Ligand-field Stabilization Energies of the First-row Transition-metal Dihalides and their Bearing on the Irving–Williams Rule

David A. Johnson[*,a] **and Peter G. Nelson**[b]
[a] *Department of Chemistry, The Open University, Milton Keynes MK7 6AA, UK*
[b] *School of Chemistry, University of Hull, Hull HU6 7RX, UK*

A new analysis of the ligand-field stabilization energy which allows for contributions from the nephelauxetic effect, is shown to give satisfactory results for solid dihalides of the first transition series. In agreement with the nephelauxetic series, this contribution increases with the size of the halide ligand, and sometimes exceeds 50% in the diiodides. The new treatment seems to be an improvement upon those which equate ligand-field and d-orbital stabilization energies; it suggests that the value of $\Delta_f H^\circ(VI_2, s)$ recommended by the National Bureau of Standards is 30–40 kJ mol^{-1} too negative. The formation of a solid dihalide from aqueous solution is used as a model for formation of an aqueous octahedral halogeno complex. It seems that the weak nephelauxetic effect of water as a ligand contributes to the emergence of the Irving–Williams order of stability in complexing and pseudo-complexing reactions for the oxidation states Mn^{II} ⟶ Zn^{II} in aqueous solution.

Recently we have shown that ligand-field stabilization energies cannot be fully explained without making an allowance for contributions from the nephelauxetic effect.[1] Thus, in the case of the hexafluorometallates(III) of the first transition series, these contributions can be as much as 75–90% of those made by orbital splittings in the octahedral field which, in a traditional treatment, are regarded as the source of ligand-field stabilization energies. The traditional treatment seems acceptable because reliable quantitative tests of it have usually only been performed upon first-row transition-metal compounds in the +2 oxidation state, and especially upon the hexaaqua +2 complexes. In this oxidation state, the nephelauxetic effect is small, and it is particularly so when water is the chosen ligand. Thus the contribution of the nephelauxetic effect to the ligand-field stabilization energies of the dipositive aqueous ions is modest, and it is then largely cancelled out by small destabilizing effects such as the reduced spin–orbit coupling in the complex, and the relaxation energy of the spherical-ion state associated with the contraction of the metal–ligand distance in the octahedral ligand field.[2]

What this suggests is that the influence of the nephelauxetic effect upon ligand-field stabilization energies of compounds in the +2 oxidation state might be detectable in a study of the dihalides. The four halide ligands differ very substantially in their positions in the nephelauxetic series: the nephelauxetic effect of fluoride is very weak; that of iodide is very strong.[3a,4] Thus the difluorides should resemble the hexaaqua +2 complexes in having ligand-field stabilization energies which owe little to the nephelauxetic effect and are well described by the traditional theory. By contrast, the diiodides should be closer to the case of the hexafluorometallates(III): their ligand-field stabilization energies should include a significant nephelauxetic contribution, and fit the traditional theory less well. In this paper, we put these conclusions to a quantitative test.

Calculations

Our approach is similar to the one used for the hexafluorometallates(III).[1] We shall study reactions of the type (1), where X = F, Cl or I, and M runs from calcium to zinc. In all cases except

$$M^{2+}(g) + 2X^-(g) \longrightarrow MX_2(s) \qquad (1)$$

those of CaF_2, $ZnCl_2$ and ZnI_2, the metal ion in the solid is octahedrally co-ordinated by halide ligands.[5] Thus if appropriate adjustments can be made for the three exceptions, reaction (1) can be regarded as a process in which the metal ion enters into octahedral co-ordination, and becomes subject to an octahedral ligand field in a high-spin configuration.

Our analysis[1] separates the departures of the standard enthalpy change of reaction (1), $\Delta H^\circ(1)$, from a smooth variation through the values at the d^0, d^5 and d^{10} configurations into four components: the orbital-stabilization energy of the complex, ΔE_{orb}, the relaxation energy, ΔE_{rlx}, the energy change, ΔE_{so}, due to changes in the spin–orbit coupling, and the change, ΔE_{rep}(irreg.), in the excess interelectronic repulsion energy of the d^n shell, relative to a smooth variation through the d^0, d^5 and d^{10} values. We now calculate a residual, $\Delta H^\circ_{res}(1)$, by subtracting the four components from $\Delta H^\circ(1)$ [equation (2)]; ΔE_{orb} and ΔE_{rep}(irreg.) are negative, ΔE_{rlx} and ΔE_{so} are positive. If the theory is sound, $\Delta H^\circ_{res}(1)$ should vary smoothly with n within experimental error. We now test this prediction by calculating each of the terms on the right-hand side of equation (2).

$$\Delta H^\circ_{res}(1) = \Delta H^\circ(1) - \Delta E_{orb} - \Delta E_{rlx} - \Delta E_{so} - \Delta E_{rep}(\text{irreg.}) \qquad (2)$$

The Values of ΔH° (1).—These were obtained from equation (3). Values of $\Delta_f H^\circ(M^{2+}, g)$ were calculated in ref. 2, and $\Delta_f H^\circ(X^-, g)$ is from the JANAF tables.[6] If a reliable value of $\Delta_f H^\circ(MX_2, s)$ exists $\Delta H^\circ(1)$ can then be calculated. The results are recorded in column 2 of Table 1 where the reference numbers give the source of $\Delta_f H^\circ(MX_2, s)$.

$$\Delta H^\circ(1) = \Delta_f H^\circ(MX_2, s) - \Delta_f H^\circ(M^{2+}, g) - 2\Delta_f H^\circ(X^-, g) \qquad (3)$$

There are special difficulties in obtaining the appropriate figures for CaF_2, $ZnCl_2$ and ZnI_2. Because we are analysing ligand-field stabilization energies in octahedral fields, we need

Table 1 Calculation of $\Delta H^{\ominus}_{\mathrm{res}}(1)$ from $\Delta H^{\ominus}(1)$ by subtraction of the contributions from ΔE_{orb}, ΔE_{rep}(irreg.), ΔE_{rlx} and ΔE_{so}. All energies in kJ mol^{-1}

	$\Delta H^{\ominus}(1)$[a]	$-\Delta E_{\mathrm{orb}}$	$-\Delta E_{\mathrm{rep}}$(irreg.)	ΔE_{rlx}	ΔE_{so}	$\Delta H^{\ominus}_{\mathrm{res}}(1)$
CaF_2[b]	−2620[c]	0	0	0	0	−2620
CrF_2	−2923[7]	92	12	0	2	−2821
MnF_2	−2868[8]	0	0	0	0	−2868
FeF_2	−2958[9]	43	12	2	3	−2908
CoF_2	−3010[8]	61	13	3	5	−2944
NiF_2	−3079[10]	108	14	7	12	−2976
CuF_2	−3082[11]	71	12	0	10	−3009
ZnF_2	−3037[12]	0	0	0	0	−3037
$CaCl_2$	−2253[12]	0	0	0	0	−2253
VCl_2	−2582[13]	134	20	19	2	−2449
$CrCl_2$	−2583[12]	80	21	6	2	−2490
$MnCl_2$	−2535[12]	0	0	0	0	−2535
$FeCl_2$	−2626[12]	33	28	2	3	−2570
$CoCl_2$	−2690[12]	57	37	3	6	−2605
$NiCl_2$	−2769[12]	110	40	6	12	−2637
$CuCl_2$	−2804[d]	—	38	0	10	—
$ZnCl_2$[b]	−2709[c]	0	0	0	0	−2709
CaI_2	−2070[12]	0	0	0	0	−2070
TiI_2	−2325[e]	68	28	18	1	−2248
VI_2	−2419[c]	113	30	18	2	−2296
CrI_2	−2423[12]	66	32	6	2	−2333
MnI_2	−2380[16]	0	0	0	0	−2380
FeI_2	−2481[17]	28	43	2	3	−2415
CoI_2	−2551[18]	52	58	4	6	−2451
NiI_2	−2639[17]	105	61	9	12	−2494
ZnI_2[b]	−2563[c]	0	0	0	0	−2563

[a] The reference numbers given in parentheses indicate the source of the value for $\Delta_f H^{\ominus}(MX_2, s)$. [b] Data refer to structures in which the metallic element is in a regular octahedral co-ordination, see text. [c] Estimated $\Delta_f H^{\ominus}(MX_2, s)$, see text. [d] From $\Delta_f H^{\ominus}(CuCl_2, s) = -218.2 \pm 2$ kJ mol^{-1} obtained by combining the heat of solution (ref. 14) with aqueous-ion data (ref. 12). [e] From ref. 15 and the value of $\Delta_f H^{\ominus}(TiI_4, g)$ in ref. 6.

values of $\Delta_f H^{\ominus}(MX_2, s)$ for these compounds in the octahedrally co-ordinated structures possessed by the other dihalides. In particular, we want values for CaF_2 with the rutile structure, and for $ZnCl_2$ and ZnI_2 with a $CdCl_2$ or CdI_2 layer structure. But CaF_2 has the fluorite structure, and in $ZnCl_2$ and ZnI_2 the zinc is tetrahedrally co-ordinated by halide.[5] Consequently, the experimental values of $\Delta_f H^{\ominus}(MX_2, s)$ refer to substances more stable than those which are relevant, and only put a lower limit on the values that we require. Previous analyses of the ligand-field stabilization energies of dihalides[19] have either ignored or been unaware of this problem.

Our solution is an adaptation of the empirical methods of estimation used by Karapet'yants[20] and Hisham and Benson.[21] A plot of $\Delta_f H^{\ominus}(MF_2, s)$ *vs.* $\Delta_f H^{\ominus}(MCl_2, s)$ for M = Mn, Fe, Co or Ni is linear with a correlation factor 0.997; from it we estimate −1205 kJ mol^{-1} and −395 kJ mol^{-1} for CaF_2 and $ZnCl_2$ respectively in octahedral co-ordination. Likewise, $\Delta_f H^{\ominus}(MF_2, s)$ *vs.* $\Delta_f H^{\ominus}(MI_2, s)$ is linear to $R^2 = 0.990$, and yields −170 kJ mol^{-1} for ZnI_2 in a CdX_2 layer structure. These three values are more positive than those of the naturally occurring forms of the compounds by 15, 20 and 38 kJ mol^{-1} respectively, the correct sign of the deviations adding credence to the estimates. It is these estimates which have provided the $\Delta H^{\ominus}(1)$ values for CaF_2, $ZnCl_2$ and ZnI_2 in Table 1.

The Values of ΔE_{orb}.—These were calculated from parameters which were obtained by assigning bands in the absorption spectra of the dihalides, and by fitting the band maxima to formulae provided by the intermediate-field approximation for O_h symmetry.[3b] For halides in which there is a marked tetragonal distortion, the t_{2g} and e_g levels are treated separately. In the case of this particular problem, that is as far as it is useful to go towards a cellular approach.[22] Extensive use was made of Rosseinsky and Dorrity's excellent review[23] for both data and assignments, although some more recent work has been included. The calculated parameters are shown in Table 2, the symbols having the meanings specified in ref. 1. Values of ΔE_{orb} were then calculated as before; the extra stabilization due to distortions in the d^4 and d^9 dihalides, and in FeF_2, was taken to be $\Delta E/4$, where ΔE is the energy of the longest-wavelength d–d transition.[2]

There are no spectroscopic data available for CrI_2, but the distortion of the octahedron is similar to that found in the other chromium dihalides and in CuF_2.[5] We have therefore estimated the value of ΔE_{orb} by assuming that the values for CrI_2 and $CrCl_2$ are in the same ratio as those for VI_2 and VCl_2. For $CuCl_2$ we have not calculated a value of ΔE_{orb}; no low-temperature spectrum is available, and published room-temperature data[23] show only a single broad band at about 12 000 cm^{-1} with a possible shoulder on the low-energy side. Moreover, the distortion is larger than for the other d^4 and d^9 dihalides in Table 1,[5] and this makes the order of the excited $^2A_{1g}$ and $^2B_{2g}$ states less certain.[41] However, our theory suggests that $-\Delta E_{\mathrm{orb}}$ should be not far short of 100 kJ mol^{-1} for this compound, and this figure is substantially larger than the value for $CrCl_2$. The final set of calculated ΔE_{orb} values is shown in Table 1.

The Values of ΔE_{rep}(irreg.).—The method of calculation is described elsewhere,[1,2] and the results are given in Table 3, the symbols having the meanings specified in ref. 1. Where spectroscopic values of ΔF_2 and/or ΔF_4 are unavailable, figures were estimated by interpolation or extrapolation. With the fluorides, as with the aqueous ions,[2] there is little variation across the series, so average values were used. For the chlorides, and especially the iodides, there is a progressive increase across the series as there is for the hexafluorometallates(III),[1] and estimates were made by linear interpolation. The calculated values of ΔE_{rep}(irreg.) are displayed in Table 1.

The Values of ΔE_{rlx}.—Our previous calculations of relaxation energies[1,2] have dealt with discrete complexes, and used the a_{1g} stretching frequency with the valence force-field approximation[42] to obtain estimates of ΔE_{rlx}. The dihalides, however,

Table 2 Values for Δ and for the Racah parameters B and C calculated from the absorption spectra of the dihalides

	Δ/cm^{-1}	B'_c/cm^{-1}	C'_c/cm^{-1}	Reference
CrF_2[a]	8400			25
MnF_2[b]		708	3640	23
FeF_2[c]	8250			23,27
CoF_2[d]	7650	905	4060	30
NiF_2[e]	7550	965	3750	32
CuF_2[f]	6750			33
VCl_2[g]	9300	615	2720	34
$CrCl_2$[f]	7300			35
$MnCl_2$[b]		623	3500	23,36
$FeCl_2$[f]	7000			23
$CoCl_2$[d]	7050	765	3820	37
$NiCl_2$[e]	7700	813	3470	38
$CuCl_2$[h]	7750			23
TiI_2[i]	8120	494	2200[j]	39
VI_2[g]	7870	529	2640	34
MnI_2[b]		573	3320	23,40
FeI_2[f]	5800			23
CoI_2	6500[k]	640[j]	3610[j]	
NiI_2[e]	7300	685	3250	38

[a] The bands observed at 10 500, 11 620 and 14 670 cm^{-1} at 6 K were assigned to transitions from a $^5B_{1g}$ ground state to the excited states $^5A_{1g}$, $^5B_{2g}$ and ^5E_g in D_{4h} symmetry. The value of Δ was then calculated as in ref. 24. [b] The values of B'_c and C'_c were calculated from the average energies of the $^6A_{1g}\rightarrow{}^4A_{1g}$, $^4E_g(^4G)$ and $^6A_{1g}\rightarrow{}^4E_g(^4D)$ transitions in the cited spectra. This selection is discussed in ref. 1. [c] The treatment was that used for the corresponding complex in ref. 2, followed by reduction of the value of Δ because iron(II) is in an axially compressed environment (ref. 26). The reduction was calculated by assigning the absorption at 1050 cm^{-1} (refs. 27 and 28) to the $^5B_{2g}\rightarrow{}^5E_g$ transition within the $^5T_{2g}$ manifold in D_{4h} symmetry. [d] Values of Δ and B'_c for CoF_2 and $CoCl_2$ were obtained by fitting the three spin-allowed transitions to the formulae given in ref. 29. The chosen values of C'_c put the ^2E_g transition within the envelope of the $^4T_{2g}$ band at about 8000 cm^{-1}. This is consistent with the asymmetry of the band, and with a shoulder at this energy in CoF_2. [e] The method was that used for nickel(II) in ref. 2, C'_c being obtained from the ^1E_g and $^1T_{2g}$ transitions. For NiF_2, the energies used were the average of those obtained when the light is polarized parallel and perpendicular to the c axis. The corrections for intermediate coupling were 300 and 350 cm^{-1} for NiF_2 and NiI_2 respectively. In $NiCl_2$, the central band of the three-band system at 12 700 cm^{-1} was assigned to the unshifted triplet, and the average of the two outer bands to the singlet as in ref. 31. [f] The treatment was that used for the corresponding complex in ref. 2. [g] As footnote f, C'_c being obtained by a best fit to the ^2E_g, $^2T_{1g}$ and $^2T_{2g}$ transitions. [h] See text. [i] Δ and B'_c were obtained by assigning the two observed bands to the $^3T_{1g}(^3F)\rightarrow{}^3T_{2g}$ and $^3T_{1g}(^3F)\rightarrow{}^3T_{1g}(^3P)$ transitions. [j] From estimates in Table 3. [k] Interpolated.

consist of edge-sharing octahedra, so our procedures must be modified. We have retained the idea of a valence force field by assuming that in compounds where the transition-metal ion is spherical and the displacement is small, the variation of the lattice energy, $F(r)$, with respect to the value at the equilibrium internuclear distance r_e, is given by equation (4). Here, k

$$F(r) - F(r_e) = 6[\tfrac{1}{2}k(r - r_e)^2] \qquad (4)$$

fulfils the role of a force constant. We now assume that in compounds containing spherical ions, the overall variation of the lattice energy of a dihalide with internuclear distance is of the form (5).[43] Then, if we take the contraction of the inter-

$$F(r) = -\frac{A}{r} + \frac{B}{r^n} \qquad (5)$$

nuclear distance in the ligand field to be Δr, and use the condition $F'(r_e) = 0$ to eliminate B, $\Delta E_{\rm rlx}$ is given by equation (6). We have estimated Δr by assuming that r_e for the spherical-ion compounds, r_e(s.i.), will vary parabolically through the experimental figures for the calcium, manganese and zinc compounds. The values of n were calculated from Pauling's data,[44] being $7\frac{2}{3}$, 9 and 11 for the fluorides, chlorides and iodides respectively. Preliminary values of $\Delta E_{\rm rlx}$ were then obtained for each series by using the $F(r_e)$ value for the manganese compound. When these were subsequently used to calculate $\Delta H^{\circ}_{\rm res}(1)$, the latter provided an improved value of $F(r_e)$ for that particular compound which, in its turn, could be used to improve $\Delta E_{\rm rlx}$. This change was significant only for the largest $\Delta E_{\rm rlx}$ values, and further cycles made no further improvement. The detailed figures are in Table 4.

$$\Delta E_{\rm rlx} = 3k(\Delta r)^2 = \tfrac{1}{2}(\Delta r)^2 F''(r_e) = -\frac{nF(r_e)(\Delta r)^2}{2r_e^{\,2}} \qquad (6)$$

In the valence force-field approximation, our force constants, k, correspond, for $MnCl_2$ and CoI_2, to a_{1g} stretching frequencies of 212 and 110 cm^{-1} in a discrete complex. The a_{1g} lattice vibration in these compounds is observed[56,57] at about 230 and 120 cm^{-1} respectively. This vibration is a combination of symmetric bending and stretching, but the reasonably good agreement between the experimental and calculated values provides some support for our estimates of $\Delta E_{\rm rlx}$.

The Values of $\Delta E_{\rm so}$.—These were mainly calculated using the procedure and sources of data given in ref. 2. For the titanium and cobalt halides, the coupling parameter was calculated by the method of Cole and Garrett.[58] For CoF_2, $CoCl_2$ and CoI_2, this gave λ = 161, 141 and 123 cm^{-1} respectively. The ratio of these values to the figure for the gaseous ion was then used to estimate λ for FeF_2, $FeCl_2$ and FeI_2 giving 93, 82 and 71 cm^{-1} respectively. The resulting values of $\Delta E_{\rm so}$ are in Table 1.

Discussion

In Table 1, the residuals, $\Delta H^{\circ}_{\rm res}(1)$, for the three kinds of halide have been calculated from equation (2) by removing $\Delta E_{\rm orb}$, $\Delta E_{\rm rep}$ (irreg.), $\Delta E_{\rm rlx}$ and $\Delta E_{\rm so}$ from $\Delta H^{\circ}(1)$. Fig. 1 shows how this eliminates cusps at manganese and leaves values which, in each case, lie close to a smoothly curved baseline. In all three cases, the fit to the parabolic curve is good to $R^2 = 0.999$ or better. Our treatment, therefore, seems to be superior to the traditional one in which $\Delta H^{\circ}_{\rm res}(1)$ is calculated from $\Delta H^{\circ}(1)$ by removal of $\Delta E_{\rm orb}$ alone. To demonstrate this, we have included in the iodide plot [Fig. 1(*c*)] points calculated in the traditional way, and it is apparent that a residual bowl remains in the second half of the series. Such deficiencies in the traditional theory are most apparent for the iodides because, as Table 1 reveals, the values of $\Delta E_{\rm rep}$(irreg.) increase from fluoride to iodide with the size of the halide ligand. This increase, as we noted in our introduction, is exactly what the relative positions of the three halides in the nephelauxetic series would suggest. Past treatments which ignored $\Delta E_{\rm rep}$(irreg.) have seemed fairly satisfactory, either because this term is small and of opposite sign to ($\Delta E_{\rm rlx} + \Delta E_{\rm so}$) as in the fluorides, or because no correction has been made for the four-co-ordinate structures of $ZnCl_2$ and ZnI_2. Without such a correction, the zinc point in Fig. 1(*c*), for example, is depressed by over 30 kJ mol^{-1}, and the traditional treatment then appears more satisfactory. One detailed consequence of our calculation concerns the thermodynamic data on vanadium diiodide. The values of $\Delta H^{\circ}(1)$ and $\Delta H^{\circ}_{\rm res}(1)$ for this compound in Table 1 were obtained using an estimated value of $\Delta_f H^{\circ}(VI_2, s)$ given by Nelson and Sharpe.[16] This was introduced because the National Bureau of Standards' value (−251.5 kJ mol^{-1}) is apparently based upon solution calorimetry[59] involving poorly determined reactions. The good fit that we obtain in Fig. 1(*c*) using the alternative estimate of −213 kJ mol^{-1} means that if the National Bureau of Standards' value is correct, it would create difficulties for our theory.

Table 3 Data used in the calculation of ΔE_{rep}(irreg.)*

	B_g/cm^{-1}	C_g/cm^{-1}	B'_g/cm^{-1}	C'_g/cm^{-1}	b	c	$-\Delta B$/cm^{-1}	$-\Delta C$/cm^{-1}	$-\Delta F_2$/cm^{-1}	$-\Delta F_4$/cm^{-1}
CrF_2									(103)	(4.1)
MnF_2	873	3515	787	3796	0.900	0.959	87	144	108	4.1
FeF_2									(103)	(4.1)
CoF_2	978	4156	971	4209	0.932	0.965	67	145	88	4.1
NiF_2	1080	4150	1056	3880	0.914	0.966	93	141	113	4.0
CuF_2									(103)	(4.1)
VCl_2	762	2906	755	2910	0.815	0.935	141	189	168	5.4
$CrCl_2$									(193)	(6.7)
$MnCl_2$	873	3515	787	3796	0.791	0.922	182	274	221	7.8
$FeCl_2$									(247)	(9.5)
$CoCl_2$	978	4156	971	4209	0.788	0.908	207	382	262	10.9
$NiCl_2$	1080	4150	1056	3880	0.770	0.894	248	440	311	12.6
$CuCl_2$									(330)	(14.0)
TiI_2	711	2516	695	2379	0.711	(0.923)	205	(194)	(233)	(5.5)
VI_2	762	2906	755	2910	0.701	0.907	228	270	267	7.7
CrI_2									(299)	(10.1)
MnI_2	873	3515	787	3796	0.728	0.875	237	439	300	12.5
FeI_2									(378)	(14.7)
CoI_2	978	4156	971	4209	(0.659)	(0.857)	(333)	(595)	(418)	(17.0)
NiI_2	1080	4150	1056	3880	0.649	0.838	379	672	475	19.2

* Values in parentheses are interpolated or extrapolated, see text.

Table 4 Calculation of ΔE_{rlx}

	r_e[a]/pm	r_e(s.i)/pm	Δr/pm	ΔE_{rlx}/kJ mol^{-1}
CaF_2[b]	229[c]	229	0	0
VF_2	208.6[d]	217.9	9.3	21
CrF_2	214[e]	214.8	0.8	0
MnF_2	212.1	212.1	0	0
FeF_2	207.2	209.7	2.5	2
CoF_2	204.0	207.6	3.6	3
NiF_2	200.6	205.8	5.2	7
CuF_2	204[f]	204.4	0.4	0
ZnF_2	203.3	203.3	0	0
$CaCl_2$	274.5[g]	274.5	0	0
VCl_2	254.0	264.9	10.9	19
$CrCl_2$	256[h]	262.1	6.1	6
$MnCl_2$	259.6	259.6	0	0
$FeCl_2$	254.1	257.3	3.2	2
$CoCl_2$	251.1	255.2	4.1	3
$NiCl_2$	247.7	253.3	5.6	6
$CuCl_2$	252[i]	251.6	0	0
$ZnCl_2$[b]	250.2[j]	250.2	0	0
CaI_2	312.0	312.0	0	0
TiI_2	292.5	304.0	11.5	18
VI_2	289.0	300.4	11.4	18
CrI_2	290.7[k]	297.1	6.4	6
MnI_2	294.0	294.0	0	0
FeI_2	288.0	291.2	3.2	2
CoI_2	283.5	288.6	5.1	4
NiI_2	279.0	286.3	7.3	9
ZnI_2[b]	282.5[j]	282.5	0	0

[a] Average values for the octahedron around the metal ion. Unless otherwise stated, fluoride values are from ref. 26, chloride values from refs. 45 and 46 (u being set at 0.25 throughout to generate a systematic comparison) and iodide values from refs. 45 and 47 (u again being set at 0.25). [b] Data refer to structures in which the metallic element is in a regular octahedral co-ordination, see text. [c] Value for a rutile structure calculated from the figure for MnF_2, and the difference in the ionic radii of Ca^{2+} and Mn^{2+} in six co-ordination (ref. 48). [d] Ref. 49. [e] Ref. 50. [f] Ref. 51. [g] Ref. 52. [h] Mean Cr–Cl distance from ref. 53. [i] Ref. 54. [j] Value for a CdX_2 structure, estimated from a linear plot of $r_e(MF_2)$ *vs.* $r_e(MX_2)$ for M = V, Mn, Fe, Co or Ni. [k] Ref. 55.

It is interesting that in the fluorides, the calcium point, where the cation has a p^6 configuration, lies close to the $\Delta H^{\circ}_{\mathrm{res}}(1)$ baseline for the d^n compounds when this is extrapolated to n = 0. A very similar situation occurs with the +2 hexaaqua complexes.[2] By contrast, in the chloride and iodide cases, the extrapolated d^n baseline lies below the calcium point in the chlorides, and well below it in the iodides. This separation of the d^1→d^{10} baseline from the p^6 point was also an outcome of our treatment of the hexafluorometallates(III).[1] We hope to explore these differences further in a subsequent paper.

Finally, we turn to the question of the Irving–Williams rule. We have suggested[2] that the unexpected persistence of this rule for the elements Mn ⟶ Zn can be explained by taking account of the contributions made by the ΔE_{rep}(irreg.) terms to the energies of complexing reactions. A typical nephelauxetic series[3a] shows that only fluoride has a weaker nephelauxetic effect than water. This then implies that, for complexing reactions in *aqueous solution*, the nephelauxetic effect will, with just one exception, *invariably* stabilize the complexes of iron(II), cobalt(II), nickel(II) and copper(II) relative to a baseline stability set by the corresponding complexes of manganese and zinc. Our study of ethylenediamine complexes suggested that the variation in ΔH° could be fully explained only when account was taken of ΔE_{rep}(irreg.) terms.

This test of our theory, however, was not an ideal one because ethylenediamine has a much greater field strength than water, but does not greatly exceed it in nephelauxetic effect. This meant that the ΔE_{rep}(irreg.) terms supported ΔE_{orb} in generating the Irving–Williams order, but played only a subordinate role. This situation seems to be the one which is by far the most common, but our theory raises the possibility of an alternative: an Irving–Williams order might still be observed if the incoming ligand was of comparable or even lower field strength than water, provided it had a substantially larger nephelauxetic effect. It is therefore especially unfortunate that the aqueous dipositive ions do not form stable hexahalogeno-complexes in aqueous solution, because the halides are weak-field ligands which are very well separated in the nephelauxetic series. However, the work done in this and in our previous paper[2] allows us to study pseudo-complexing reactions of the type (7), where X is a halogen. If, as in the case of ZnI_2, the

$$[M(H_2O)_6]^{2+}(aq) + 2X^-(aq) \longrightarrow MX_2(s) + 6H_2O(l) \quad (7)$$

metal ion is not in octahedral co-ordination, we can make it so by an adjustment of $\Delta_f H^{\circ}(MX_2, s)$.

In Table 5, we give $\Delta H^{\circ}(7)$ for X = F or I. Values of $\Delta_f H^{\circ}(X^-, aq)$ were taken from ref. 12. They were combined with $\Delta_f H^{\circ}(M^{2+}, aq)$ from ref. 2, and the values of $\Delta_f H^{\circ}(MX_2, s)$ recommended in this work, to obtain $\Delta H^{\circ}(7)$. The same two sources give us the contributions made by the ΔE_{orb},

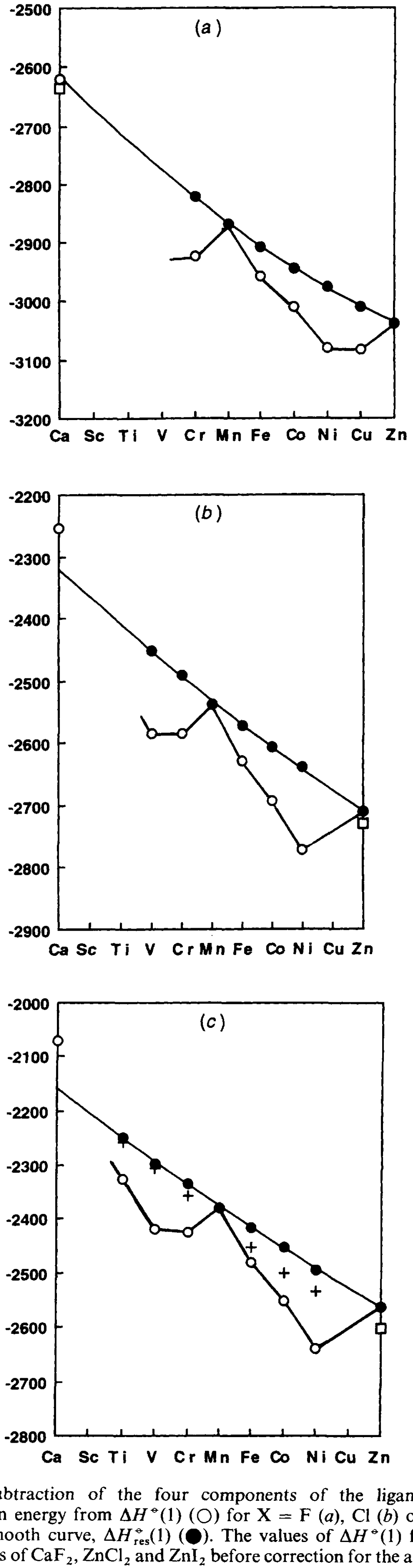

Fig. 1 Subtraction of the four components of the ligand-field stabilization energy from $\Delta H^{\ominus}(1)$ (○) for X = F (*a*), Cl (*b*) or I (*c*) leaves a smooth curve, $\Delta H^{\ominus}_{\text{res}}(1)$ (●). The values of $\Delta H^{\ominus}(1)$ for the stable forms of CaF_2, $ZnCl_2$ and ZnI_2 before correction for the absence of octahedral co-ordination (□) and, for the iodides, the result of subtracting ΔE_{orb} contributions alone (+) are also indicated

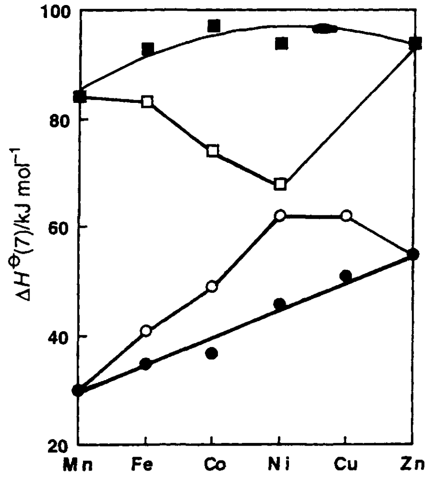

Fig. 2 Values of $\Delta H^{\ominus}(7)$ for X = F (○) or I (□). The residuals left after removal of the contributions from ΔE_{orb}, ΔE_{rep}(irreg.), ΔE_{rlx} and ΔE_{so} are also shown (●, X = F; ■, X = I)

ΔE_{rep}(irreg.), ΔE_{rlx} and ΔE_{so} terms to $\Delta H^{\ominus}(7)$ and these are also shown in Table 5. The values in Table 5 suggest that the ΔE_{rlx} and ΔE_{so} terms make negligible contributions to any irregularities in $\Delta H^{\ominus}(7)$ as one moves across the series. Those irregularities must therefore arise mainly from the ΔE_{orb} and ΔE_{rep}(irreg.) terms. Fluoride has both a lower field strength and a weaker nephelauxetic effect than water,[3a] so, for the $d^6 \rightarrow d^9$ configurations, we expect both the ΔE_{orb} and ΔE_{rep}(irreg.) terms to be positive. Table 5 confirms this expectation. Both d-orbital splittings and the nephelauxetic effect therefore act together to destabilize the fluorides of iron(II), cobalt(II), nickel(II) and copper(II) with respect to the corresponding hexaaqua ions, and the values of $\Delta H^{\ominus}(7)$ should be raised above a manganese–zinc baseline. As Fig. 2 shows, this expectation is fulfilled: the $\Delta H^{\ominus}(7)$ values imply that the stability of the fluorides with respect to reaction (7) follows the sequence Mn > Fe > Co > Ni < Cu < Zn which is the exact opposite of the Irving–Williams order.

If, as current explanations assume, the deviations from the manganese–zinc baseline were due to orbital stabilizations alone, then in the case of the iodides, those deviations should have the same sense as in the fluorides, but they should be of even greater magnitude, because iodide has a lower field strength than both fluoride and water. This low field strength is confirmed by the larger positive ΔE_{orb} contributions for the iodide series in Table 5, but Fig. 2 shows that the values of $\Delta H^{\ominus}(7)$ vary in a way which is the exact opposite of that seen in the fluorides, and that they generate a stability sequence which follows the Irving–Williams order.

According to our theory, the reason for this reversal is the high nephelauxetic effect of the iodide ion: in reaction (7), this stabilizes the iodides of iron, cobalt and nickel with respect to a manganese–zinc baseline, generates the large negative values of ΔE_{rep}(irreg.) in Table 5, and more than offsets the destabilizations introduced by iodide's low ligand-field strength.

In Table 5, we have tried to fix the baseline positions by subtracting the ΔE_{orb}, ΔE_{rep}(irreg.), ΔE_{rlx} and ΔE_{so} contributions from $\Delta H^{\ominus}(7)$ to obtain values of a residual, $\Delta H^{\ominus}_{\text{res}}(7)$. Not much reliance can be placed upon individual values because they have been calculated from the differences between larger quantities like those in Table 1 which themselves have substantial uncertainties. However, Fig. 2 shows that, for both the fluorides and the iodides, the irregularities in $\Delta H^{\ominus}(7)$ are largely eliminated when $\Delta H^{\ominus}_{\text{res}}(7)$ is calculated using our analysis. This is especially significant for the iodides, because the conventional theory would have the opposite effect: consideration of only ΔE_{orb} would cause those irregularities to be magnified.

Table 5 The values of $\Delta H^\circ(7)$ for X = F or I and the calculation of $\Delta H^\circ_{\text{res}}(7)$ by removal of the contributions from ΔE_{orb}, ΔE_{rep}(irreg.), ΔE_{rlx} and ΔE_{so}. All energies in kJ mol^{-1}

	$\Delta H^\circ(7)$	ΔE_{orb}	ΔE_{rep}(irreg.)	ΔE_{rlx}	ΔE_{so}	$\Delta H^\circ_{\text{res}}(7)$
MnF_2	30	0	0	0	0	30
FeF_2	41	2	4	0	0	35
CoF_2	49	7	6	−2	−1	39
NiF_2	62	15	4	−3	0	46
CuF_2	62	9	4	−2	0	51
ZnF_2	55	0	0	0	0	55
MnI_2	84	0	0	0	0	84
FeI_2	83	17	−27	0	0	93
CoI_2	74	16	−39	−1	0	98
NiI_2	68	18	−43	−1	0	94
ZnI_2*	94	0	0	0	0	94

* Data refer to a hypothetical CdI_2 or $CdCl_2$ structure.

The iodide example supports Williams' objections[60] to the traditional explanation of the Irving–Williams rule. Our nephelauxetic contribution corresponds, to some extent, to his ideas about the importance of radially or spherically symmetrical polarization. The energy changes affected by this polarization do not change smoothly between d^5 and d^{10}. Our physical explanation[1] attributes this to the fact that the ground states of $d^6 \longrightarrow d^9$ configurations have fewer pairs of parallel spins than the $d^5 \longrightarrow d^{10}$ baseline implies, and they are therefore relatively destabilized by excess interelectronic repulsion within the d shell. This destabilization generates a corresponding stabilization in a process such as reaction (7) for X = I, when the enhanced nephelauxetic effect of the iodide ion relieves the excess repulsion.

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