis at a fixed metal–ligand distance. We assume that this distance is the same in both octahedral and tetrahedral systems so that S_σ will be equivalent in both co-ordination frameworks. Two points concerning Figure 3 are of immediate interest. (*i*) The total destabilisation energy associated with the e_g* pair of d orbitals is $6\beta_\sigma S_\sigma^2$, whereas that associated with the t_2* trio is $4\beta\sigma S\sigma^2$. This is simply $x\beta_\sigma S_\sigma^2$ where x is the number of σ ligands. (*ii*) $\Delta_{\text{tet}} = (1.33/3)\ \Delta_{\text{oct}} = (4/9)\ \Delta_{\text{oct}}$ as in the c.f. model. (The result will be slightly different if π bonding is included, as noted below.)

Stabilisation energies of d^n configurations in crystal-field and molecular-orbital models

	Crystal field					Molecular orbital (units $\beta_\sigma S_\sigma{}^2$)		
	octahedral		tetrahedral		square-pyramidal			
d^n	units, Δ_{oct}	Dq	units,	Δ_{tet}/Dq	units (Dq)	octahedral	tetrahedral	square-pyramidal
0	0		0	(0)	0	12	8	10
1	2/5	(4)	3/5	(2.67)	4.57	12	8	10
2	4/5	(8)	6/5	(5.33)	9.14	12	8	10
3	6/5	(12)	4/5	(3.56)	10.0	12	6.67	10
4	3/5	(6)	2/5	(1.78)	9.14	9	5.33	8
5	0	(0)	0	(0)	0	6	4	5
6	2/5	(4)	3/5	(2.67)	4.57	6	4	5
7	4/5	(8)	6/5	(5.33)	9.14	6	4	5
8	6/5	(12)	4/5	(3.56)	10.0	6	2.67	5
9	3/5	(6)	2/5	(1.78)	9.14	3	1.33	3
10	0	(0)	0	(0)	0	0	0	0

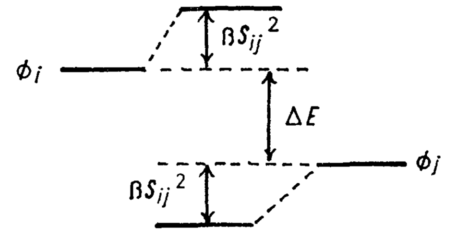

FIGURE 2 Basis of the angular-overlap model; the stabilisation energy of the bonding orbital (assumed equal to the destabilisation energy of the antibonding orbital) is proportional to the square of the overlap integral between them

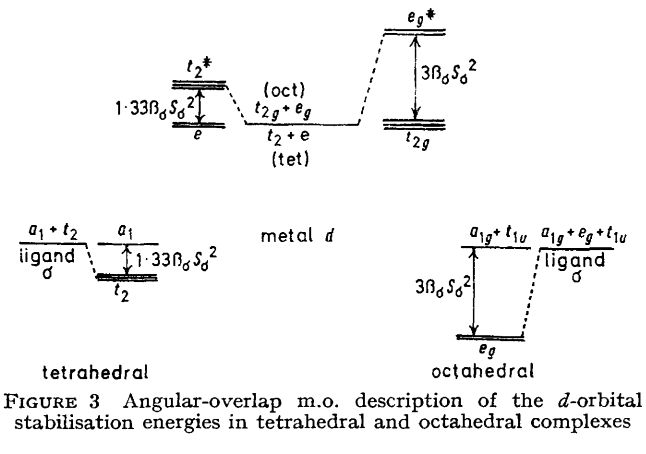

FIGURE 3 Angular-overlap m.o. description of the *d*-orbital stabilisation energies in tetrahedral and octahedral complexes

The total *d*-orbital molecular-orbital stabilisation energy (m.o.s.e.) may readily be calculated from Figure 3 by computing the total stabilisation energy afforded by the six electrons in the t_2 orbitals, $8\beta_\sigma S_\sigma{}^2$ (or four electrons in the e_g orbital, $12\beta_\sigma S_\sigma{}^2$) minus any destabilisation produced *via* population of t_2* (or e_g*). The results are given in the Table, alongside their c.f. counterparts. This stabilisation is relative to an energy zero of the d^n ion plus ligands in closed-shell form ($M^{2+} + 4X^-$, for example).

Heats of Hydration.—At first sight there seems to be little correlation between the stabilisation energies arrived at using the two methods, but on plotting $\Delta H^\ominus(\text{hyd})_{\text{obs.}}$ — m.o.s.e. and $\Delta H^\ominus(\text{hyd})_{\text{obs.}}$ — c.f.s.e. in

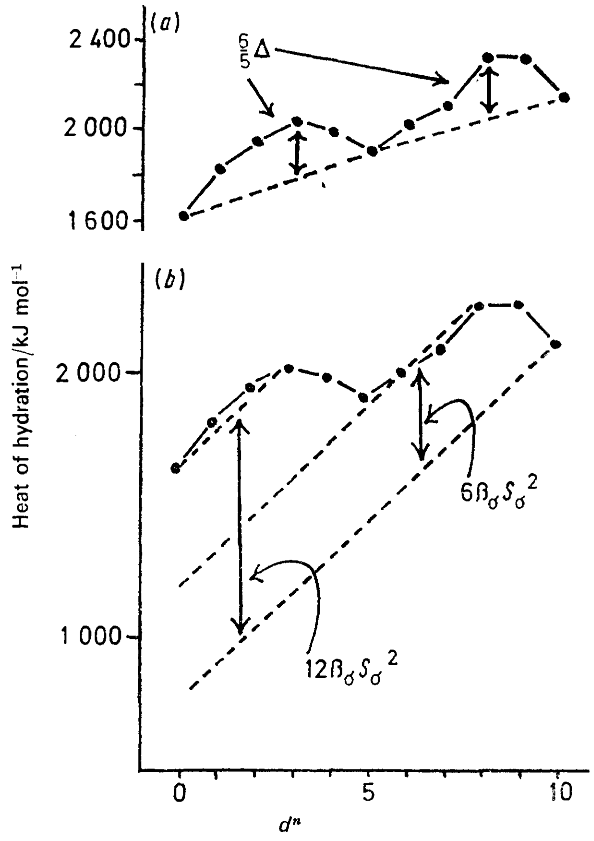

FIGURE 4 Observed heats of hydration of M^{2+} ions with (*a*) c.f.s.e. values qualitatively subtracted, (*b*) m.o.s.e. values subtracted (with $\beta_\sigma S_\sigma{}^2$ = 84 kJ mol^{-1})

standard fashion for the first-row M^{2+} ions (Figure 4) we see that in both cases a smooth variation of $\Delta H^{\ominus}$(hyd)$_{\mathrm{corr.}}$ with d^n results. The gradients of these two lines are however very different. The c.f. explanation is that some stabilising force in addition to the c.f.s.e. changes in monotonic fashion across the series from Ca^{2+} to Zn^{2+}. The m.o. rationalisation is much more specific; $\Delta H^{\ominus}$(hyd) contains the sum of the total interactions of s, p, and d orbitals on the metal centre with the ligands. The difference $\Delta H^{\ominus}$(hyd)$_{\mathrm{obs.}}$ − m.o.s.e. is thus the total stabilisation energy associated with $(n + 1)s$ and $(n + 1)p$ orbitals on the central atom. The $(n + 1)s$ and $(n + 1)p$ orbitals are able to interact with the ligand σ orbitals of species a_{1g} and t_{1u} respectively in the octahedral case and $a_1 + t_2$ respectively in the tetrahedral case. As the metal ionisation potentials increase across the series from Sc to Zn so the energy separation between these higher orbitals and the ligand σ orbitals decreases. The result is a larger interaction between the two (larger overall stabilisation energy) as the transition-metal series is traversed. We may immediately deduce the relative importance of the two sorts of interaction in this series. Thus, although the d-orbital contribution to $\Delta H^{\ominus}$(hyd) is *ca.* 50% for Ti^{2+} it is only *ca.* 15% of the total stabilisation energy for Cu^{2+}. It is wholly responsible however for the so-called ' double-hump ' behaviour of this curve. The m.o. rationalisations of similar variations in other properties with d^n are along the same lines. Examples include variations of MO bond lengths, MX_2 (X = halogen) lattice energies, and decomposition temperatures of carbonates.[9]

Rates of Reaction of Aqua-ions.—This is a field in which c.f. theory has been used to correlate in semi-quantitative terms the relative rates of reaction (1). The

$$[M(OH_2)_6]^{2+} \overset{k_1}{\rightleftharpoons} [M(OH_2)_5]^{2+} + H_2O \qquad (1)$$

difference in c.f.s.e. for the six-co-ordinate and square-pyramidal five-co-ordinate molecule has been used directly as a measure of the activation energy for the loss of water.[9] Let us see how the m.o. approach is able to view this reaction, by calculating the difference in *total* stabilisation energy between the two molecules.

We have noted above that the total hydration energy was the sum of two parts: (*i*) the d-orbital contribution, a function of $\beta_{\sigma}S_{\sigma}^2$ which varied with the number of d electrons; and (*ii*) a contribution from the $(n + 1)s$ and $(n + 1)p$ orbitals on the metal which seemed to vary smoothly across the transition-metal series. This latter contribution from the higher orbitals may be parametrised along similar lines to the way we have treated the d orbitals. Since all the bonding orbitals involving metal $(n + 1)s$–ligand and metal $(n + 1)p$–ligand interactions are filled, the total metal–ligand stabilisation energy is simply $x(\beta_s S_s^2 + \beta_p S_p^2)$ where x is the total number of σ ligands[10] and the meaning of the other symbols is obvious by comparison with Figure 3. Thus, the total stabilisation energy from this source for the five-co-ordinate $[M(OH_2)_5]^{2+}$ species is simply five sixths of that for the $[M(OH_2)_6]^{2+}$ species. The d orbitals of this C_{4v} fragment transform as $a_1 + e + b_1 + b_2$ and on a σ model alone the d-orbital region of the m.o. diagram is quantitatively described by Figure 5, where the c.f.s.e. values of the square pyramid are also shown. The d-orbital stabilisation energies and c.f.s.e.'s of this fragment as a function of d^n are given in the Table.

For each M^{2+} ion of the series therefore we may calculate the stabilisation energy loss on forming $[M(OH_2)_5]^{2+}$ by subtracting the sum of one sixth of the $(s + p)$ stabilisation energy from the experimental values of the heats of hydration (Figure 4) and adding the loss of d-orbital stabilisation energy from the Table. The results are shown in Figure 6 for the first-row transition-metal aqua-species. We see immediately that the m.o. method [6(*d*)] reproduces the observed monotonic increase [6(*c*)] in reaction rate for d^4—d^8 which is not the case for the c.f. calculation of the same parameter [Figure 6(*b*)]. Figure 7 shows a similar calculation for trivalent ions using in this case the rate of M^{3+}–M^{2+} exchange and assuming that the rate is determined by the reaction of the M^{3+} ion.

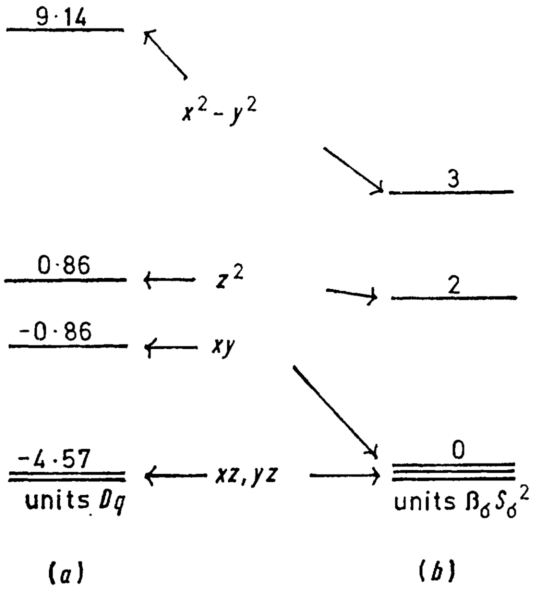

FIGURE 5 d-Orbital energies of a square-pyramidal molecule in (*a*) c.f. and (*b*) simple m.o. terms

It is difficult to rationalise conceptually the sometimes positive and sometimes negative change in c.f.s.e. on going from the six- to five-co-ordinate species on the c.f. model. In the m.o. approach however, both the change in m.o.s.e. associated with the d orbitals alone and the total $s + p + d$ energy change are never positive, *i.e.* the five-co-ordinate species is never more stable than the six-co-ordinate one.

The origin of the stepped function of Figure 6(*d*) is

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[9] For a large number of such plots see C. S. G. Phillips and R. J. P. Williams, ' Inorganic Chemistry,' Oxford University Press, 1966, vol. 2.

recognised if simply the difference in d-orbital stabilisation energy between the two structures is plotted [Figure 6(e)]. The form of Figure 6(d) is produced if a smoothly increasing energy difference associated with the $s + p$ stabilisation is added to this d-orbital term as we saw in the previous section with the hydration energies themselves. [The m.o. plot of Figure 6(d) gives a better fit to the experimental plot if the gradient of the $(s + p)$ contribution was in fact slightly smaller than we have calculated by taking one sixth of the value for the six-co-ordinate species.] The considerably better fit for the m.o. method is worth commenting on. For the hydration energies themselves similar behaviour is expected on the two models since only one parameter (the t_{2g}/e_g* separation) is involved. For the d-orbital energy levels in the square-based pyramid the two methods indicate radically different energetic arrangements; they are not just differently parametrised versions of the same energy diagram. In the absence of π bonding, d_{xy}, d_{xz}, and d_{yz} are equi-energetic on the m.o. approach, but d_{xy} is firmly split off in the c.f. method. The result of this section casts some doubt on the quantitative validity of the c.f. method.

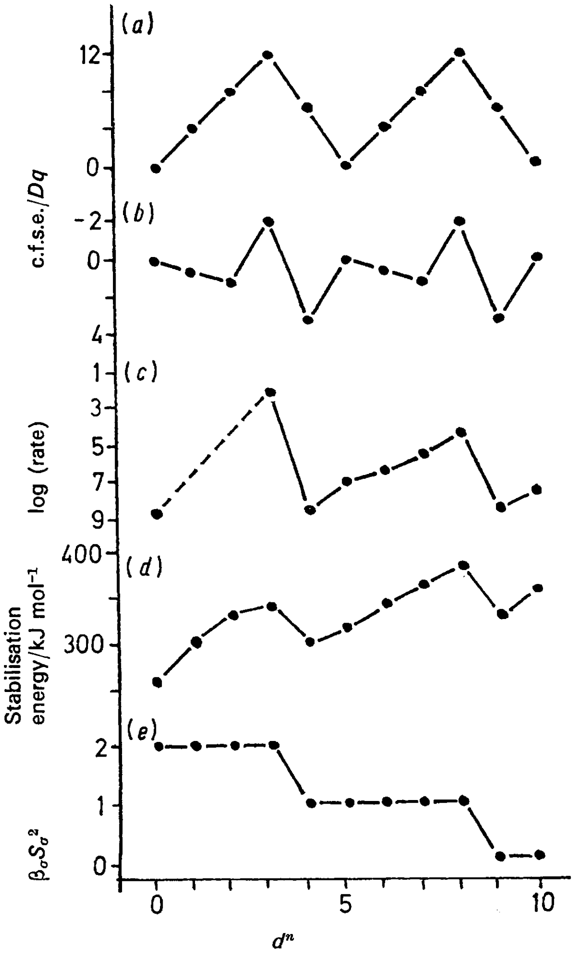

FIGURE 6 Rates of aqua-substitution reactions in the M^{2+} series: (a) c.f.s.e. of $[M(OH_2)_6]^{2+}$; (b) difference in c.f.s.e. of $[M(OH_2)_6]^{2+}$ and square-pyramidal $[M(OH_2)_5]^{2+}$; (c) observed rates of reactions; (d) differences in total $(s + p + d)$ stabilisation energies of $[M(OH_2)_6]^{2+}$ and square-pyramidal $[M(OH_2)_5]^{2+}$ using the m.o. method; and (e) differences in d-orbital stabilisation energies only of the two ions using the m.o. method

Tetrahedral versus *Octahedral Co-ordination*.—We may employ a similar calculation to the one in the previous section to estimate the energy difference between octahedral and tetrahedral co-ordination for these hydrates. Here we take two thirds of the $(s + p)$ stabilisation and add to it the difference in d-orbital stabilisation energy from the Table. The results are shown in Figure 8(a) and 8(b) for the two methods. Both m.o. and c.f. approaches show that the d^3 and d^8 configurations form tetrahedral complexes the least easily, as elegantly demonstrated by Gruen and his co-workers[11] in studies on $CsCl{\cdot}MCl_2$ melts. Tetrahedrally co-ordinated species could be found in the resulting solids for all the first-row d^n ions with the exceptions of V^{2+} and Ni^{2+}.

The plot of Figure 8(b) shows a gradually decreasing tendency for tetrahedral co-ordination as the series is progressed, yet experimentally one finds substantially more d^{10} (Zn^{2+}) tetrahedral complexes than d^5 or d^0. However, $\Delta H^\ominus$ values for process (2) have been calculated

$$[MCl_4]^{2-} + 6H_2O \longrightarrow [M(OH_2)_6]^{2+} + 4Cl^- \quad (2)$$

by Blake and Cotton[12] and the gradient of the curve

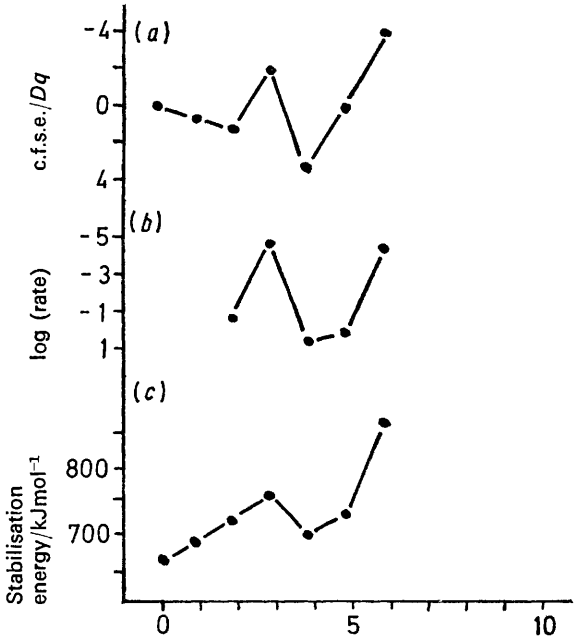

FIGURE 7 Rates of reaction of $[M(OH_2)_6]^{3+}$ ions: (a) difference in c.f.s.e. between $[M(OH_2)_6]^{3+}$ and square-pyramidal $[M(OH_2)_5]^{3+}$; (b) observed reaction rates; (c) difference in total $(s + p + d)$ stabilisation energies between the two ions using the m.o. approach

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[10] C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, 1965, **4**, 401.

[11] E. Iberson, R. Gut, and D. M. Gruen, *J. Phys. Chem.*, 1962, **66**, 65.

[12] A. B. Blake and F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 9.

[Figure 8(*c*)] is in the opposite direction to that for the aqua-complexes in Figure 8(*b*). A glance at these two figures together should be sufficient to warn against straightforward use of the c.f.s.e. values alone to predict when octahedral or tetrahedral co-ordination is favoured. Thus for the aqua-ions [Figure 8(*b*)] tetrahedral co-ordination is favoured more for Mn^{2+} than for Zn^{2+}; for the aqua-halide exchange [Figure 8(*c*)] the reverse is true.

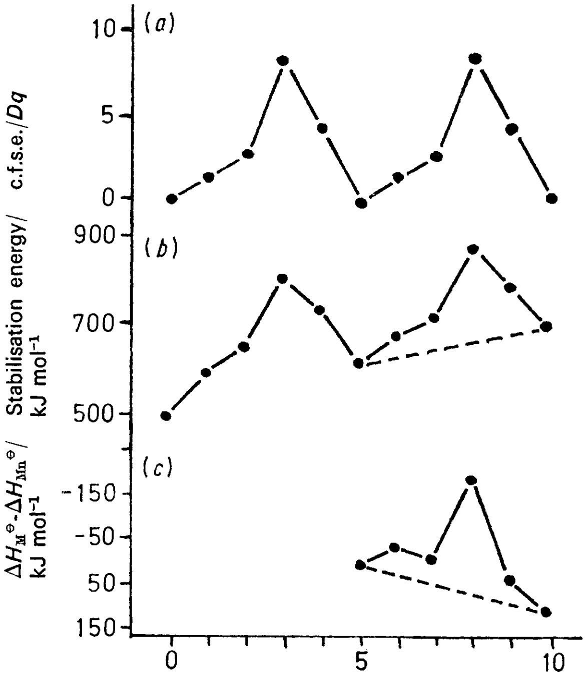

FIGURE 8 Energy difference between octahedral and tetrahedral co-ordination: (*a*) difference in c.f.s.e. between the two co-ordinations; (*b*) total ($s + p + d$) m.o. stabilisation energy difference between $[\mathrm{M(OH_2)_6}]^{2+}$ and tetrahedral $[\mathrm{M(OH_2)_4}]^{2+}$; (*c*) plot of $\Delta H_{\mathrm{M}}^{\ominus} - \Delta H_{\mathrm{Mn}}^{\ominus}$ for the reaction (2) (after Blake and Cotton [12])

On c.f. grounds alone equal tendency to form both octahedral and tetrahedral co-ordination is predicted since both configurations have zero c.f.s.e. in the two (and indeed all) environments. This is not the first time that the importance of this effect has been noted. Katzin [4,5] made similar strong objections in c.f. language to the general use of the c.f. method to rationalise trends in equilibria linking species of different co-ordination number.

The use of c.f.s.e. values *alone* will therefore only be a viable method to view such trends when the gradient of the line joining d^0, d^5, and d^{10} octahedral stabilisation energies [of Figure 8(*b*) or 8(*c*)] is close to zero. This requires the change in ($s + p$) stabilisation energy from d^0 to d^{10} to be exactly counterbalanced by the change in *d*-orbital stabilisation energy ($4\beta_\sigma S_\sigma^2$). An impressive case where this is seems to be true is the well known series of inverse and normal spinel structures ($\mathrm{A^{II}B^{III}_2O_4}$), where a knowledge of the o.s.p.e. (octahedral site preference energy) values alone is often sufficient to predict which structure will be adopted.[13,14] In the case where A and B are transition metals the method works well but it fails to allow Al^{3+} ions (*d*-orbital c.f.s.e. = 0) to occupy octahedral sites for those cases where A = Mn^{2+}–Ni^{2+}. More than most other observations, this is clear evidence that a stabilising force other than c.f.s.e. exists on co-ordination. Our conclusion here is therefore that the success of the c.f. method in the spinel field is weighted heavily by a fortunate balance of terms, the objections to its general use in this field being strong indeed.

Inclusion of π Bonding.—In the octahedral case the t_{2g} orbitals are involved in π interactions with the ligands. Using the same nomenclature as before, this t_{2g} set is raised in energy by an amount $4\beta_\pi S_\pi^2$ for π-donor ligands and depressed by this amount for π-acceptor ligands. [S_π is the overlap integral of d_{xz} (or d_{yz}) with the π orbital of a ligand lying along the *z* axis.] The figures of the Table should then be modified by the addition of a term $(12 - 4m)\beta_\pi S_\pi^2$ for π donors or a term $4m\beta_\pi S_\pi^2$ for π acceptors where *m* is the number of t_{2g} electrons; Δ_{oct} thus becomes $3\beta_\sigma S_\sigma^2 + 4\beta_\pi S_\pi^2$ for π acceptors and $3\beta_\sigma S_\sigma^2 - 4\beta_\pi S_\pi^2$ for π donors. The inclusion of π bonding means that the resulting curve of Figure 4(*b*) will be shallower (for π donors) and steeper (for π acceptors). Similar considerations apply for the other geometries. We generally consider however that σ interactions are larger than π interactions in such systems, and in the discussion above for high-spin systems have ignored π interactions completely for simplicity.

Conclusion.—Apart from describing a molecular-orbital alternative to the crystal-field description of thermodynamic and allied properties of transition-metal complexes, the relative importance of *d* and *s* and *p* orbital interactions with the ligands across the transition-metal series has been demonstrated. The contribution to the total stabilisation energy by these *s* and *p* orbitals on the metal is very large and usually much more important in magnitude than *d*-orbital interactions. We should therefore exercise care in trying to rationalise transition-metal chemistry on a purely *d*-orbital basis, using either the c.f. or simple m.o. methods.

[6/308 *Received, 13th February*, 1976]

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[13] D. S. McClure, *J. Chem. Phys. Solids*, 1957, **3**, 311.

[14] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys. Solids*, 1957, **3**, 318.