

# A New Analysis of the Ligand Field Stabilization Energy

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Received December 7, 1994<sup>⊗</sup>

The lattice enthalpies of the compounds  $K_3MF_6$ , where M runs from scandium to gallium, are used to show that conventional explanations of the origin of ligand field stabilization energies are incomplete. The usual double-bowl shape is observed, but the bowls are substantially larger than the orbital stabilization energies alone would imply. A new analysis suggests that the discrepancy is due almost entirely to irregularities in the variation in the interelectronic repulsion of the  $d^n$  shell with  $n$ , coupled with the nephelauxetic effect.

## Introduction

One of the most important chemical tests of ligand field theory is the explanation of the energy change that occurs when a gaseous ion,  $M^{n+}$ , of the first transition series forms an octahedral high-spin complex with a ligand  $L^{q-}$ . If  $n$  and  $L$  are fixed, the energy variation across the series is double bowl-shaped with a cusp between the bowls at the point where the transition metal ion has a  $d^5$  configuration. The variation is explained by breaking up the complexing reaction into two steps, as shown in Figure 1. In step 1, the gaseous ion interacts with the ligands to give a complex in which the ion is spherically symmetrical, as it is when it has a configuration of the type  $d^0$ ,  $d^5$ , or  $d^{10}$ ; the energy change for this step varies smoothly across the series. In step 2, the spherical ion complex is transformed into the real complex, and  $\Delta H$  is negative,<sup>1</sup> except at  $d^0$ ,  $d^5$ , and  $d^{10}$ . Consequently, the overall enthalpy of complexing  $\Delta H_c^\ominus$  is found to be double-bowl shaped, and the values fall below a smooth curve through the points at the  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations by an amount which we call the thermodynamic ligand field stabilization energy,  $\Delta H_{lf}^\ominus$ .

Ligand field theory attributes this stabilization to the loss of spherical symmetry when the octahedral ligand field exerts its influence in step 2. The field causes a splitting of the  $d$  orbitals into  $t_{2g}$  and  $e_g$  sets with separation  $\Delta$  or  $10Dq$ . Values of  $\Delta$  can be determined from the absorption spectra of complexes and used to calculate the orbital stabilization energy,  $\Delta E_{orb}$ , from the equation

$$\Delta E_{orb} = -\frac{\Delta}{5}(2n_t - 3n_e) \quad (1)$$

Here,  $n_t$  is the number of electrons in the  $t_{2g}$  orbitals and  $n_e$  is the number in the  $e_g$  set. Penney<sup>2</sup> and Orgel<sup>3</sup> showed that when, in Figure 1,  $n = 2$  and  $L = H_2O$ , the thermodynamic ligand field stabilization energies, and the values of  $\Delta E_{orb}$  calculated from eq 1, are almost identical. Thus, when the orbital stabilization energies are subtracted from  $\Delta H_c^\ominus$ , a smooth curve through the points at the  $d^0$ ,  $d^5$ , and  $d^{10}$  configuration is

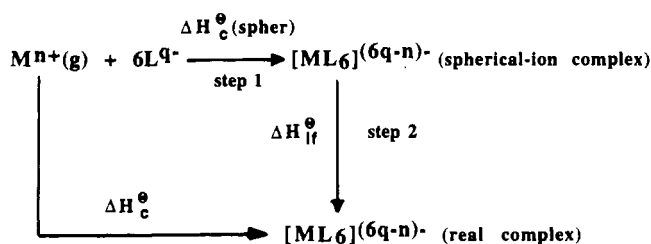


Figure 1. Two steps which separate the ligand field stabilization energy from the total metal–ligand interaction in a complex.

obtained. This proof of the validity of ligand field theory is presented in nearly all standard textbooks of inorganic chemistry.<sup>4–6</sup> What we shall do in this paper is show that this proof is oversimplified and pursue a more thorough analysis of the problem along the same lines. We shall adhere to a ligand field approach because all-electron calculations are not yet a sufficiently accurate alternative. Thus Åkesson *et al.*<sup>7</sup> carried out *ab initio* SCF calculations on  $[M(H_2O)_6]^{2+}$  ions of the first transition series and could only reproduce about 60% of the observed ligand field stabilization energies. Preliminary results of more detailed calculations also indicated that inclusion of correlation would not improve this figure very much.

A suitable starting point for our analysis is the review of George and McClure<sup>8</sup> which surveyed many complexing reactions of the type shown in Figure 1. In nearly all the cases that they examined,  $n = 2$ , and they found good agreement between thermodynamic ligand field and orbital stabilization energies. There were, however, signs that the former slightly exceeded the latter, the difference being quite significant for the case of the tripositive aqueous ions ( $n = 3$ ,  $L = H_2O$ ). In other words, the double bowl-shaped variation in  $\Delta H_c^\ominus$  was not wholly eliminated by the subtraction of  $\Delta E_{orb}$ , and a residual double bowl remained. In searching for the source of such

(4) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1987; pp 467–9.

(5) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1984; pp 1096–7.

(6) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry; Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; pp 408–9.

(7) Åkesson, R.; Petterson, L. G. M.; Sandstrom, M.; Siegbahn, P. E. M.; Wahlgren, U. *J. Phys. Chem.* **1992**, *96*, 10773.

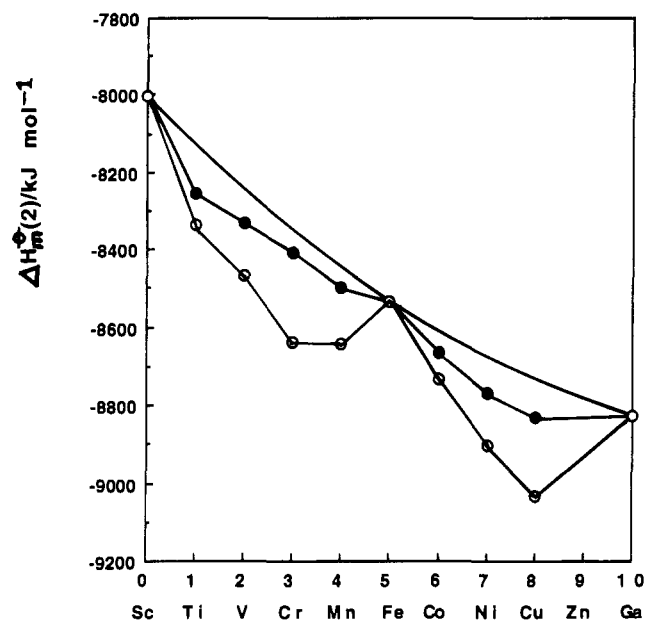
(8) George, P.; McClure, D. S. *Prog. Inorg. Chem.* **1959**, *1*, 381.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1995.

(1) Throughout this paper, enthalpies ( $H$ ) and energies ( $E$ ) are molar quantities.

(2) Penney, W. G. *Trans. Faraday Soc.* **1940**, *36*, 627.

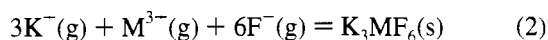
(3) Orgel, L. E. *J. Chem. Soc.* **1952**, 4756.



**Figure 2.** Plot showing that when the orbital stabilization energies of  $\text{MF}_6^{3-}$  are subtracted from the values of  $\Delta H_m^{\ominus}(2)$  (open circles), they prove insufficient to eliminate the cusp at  $d^5$ . They leave a residual (filled circles) which falls below a smooth curve through the values at  $d^0$ ,  $d^5$ , and  $d^{10}$ .

discrepancies, George and McClure considered the effects of what we call the relaxation energy,  $\Delta E_{\text{rlx}}$ . Suppose that the energy of metal–ligand interaction in the spherical complex of Figure 1 is described by a function of internuclear distance,  $F(r)$ . Then this function should be a minimum at a value of  $r$  that varies smoothly across the series. Now, when the spherical ion complex is converted into the real one in step 2, the concentration of electrons in the  $t_{2g}$  orbitals results in a contraction of the M–L distance in the  $d^1$ – $d^4$  and  $d^6$ – $d^9$  cases. This contraction leads to an increase in the value of  $F(r)$  and is destabilizing. Thus, removal of this increase ( $\Delta E_{\text{rlx}}$ ), along with  $\Delta E_{\text{orb}}$ , from  $\Delta H_c^{\ominus}$  leaves an even larger residual double bowl, and further increases the discrepancy between theory and experiment.

The seriousness of such discrepancies has been most clearly exposed by Pearse,<sup>9</sup> who examined the case  $n = 3$  and  $L^q = F^-$ . He determined the values of  $\Delta H_m^{\ominus}$  for the reaction



where M is one of the elements scandium to gallium inclusive. The compounds  $\text{K}_3\text{MF}_6$  have similar structures, the metallic element is in octahedral coordination, and of the 11 possible compounds in the sequence, only that of nickel is not high spin and only that of zinc has not been prepared. Figure 2 shows the values of  $\Delta H_m^{\ominus}$  (open circles) and the size of the double bowl (filled circles) which remains when  $\Delta E_{\text{orb}}$  is removed. There is a marked cusp in the residual at  $d^5$ , and in the second half of the series, the points on the residual at  $d^7$  and  $d^8$  lie some 110–130  $\text{kJ mol}^{-1}$  below a straight line between the  $d^5$  and  $d^{10}$  points.

In this paper, we show how such discrepancies can be explained by a refinement of the existing theory. We are interested in why  $\Delta H_m^{\ominus}(2)$  does not vary smoothly with  $n$ , the number of d electrons in both the gaseous ion and the complex.

In Figure 1, the reaction is divided into steps 1 and 2, the energy of step 1 varying smoothly through the values for the  $d^0$ ,  $d^5$ , and  $d^{10}$  ions. If this is to be the case, then the spherical ion complex of Figure 1 should have the following properties: (1) There must be no stabilization of the complex from d-orbital splitting. (2) The metal–ligand distance in the complex must vary smoothly along a curve through the values at the  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations. (3) Any stabilization of the complex by spin–orbit coupling must be identical with that of the gaseous ion, as it is at  $d^0$ ,  $d^5$ , and  $d^{10}$ . (4) The change in the interelectronic repulsion energy of the  $d^n$  shell when the complex is formed from the gaseous ion must vary smoothly along a curve through the values for the  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations.

As we have noted, George and McClure considered the consequences of the removal of conditions 1 and 2 in step 2 of Figure 1; they also made an allowance for condition 3. We now consider the removal of condition 4 as well. It transpires that the loss of condition 4 is almost entirely responsible for the missing, stabilizing component. When a gaseous transition metal ion enters into octahedral coordination and forms a complex, one factor that favors complex formation is the nephelauxetic effect—the decrease in the repulsion energy between the d electrons. According to the theory of many electron atoms, this decrease in energy does not vary smoothly across the series. The decrease is greater in the  $d^1$ – $d^4$  and  $d^6$ – $d^9$  regions than at  $d^0$ ,  $d^5$ , and  $d^{10}$ . Table 1 shows the interelectronic repulsion energy,  $E_{\text{rep}}(d^n)$ , of the ground terms of the  $d^n$  configurations as a linear combination of the Slater–Condon parameters,  $F_0$ ,  $F_2$ , and  $F_4$ .<sup>10a</sup> The next column shows what the repulsion energies would be if they varied smoothly along a curve through the  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations. They are given by the function

$$f(n) = \frac{1}{2}n(n-1)F_0 - 7n(F_2 + 9F_4) \quad (3)$$

In the next column, we give the values of  $[E_{\text{rep}}(d^n) - f(n)]$ ; they generate two humps linked at  $d^5$ , the expressions being  $(7F_2 + 63F_4)$  at  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$ ,  $(6F_2 + 117F_4)$  at  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$ , and zero at other places. From now on, we shall write this irregularly varying part of the interelectronic repulsion energy as  $E_{\text{rep}}(\text{irreg})$ , where

$$E_{\text{rep}}(\text{irreg}) = [E_{\text{rep}}(d^n) - f(n)] \quad (4)$$

We have chosen to perform the analysis with the Slater–Condon parameters, because the smoothly varying function  $f(n)$  then appears quite naturally. It is, however, a straightforward matter to express the formulas of Table 1 in terms of the more common, Racah parameters,  $A$ ,  $B$ , and  $C$ . The last column of Table 1 shows  $E_{\text{rep}}(\text{irreg})$  when it is written in this fashion. Given the way that we have defined the characteristics of the spherical ion complex, these irregularities appear in step 2 of Figure 1 as the terms  $(7\Delta B + 2.8\Delta C)$  at  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$  and  $(6\Delta B + 4.2\Delta C)$  at  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$ , where  $\Delta B$  and  $\Delta C$  are changes in the Racah parameters  $B$  and  $C$ . Because of the nephelauxetic effect,  $\Delta B$  and  $\Delta C$  are negative, so such terms make a stabilizing contribution to  $\Delta H_c^{\ominus}$  and together have the shape needed to eliminate the discrepancy in the present theory. As we shall now show, they also have the right size.

The way that we shall do this is to calculate the standard enthalpy change of step 1 in Figure 1,  $\Delta H_c^{\ominus}(\text{spher})$ . The calculation is performed by subtracting from  $\Delta H_c^{\ominus}$  the enthalpy change of step 2. The latter is the sum of the energy

(9) (a) Pearse, R. V. Ph.D. Thesis, University of Hull, 1966. (b) Nelson, P. G.; Pearse, R. V. *J. Chem. Soc., Dalton Trans.* **1983**, 1977. In eq 16 of ref 9b, the second term should read  $\frac{3}{5}F(R_c)$ .

(10) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1961: (a) Chapter 4; (b) p 300.

**Table 1.** Separation of the Interelectronic Repulsion of the Ground Term of a  $d^n$  Configuration (Column 2) into a Part That Varies Smoothly through  $d^0$ ,  $d^5$ , and  $d^{10}$  (Column 3) and a Part That Varies Irregularly (Column 4)<sup>a</sup>

$n$	$E_{\text{rep}}(d^n)$	$f(n)$	$[E_{\text{rep}}(d^n) - f(n)]$	
0	0	0	0	0
1	0	$-7F_2 - 63F_4$	$7F_2 + 63F_4$	$7B + 2.8C$
2	$F_0 - 8F_2 - 9F_4$	$F_0 - 14F_2 - 126F_4$	$6F_2 + 117F_4$	$6B + 4.2C$
3	$3F_0 - 15F_2 - 72F_4$	$3F_0 - 21F_2 - 189F_4$	$6F_2 + 117F_4$	$6B + 4.2C$
4	$6F_0 - 21F_2 - 189F_4$	$6F_0 - 28F_2 - 252F_4$	$7F_2 + 63F_4$	$7B + 2.8C$
5	$10F_0 - 35F_2 - 315F_4$	$10F_0 - 35F_2 - 315F_4$	0	0
6	$15F_0 - 35F_2 - 315F_4$	$15F_0 - 42F_2 - 378F_4$	$7F_2 + 63F_4$	$7B + 2.8C$
7	$21F_0 - 43F_2 - 324F_4$	$21F_0 - 49F_2 - 441F_4$	$6F_2 + 117F_4$	$6B + 4.2C$
8	$28F_0 - 50F_2 - 387F_4$	$28F_0 - 56F_2 - 504F_4$	$6F_2 + 117F_4$	$6B + 4.2C$
9	$36F_0 - 56F_2 - 504F_4$	$36F_0 - 63F_2 - 567F_4$	$7F_2 + 63F_4$	$7B + 2.8C$
10	$45F_0 - 70F_2 - 630F_4$	$45F_0 - 70F_2 - 630F_4$	0	0

<sup>a</sup> In column 5, the irregular part is expressed in terms of the Racah parameters,  $B$  and  $C$ .

changes<sup>11</sup> associated with the replacement of the state specified by properties 1–4 above by the real complex. Thus,

$$\begin{aligned} \Delta H_c^\ominus(\text{spher}) &= \Delta H_c^\ominus - \Delta H_{\text{lf}}^\ominus \\ &= \Delta H_c^\ominus - \Delta E_{\text{orb}} - \Delta E_{\text{rep}}(\text{irreg}) - \\ &\quad \Delta E_{\text{rlx}} - \Delta E_{\text{so}} \quad (5) \end{aligned}$$

where  $\Delta E_{\text{so}}$  is the energy associated with the loss of spin–orbit coupling. In the equation,  $\Delta E_{\text{orb}}$  and  $\Delta E_{\text{rep}}(\text{irreg})$  are negative and  $\Delta E_{\text{rlx}}$  and  $\Delta E_{\text{so}}$  are positive. The calculation of each term is described in the following sections. We shall neglect the vibrational effects discussed in ref 9b, as these are small and largely cancel.

### Calculation of $\Delta H_c^\ominus$ , the Standard Enthalpy Change of the Complexing Reaction

In this particular case,  $\Delta H_c^\ominus$  is  $\Delta H_m^\ominus$  for reaction 2 at 298.15 K. Values were calculated by using  $\Delta H_f^\ominus(\text{K}_3\text{MF}_6, \text{s})$ ,<sup>9</sup>  $\Delta H_f^\ominus(\text{K}^+, \text{g})$ ,<sup>12</sup> and  $\Delta H_f^\ominus(\text{F}^-, \text{g})$ .<sup>13</sup> Standard enthalpies of formation of the gaseous tripositive ions were obtained from the equation

$$\begin{aligned} \Delta H_f^\ominus(\text{M}^{3+}, \text{g}) &= \Delta H_f^\ominus(\text{M}, \text{g}) + \sum_{n=1}^{n=3} I_n + \\ & [H_{298}^\ominus - H_0^\ominus](\text{M}^{3+}, \text{g}) + 3[H_{298}^\ominus - H_0^\ominus](\text{e}^-, \text{g}) - \\ & [H_{298}^\ominus - H_0^\ominus](\text{M}, \text{g}) \quad (6) \end{aligned}$$

Here,  $\Delta H_f^\ominus(\text{M}, \text{g})$  was taken from ref 13, except in the case of scandium,<sup>12</sup> and the ionization potentials,  $I_n$ , from ref 14, except for copper<sup>15</sup> and gallium.<sup>12</sup> The necessary values of  $[H_{298}^\ominus - H_0^\ominus]$  have been published,<sup>12</sup> except for those of  $\text{Co}^{3+}(\text{g})$ ,  $\text{Ni}^{3+}(\text{g})$ , and  $\text{Cu}^{3+}(\text{g})$  for which the figures 6.506, 6.234, and 6.200  $\text{kJ mol}^{-1}$ , respectively, were calculated from the energy levels<sup>14,15</sup> of the ions. The resulting values of  $\Delta H_f^\ominus(\text{M}^{3+}, \text{g})$  and  $\Delta H_c^\ominus$ , which in this case is the value of  $\Delta H_m^\ominus(2)$ , are recorded in Table 5. The main uncertainties in the latter arise from those in  $\Delta H_f^\ominus(\text{K}_3\text{MF}_6, \text{s})$ . In ref 9b, these are estimated

- (11) The difference between  $\Delta H_{\text{lf}}^\ominus$  and  $\Delta E_{\text{lf}}^\ominus$  arises from  $p\delta V$  terms and is negligible.  
 (12) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties*; American Institute of Physics: New York, 1982.  
 (13) Chase, M. W.; Davies, C. A.; Downey, J. R.; Fruij, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; American Institute of Physics: New York, 1986.  
 (14) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement 2.  
 (15) Sugar, J.; Musgrove, A. J. *J. Phys. Chem. Ref. Data* **1990**, *19*, 549.

**Table 2.** Values of  $\Delta$ , and of the Racah Parameters,  $B$  and  $C$ , Calculated from the Absorption Spectra of  $[\text{MF}_6]^{3-}$  Complexes

compd	$\Delta/\text{cm}^{-1}$	$B/\text{cm}^{-1}$	$C/\text{cm}^{-1}$	ref
$\text{K}_3\text{TiF}_6$	17 500			17
$\text{K}_3\text{VF}_6$	16 170	645	2662	18
$\text{K}_3\text{CrF}_6$	16 100	647	3334	20
$\text{K}_3\text{MnF}_6$	14 400			23
$\text{K}_3\text{FeF}_6$		700	4000	24
$\text{K}_3\text{CoF}_6$	14 100	765	3672	19
$\text{Rb}_2\text{KNiF}_6$	13 900	750	3375	25
$\text{Cs}_2\text{KCuF}_6$	14 100	658	2285	26

to be  $\pm 20$  (Sc, Ti, V, Cr, Fe, Ga),  $\pm 30$  (Co, Cu), or  $\pm 40$   $\text{kJ mol}^{-1}$  (Mn, Ni). However, these include systematic errors; the uncertainties in the relative values of  $\Delta H_m^\ominus(2)$  are less (ca.  $\pm 10$ ,  $\pm 20$ , or  $\pm 30$   $\text{kJ mol}^{-1}$ , respectively).

### Calculation of $\Delta E_{\text{orb}}$ , the Orbital Stabilization Energy

$\Delta E_{\text{orb}}$  values were calculated from parameters which were obtained by assigning bands in the absorption spectra of  $[\text{MF}_6]^{3-}$  complexes and then fitting the band maxima in the intermediate field approximation.<sup>16</sup> The parameters are shown in Table 2. In all cases except those of  $[\text{VF}_6]^{3-}$ ,  $[\text{MnF}_6]^{3-}$ , and  $[\text{NiF}_6]^{3-}$  eq 1 is valid for high-spin complexes at any field strength, so  $\Delta E_{\text{orb}}$  values could be calculated from it. For the  $d^2$  and  $d^7$  cases, this is not so, and in the intermediate field approximation which we have used in the assignments<sup>16</sup>

$$\Delta E_{\text{orb}} = 7^1/2 B - 3^1/10 \Delta - 1^1/2 \sqrt{(225B^2 + 18B\Delta + \Delta^2)} \quad (7)$$

With  $[\text{NiF}_6]^{3-}$ , this must be supplemented by the small stabilization of the low-spin complex with respect to the high-spin state. The supplement is about  $-1380 \text{ cm}^{-1}$ .<sup>25</sup>

- (16) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; pp 126–7.  
 (17) Reference 9a;  $\Delta$  is the maximum of the envelope of the two bands at 15 600 and 19 200  $\text{cm}^{-1}$ .  
 (18) From the spectrum of ref 9a; bands at 9700, 14 900, and 23 300  $\text{cm}^{-1}$  were assigned like the similar bands of ref 19.  
 (19) Allen, G. C.; El-Sharkawy, G. A. M.; Warren, K. D. *Inorg. Chem.* **1971**, *10*, 2538.  
 (20) The spectrum of ref 19 with the assignment used in refs 21 and 22.  
 (21) Wong, K. Y.; Manson, N. B.; Osborne, G. A. *J. Phys. Chem. Solids* **1977**, *38*, 1017.  
 (22) Dubicki, L.; Ferguson, J.; van Oosterhout, B. *J. Phys. C* **1980**, *13*, 2791.  
 (23) The  $\Delta$  value is an estimate for the regular octahedral complex, obtained from the spectrum of ref 19 using the method of ref 9b.  
 (24) Calculated from the assignment of the bands at 27 000 and 31 900  $\text{cm}^{-1}$  given in ref 19.  
 (25) Reinen, D.; Friebel, C.; Propach, V. *Z. Anorg. Allg. Chem.* **1974**, *408*, 187.  
 (26) Calculated from the spectrum and assignment of the following: Allen, G. C.; Warren, K. D. *Inorg. Chem.* **1969**, *8*, 1895. Pearse's spectrum for  $\text{K}_3\text{CuF}_6$ <sup>26</sup> is similar but less detailed.

**Table 3.** Data Used in the Calculation of  $\Delta E_{\text{rep(irreg)}}$ <sup>a</sup>

	$B_g$	$C_g$	$B'_g$	$C'_g$	$b$	$c$	$-\Delta B$	$-\Delta C$	$-\Delta F_2$	$-\Delta F_4$
TiF <sub>6</sub> <sup>3-</sup>									(310)	(12)
VF <sub>6</sub> <sup>3-</sup>	881	3364	862	3114	0.748	0.855	222	488	292	13.9
CrF <sub>6</sub> <sup>3-</sup>	929	3705	917	3677	0.706	0.907	273	345	322	9.9
MnF <sub>6</sub> <sup>3-</sup>									(325)	(13)
FeF <sub>6</sub> <sup>3-</sup>	1047	4245	941	4574	0.744	0.875	268	531	344	15.2
CoF <sub>6</sub> <sup>3-</sup>	1100	4540	1100	4540	0.695	0.809	336	867	460	24.8
NiF <sub>6</sub> <sup>3-</sup>	1152	4828	1146	4864	0.654	0.694	399	1477	610	42.2
CuF <sub>6</sub> <sup>3-</sup>	1263	4756	1237	4355	0.532	0.525	591	2259	914	64.5

<sup>a</sup> All values in cm<sup>-1</sup> except for  $b$  and  $c$ .

Finally, with [MnF<sub>6</sub>]<sup>3-</sup>, the value obtained from eq 1 must be supplemented by the stabilization brought about by a distortion of regular octahedral coordination. In ref 9b, this was taken to be half the observed separation<sup>19</sup> of the <sup>5</sup>B<sub>1g</sub> and <sup>5</sup>A<sub>1g</sub> states, its contribution to  $\Delta E_{\text{orb}}$  then being -4500 cm<sup>-1</sup>. However, because of the form of the potential energy surfaces for the two states, this is an upper limit, and the value lies between this and a quarter of the observed separation.<sup>10b</sup> We take the average of the two limits (-3400 cm<sup>-1</sup>). The complete set of  $\Delta E_{\text{orb}}$  values, obtained in these ways, is shown in Table 5.

### Calculation of $\Delta E_{\text{rep(irreg)}}$ , the Changes in the Irregularly Varying Part of the Repulsion Energy

The basic method for calculating  $\Delta F_2$  and  $\Delta F_4$  is best illustrated by [VF<sub>6</sub>]<sup>3-</sup>, [CrF<sub>6</sub>]<sup>3-</sup>, [NiF<sub>6</sub>]<sup>3-</sup>, and [CuF<sub>6</sub>]<sup>3-</sup>. In these cases, the bands which are observed in the absorption spectra arise from just three terms of the gaseous M<sup>3+</sup> ions, one of which is the ground term. From the baricenters of the corresponding multiplets in the gaseous ion spectra,<sup>14,15</sup> and the formulas provided by the theory of atomic spectra,<sup>10a</sup> values of the Racah parameters,  $B$  and  $C$ , can be obtained. We call these values  $B'_g$  and  $C'_g$ , where the primes mark the limitation in the range of terms from which they have been derived and the subscripts distinguish gaseous ion values from those of the complex ions in Table 2, which we hereafter denote  $B_c$  and  $C_c$ . The ratios  $B'_c/B'_g$  and  $C'_c/C'_g$  then compare gaseous and complex ion values which have been derived in comparable ways. We call these ratios  $b$  and  $c$ , respectively, and they appear in Table 3 along with the parent values of  $B'_g$  and  $C'_g$ . Table 3 also contains  $B$  and  $C$  values for the gaseous ions obtained without the limitation described above: by a least squares fit of the baricenters of *all* terms arising from the d<sup>n</sup> configurations<sup>14,15</sup> to the formulas given by the theory of atomic spectra.<sup>10a</sup> These figures are denoted  $B_g$  and  $C_g$ . The values of  $\Delta B$  and  $\Delta C$  in step 2 of Figure 1 were then calculated from the following expressions:

$$\Delta B = B_c - B_g = -B_g(1 - b) \quad (8)$$

$$\Delta C = C_c - C_g = -C_g(1 - c) \quad (9)$$

This procedure minimizes errors arising from the variation of parameters with the free-ion value of  $L$ .<sup>27</sup> Table 3 contains the figures for  $\Delta B$  and  $\Delta C$ , along with the corresponding  $\Delta F_2$  and  $\Delta F_4$  which can be obtained from the relations

$$\Delta F_2 = \Delta B + \frac{1}{7}\Delta C \quad (10)$$

$$\Delta F_4 = \frac{1}{35}\Delta C \quad (11)$$

With a slight modification, this procedure can also be used for [FeF<sub>6</sub>]<sup>3-</sup>. Here,  $B'_g$  and  $C'_g$  were calculated from the <sup>6</sup>S → <sup>4</sup>G and <sup>6</sup>S → <sup>4</sup>D transitions in the spectrum of Fe<sup>3+</sup>(g), and  $B'_c$  and  $C'_c$  from the <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>(<sup>4</sup>G) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>(<sup>4</sup>D) transitions in the spectrum of [FeF<sub>6</sub>]<sup>3-</sup>. Such a procedure is appropriate because, for iron(III), the corresponding transitions in the gaseous ion and in the complex are given by the same linear combinations of  $B$  and  $C$ .

In the case of [CoF<sub>6</sub>]<sup>3-</sup>, the low-lying terms of Co<sup>3+</sup>(g), from which the transitions in the complex arise, are very poorly fitted by the theoretical expressions in  $B$  and  $C$ . Here, therefore, we have taken  $B'_c$  and  $C'_c$  from ref 19 and assumed  $B'_g$  and  $C'_g$  to be equal to  $B_g$  and  $C_g$ . With [MnF<sub>6</sub>]<sup>3-</sup>, such calculations are impossible because insufficient levels have been identified in the spectrum of Mn<sup>3+</sup>(g). For K<sub>3</sub>MnF<sub>6</sub> and K<sub>3</sub>TiF<sub>6</sub>, therefore, estimates of  $\Delta F_2$  and  $\Delta F_4$  were read off plots of  $\Delta F_2$  and  $\Delta F_4$  against atomic number which are shown in Figure 3. These estimates are given in parentheses in Table 3.

Values of  $\Delta E_{\text{rep(irreg)}}$  were then calculated as (7 $\Delta F_2$  + 63 $\Delta F_4$ ) for K<sub>3</sub>TiF<sub>6</sub>, K<sub>3</sub>MnF<sub>6</sub>, and K<sub>3</sub>CoF<sub>6</sub> and as (6 $\Delta F_2$  + 117 $\Delta F_4$ ) for K<sub>3</sub>CrF<sub>6</sub> and K<sub>3</sub>CuF<sub>6</sub>. In the d<sup>2</sup> and d<sup>7</sup> cases of K<sub>3</sub>VF<sub>6</sub> and K<sub>3</sub>NiF<sub>6</sub>, the situation is complicated by the fact that the expression for  $\Delta E_{\text{rep(irreg)}}$  depends upon the field strength. In the weak field case when the orbital stabilization energy is -<sup>3</sup>/<sub>5</sub> $\Delta$ , it is (6 $\Delta F_2$  + 117 $\Delta F_4$ ) as in Table 1; in the strong field case, when the orbital stabilization energy is -<sup>4</sup>/<sub>5</sub> $\Delta$ , it is (9 $\Delta F_2$  + 102 $\Delta F_4$ ). As the spectra were assigned in the intermediate field case, when  $\Delta E_{\text{orb}}$  is given by eq 7, we have used the position of  $\Delta E_{\text{orb}}$  between the weak and strong field limits to interpolate the value of  $\Delta E_{\text{rep(irreg)}}$  for the d<sup>2</sup> and d<sup>7</sup> configurations by using the equation

$$\Delta E_{\text{rep(irreg)}} = 6\Delta F_2 + 117\Delta F_4 - \left(\frac{5\Delta E_{\text{orb}}}{\Delta} + 3\right)(3\Delta F_2 - 15\Delta F_4) \quad (12)$$

Table 5 contains the required set of  $\Delta E_{\text{rep(irreg)}}$  values obtained by these different procedures.

### Calculation of the Relaxation Energy, $\Delta E_{\text{rlx}}$

To estimate this quantity, we require the M-F distances in the compounds K<sub>3</sub>MF<sub>6</sub>. Unfortunately these have not yet been determined. However, the M-F distances in the trifluorides ScF<sub>3</sub>, TiF<sub>3</sub>, VF<sub>3</sub>, CrF<sub>3</sub>, FeF<sub>3</sub>, CoF<sub>3</sub>, and GaF<sub>3</sub> are known, and in all these compounds, the metal ion is in octahedral coordination.<sup>28-32</sup> Moreover, scattered determinations of the

(28) Jack, K. H.; Gutmann, V. *Acta Crystallogr.* **1951**, *4*, 246.

(29) Siegel, S. *Acta Crystallogr.* **1956**, *9*, 684.

(30) Hepworth, M. A.; Jack, K. H.; Peacock, R. D.; Westland, G. J. *Acta Crystallogr.* **1957**, *10*, 63.

(31) Knox, K. *Acta Crystallogr.* **1960**, *13*, 507.

(32) Brewer, F. M.; Garton, G.; Goodgame, D. M. L. *J. Inorg. Nucl. Chem.* **1959**, *9*, 56.

(27) Gerloch, M.; Slade, R. C. *Ligand-Field Parameters*; Cambridge University Press: Cambridge, U.K., 1973; pp 54-9.

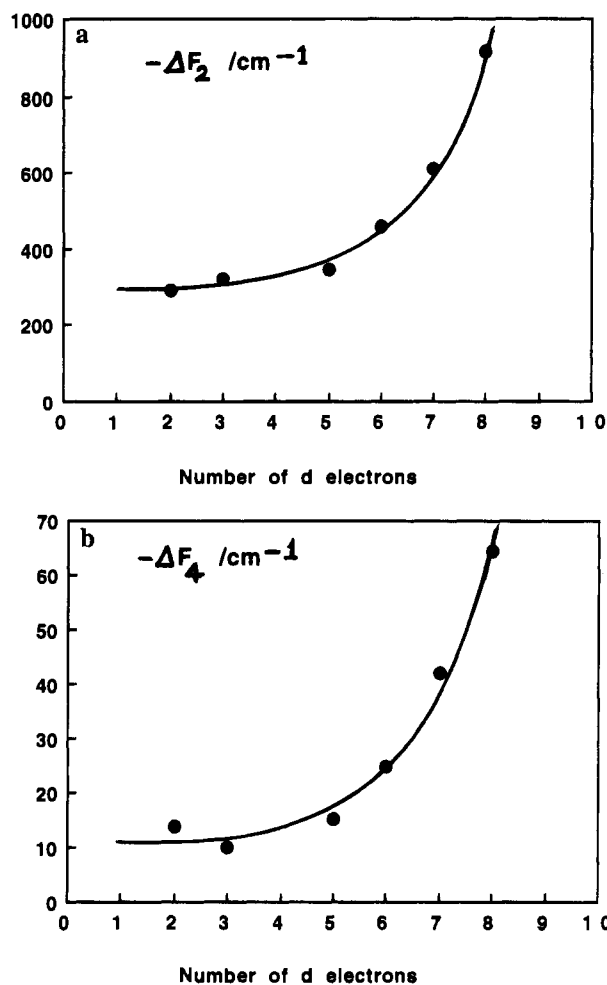


Figure 3. Values of (a)  $-\Delta F_2$  and (b)  $-\Delta F_4$ , for the complexes  $MF_6^{3-}$ , plotted against the number of d electrons in the  $M^{3+}$  ions.

Table 4. Data Used in the Estimation of  $\Delta E_{rlx}$

	$r(M-F)/\text{pm}$	$r_{\text{spher}}(M-F)/\text{pm}$	$\Delta r/\text{pm}$	$\Delta E_{rlx}/\text{kJ mol}^{-1}$
Sc	202	202	0	0
Ti	197	199	2	2
V	194	197	3	5
Cr	190	195	5	14
Mn	(191)	193	2	2
Fe	192	192	0	0
Co	189	191	2	2
Ni		190	(3)	5
Cu		189	(5)	14
Zn				
Ga	189	189	0	0

internuclear distances in compounds containing the  $[MF_6]^{3-}$  complexes suggest a close similarity to those in the trifluorides.<sup>33</sup> We have therefore taken the M–F distances in  $K_3ScF_6$ ,  $K_3TiF_6$ ,  $K_3VF_6$ ,  $K_3CrF_6$ ,  $K_3FeF_6$ ,  $K_3CoF_6$ , and  $K_3GaF_6$  to be identical with those in the trifluorides, and these are recorded in Table 4 as  $r(M-F)$ . For  $K_3MnF_6$ , we require the value in regular octahedral coordination, and this was taken to be the average of  $r(Cr-F)$  and  $r(Fe-F)$ .

The M–F distances in the hypothetical spherical-ion complexes are shown in column 3 of Table 4. These were estimated from a parabolic baseline through the values for scandium, iron, and gallium.  $\Delta E_{rlx}$  can then be estimated by using the valence

Table 5. Data Used in the Calculation of  $\Delta H_c^\ominus(\text{spher})$  from  $\Delta H_c^\ominus$  (Columns 8 and 3) by Using Eq 5<sup>a</sup>

	$\Delta H_c^\ominus(M^{3+}, g)$	$\Delta H_c^\ominus$	$\Delta E_{orb}$	$\Delta E_{rep}(\text{irreg})$	$\Delta E_{rlx}$	$\Delta E_{so}$	$\Delta H_c^\ominus(\text{spher})$
Sc	4652	-8001	0	0	0	0	-8001
Ti	5112	-8337	-84	-35	2	1	-8221
V	5426	-8464	-140	-45	5	3	-8287
Cr	5648	-8637	-231	-37	14	5	-8388
Mn	5779	-8640	-144	-37	2	4	-8465
Fe	5715	-8534	0	0	0	0	-8534
Co	6084	-8730	-67	-57	2	5	-8613
Ni	6333	-8903	-134	-110	5	14	-8678
Cu	6614	-9034	-202	-156	14	16	-8706
Zn	6621						
Ga	5812	-8825	0	0	0	0	-8825

<sup>a</sup> All values in  $\text{kJ mol}^{-1}$ .

force field approximation<sup>34,35</sup> in the following form:

$$\Delta E_{rlx} = 12\pi^2\nu^2[m(F^-)](\Delta r)^2 \quad (13)$$

Here,  $\Delta r$  is the contraction when the spherical ion complex is converted to the real complex,  $\nu$  is the symmetrical stretching frequency, and  $m(F^-)$  is the mass of the ligand. The frequency  $\nu$  is typically<sup>36-39</sup> about  $520 \text{ cm}^{-1}$ , and eq 13 then becomes

$$\Delta E_{rlx}/\text{kJ mol}^{-1} = 0.5468(\Delta r/\text{pm})^2 \quad (14)$$

$\Delta r$  is the difference between columns 2 and 3 of Table 4. To estimate the unknown values of  $\Delta r$  for high-spin  $K_3NiF_6$  and for  $K_3CuF_6$ , it was assumed that the  $\Delta r$  values for the  $d^6 \rightarrow d^8$  complexes are identical with those observed for  $d^1 \rightarrow d^3$  in the first half of the series. Equation 14 then gives the values of  $\Delta E_{rlx}$  shown in column 6 of Table 4.

#### Calculation of the Spin–Orbit Coupling Energy, $\Delta E_{so}$

This was taken to be equal to the stabilization of the ground state of the gaseous  $M^{3+}$  ion, with respect to the barycenter of the ground term, minus the corresponding quantity for the complex, each adjusted for the thermal population of excited states at 298.15 K. Energy levels for the gaseous ions were taken from the literature.<sup>14,15</sup> Spin–orbit splittings in the complexes were calculated from the formulas given by Figgis,<sup>40</sup> with the coupling parameter  $\lambda$  equal to  $1/2(b+c)$  times the value for the gaseous ion. The value of  $\lambda$  that was obtained in this way for  $VF_6^{3-}$  ( $84 \text{ cm}^{-1}$ ) compares very favorably with the experimental value<sup>41</sup> of  $80 \text{ cm}^{-1}$ . The factor  $A$  for the  $d^2$  ion was interpolated between 1.5 (weak-field limit) and 1.0 (strong-field limit) by following the procedure used for  $\Delta E_{rep}(\text{irreg})$  (eq 12).

#### Discussion

In Table 5,  $\Delta H_c^\ominus(\text{spher})$  has been calculated by removing  $\Delta E_{orb}$ ,  $\Delta E_{rep}(\text{irreg})$ ,  $\Delta E_{rlx}$ , and  $\Delta E_{so}$  from  $\Delta H_c^\ominus$ . Figure 4 shows how this eliminates the cusp at iron and leaves values which lie on, or close to, a smoothly curved baseline. As Figure 2 has shown, the usual treatment which removes  $\Delta E_{orb}$  alone

(34) Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand-Reinhold: New York, 1945; pp 168–186.

(35) Johnson, D. A.; Nelson, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 1.

(36) Wiegardt, K.; Eysel, H. H. *Z. Naturforsch. B* **1970**, 25, 105.

(37) Becker, R.; Sawodny, W. *Z. Naturforsch. B* **1973**, 28, 360.

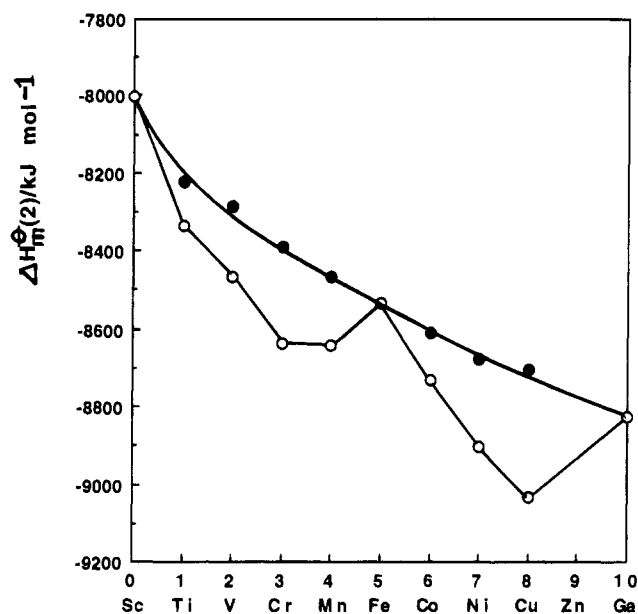
(38) Barker, S. L.; Kettle, S. F. A. *Spectrochim. Acta, Part A* **1978**, 34, 83.

(39) Sliwczuk, U.; Bartram, R. H.; Gabbe, D. R.; McCollum, B. C. *J. Phys. Chem. Solids* **1991**, 52, 357.

(40) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966; p 269.

(41) Machin, D. J.; Murray, K. S. *J. Chem. Soc. A* **1967**, 1498.

(33) See, for example: Yin, Y.; Kexler, A. *Chem. Mater.* **1992**, 4, 645. Kummer, S.; Babel, D. *Z. Naturforsch. B: Chem. Sci.* **1987**, 42, 1403.



**Figure 4.** Plot showing that removal of all four contributions to the ligand field stabilization energy that have been considered in this paper from  $\Delta H_m^{\ominus}(2)$  (open circles) leaves values (filled circles) that lie close to a smooth curve through the values at the  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations.

does not do this. The difference is due mainly to the term  $\Delta E_{\text{rep}}(\text{irreg})$ , which is 15–45% of  $\Delta E_{\text{orb}}$  in the first half of the series and 75–100% of  $\Delta E_{\text{orb}}$  in the second. The higher values in the second half of the series are due to the greater nephelauxetic effect in the later members, as shown by the values of  $b$  and  $c$  in Table 3.

In Figure 4, the smooth curve through the elements with  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations is not parabolic: there is a steep fall from scandium to titanium, but this is followed by a leveling off toward a more gentle, nearly linear decrease in the remainder of the series. On reflection, the discontinuity is not surprising: the so-called outer  $d^0$  configuration of  $\text{Sc}^{3+}$  is actually  $3p^6$ , and the step in which the first  $d$  electron is added to it is qualitatively different from those in which subsequent  $d$  electrons are acquired. Strictly speaking, the  $3p^1 \rightarrow 3p^6$  series should be treated separately from the  $3d^1 \rightarrow 3d^{10}$ . Indeed, what is surprising is that although the  $3d$  orbitals are higher in energy than the  $3p$ , Figure 4 suggests that, at zero ligand field, there is a contraction in size between  $\text{Sc}^{3+}$  and  $\text{Ti}^{3+}$  akin to that which occurs subsequently in the series. However, the contraction is consistent with the outer radial maxima in the charge density distributions provided by self-consistent field calculations.<sup>42</sup> In  $\text{Sc}^{3+}$ , the  $3p$  maximum occurs at 51 pm; in  $\text{Ti}^{3+}$ , the  $3p$  and  $3d$  maxima are both at 48 pm. Presumably the inner parts of the charge density distribution determine the energy and are more compact for  $3p$  than for  $3d$ , but the outer parts which determine ionic size are not.

The arguments of this paper have been developed through the hexafluorometalates(III) because these provide the clearest illustrative example. The arguments are, however, quite general, and they raise wider questions. First, there is the problem of a physical explanation of the important contribution from the interelectronic repulsion energy that we have introduced. This can be analyzed by dividing the energy into the Coulomb part and the exchange part.<sup>43,44a</sup> The former increases approximately uniformly as  $1/2n(n-1)$  and therefore changes smoothly with  $n$ , but the latter, which exercises a stabilizing influence, does

**Table 6.** Number of Pairs of Electrons with Parallel Spins in the Ground States of  $d^n$  Configurations, Compared with That Given by a Linear  $d^0$ ,  $d^5$ , and  $d^{10}$  Baseline

	pairs of parallel spins		
	ground state	baseline	baseline excess
$d^0$	0	0	0
$d^1$	0	2	2
$d^2$	1	4	3
$d^3$	3	6	3
$d^4$	6	8	2
$d^5$	10	10	0
$d^6$	10	12	2
$d^7$	11	14	3
$d^8$	13	16	3
$d^9$	16	18	2
$d^{10}$	20	20	0

not: it is roughly proportional to the number of pairs of electrons with parallel spins. In Table 6, we give the number of such pairs for the ground state of each configuration,<sup>44</sup> alongside the values implied by the linear variation through those for  $d^0$ ,  $d^5$ , and  $d^{10}$ . There is a deficiency of two at  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$  and of three at the  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$  configurations.<sup>45</sup> Thus these states are destabilized with respect to the baseline variation in both the gaseous ion and the complex, but the *reduction* in the destabilizations caused by the nephelauxetic effect in reactions such as eq 2 amounts to a contribution to the ligand field stabilization energy. Put another way, the  $d^5$  and  $d^{10}$  ions lose some of their exchange energy advantage in their complexes, making the complexes of the other  $d^n$  ions ( $n > 0$ ) relatively more stable. This is why the  $d^1$  complex is stabilized by changes in interelectronic repulsion energy, even though the  $d^1$  ion itself experiences no  $d$ -electron repulsion whatsoever. This physical interpretation of the irregularities in interelectronic repulsion distinguishes our treatment from a recent nonquantitative discussion of the problem<sup>46</sup> which does not mention the nephelauxetic effect. There the irregularities are attributed to the elimination of exchange interactions between electrons in different orbitals when the degeneracy of those orbitals is removed by the ligand field. If this occurred, the irregularities would be very much greater than they are.

A general explanation of this kind suggests that the influence of irregularities in the changes in interelectronic repulsion energy during complexing reactions should be evident in other series. In fact, they have long been recognized in lanthanide and actinide chemistry. A consistent pattern of irregularities in distribution coefficients of lanthanide(III) complexes was noted by Fidelis and Siekierski<sup>47,48</sup> and has become known as the double-double<sup>48</sup> or tetrad<sup>49</sup> effect. Calls for an explanation were answered by Jørgensen<sup>50</sup> and Nugent<sup>51</sup> in terms which are closely related to the arguments used in this paper. In the lanthanide series, such effects are small because of the small nephelauxetic effect, but recognition is easier because symmetry-

(42) Fraga, S.; Karwowski, J.; Saxena, K. M. S. *Handbook of Atomic Data*; Elsevier: New York, 1976.

(43) Nelson, P. G. Ph.D. Thesis, University of Cambridge, 1962.

(44) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed.; Cambridge Univ. Press: Cambridge, U.K., 1982: (a) pp 154–6; (b) pp 161–2 and problems 6.6–6.9.

(45) These figures are in accord with the formulas of Table 1, if allowance is made for the small stabilization of  $4.5B$  for the ground state of  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$  ions discussed in ref 44b. This changes  $E_{\text{rep}}(\text{irreg})$  in these cases to  $(10.5B + 4.2C)$ . The ratio of this to the value for the  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$  ions ( $7B + 2.8C$ ) is then 3:2.

(46) Gerloch, M.; Constable, E. C. *Transition Metal Chemistry*; VCH: New York, 1994; p 152.

(47) Fidelis, I.; Siekierski, S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 185.

(48) Siekierski, S. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3191.

(49) Peppard, D. F.; Bloomquist, C. A. A.; Horwitz, E. P.; Lewey, S.; Mason, G. W. *J. Inorg. Nucl. Chem.* **1970**, *32*, 339.

(50) Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3127.

(51) Nugent, L. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3485.

related ligand field effects are negligible and so cannot exert the masking effect that they do in the first transition series.

An important challenge to the treatment given here is provided by the hydration energies of the dipositive aqueous ions of the elements  $\text{Ca}^{2+} \rightarrow \text{Zn}^{2+}$ . This is the example which is usually chosen to demonstrate the influence of ligand field stabilization energies. How is it that an approach which simply uses  $\Delta E_{\text{orb}}$  values, and fails to include the other terms considered

here, is so successful? The main reason seems to be that, in the dipositive state, the nephelauxetic effect is smaller. Consequently,  $\Delta E_{\text{rep}}(\text{irreg})$  is of similar magnitude, but of opposite sign, to  $(\Delta E_{\text{rlx}} + \Delta E_{\text{so}})$ , so the sum of these three quantities is small. This will be discussed in a further paper.<sup>52</sup>

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(52) Johnson, D. A.; Nelson, P. G. Submitted for publication.