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Factors Determining the Ligand Field Stabilization Energies of the Hexaaqua 2+ Complexes of the First Transition Series and the Irving−Williams Order

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A new analysis of the ligand field stabilization energy, which makes allowance for the nephelauxetic effect, is shown to give satisfactory results for the hexaaqua 2+ complexes of the first transition series. Previous treatments only considered d-orbital splitting energies, and they seem successful because irregularities in the changes in interelectronic repulsion energy during complex formation are counterbalanced by those in spin-orbital coupling energies, and in the relaxation energies associated with the contraction in internuclear distance brought about by the effects of the ligand field. The weak nephelauxetic effect of water as a ligand contributes to the emergence of the Irving−Williams order of stability in complexing reactions of $Mn^{2+} \rightarrow Zn^{2+}$ ions in aqueous solution. This is established with thermodynamic and spectroscopic data on ethylenediamine complexes.

Recently, there has been a renewed interest in those properties of the dipositive aqueous ions of the first transition series that are usually explained by using ligand field theory. Careful determinations of metal−oxygen distances in the $[M(H_2O)_6]^{2+}$ complexes have been made,[1,2] along with *ab initio* SCF calculations of both Jahn−Teller stabilization energies in the chromium(II) and copper(II) complexes[3] and the energies of hydration of the gaseous ions.[4] These all-electron calculations obtained binding energies for the gaseous complexes, $[M(H_2O)_6]^{2+}$, which lie on a double-humped shaped curve. The ligand field stabilization energies, relative to a parabolic baseline, are about 60% of those in the experimentally observed variation in the hydration energies of $M^{2+}(g)$ when the latter are calculated from the data in our Table 1 (e.g. for cobalt, the respective values are 43 and 74 kJ mol^{-1}). The discrepancy was attributed to the hydration energies of $[M(H_2O)]_6^{2+}$, but these seem to be too small to explain the differences completely. Thus, estimated values for manganese, cobalt and zinc[5] give, relative to a linear baseline, a stabilization for cobalt of 15 kJ mol^{-1}. This is only half the observed discrepancy of 31 kJ mol^{-1} for this element. Such difficulties suggest that the empirical ligand field approach still retains an important explanatory role in the interpretation of thermodynamic properties.

In a recent paper,[6] we have shown that the customary interpretation of ligand field stabilization energies is defective: the ligand field stabilization energies of the hexafluorometalate(III) complexes of the first transition series cannot be adequately explained without consideration of the nephelauxetic effect. According to the Slater−Condon−Shortley theory of many electron atoms, the interelectronic repulsion in the $3d^n$ subshell does not vary smoothly with n: when the d^1, d^4, d^6, and d^9 configurations are compared with a smooth curve through d^0, d^5, and d^{10}, they have an excess repulsion energy of $(7F_2 + 63F_4)$ or, in terms of the Racah parameters, $(7B + 2.8C)$. For the d^2, d^3, d^7, and d^8 configurations, this excess is $(6F_2 + 117F_4)$ or $(6B + 4.2C)$. When a complex is formed by the combination of a gaseous transition metal ion with ligands, the nephelauxetic effect ensures that ΔB and ΔC are negative, and the excess repulsion energies emerge as stabilizing contributions to the ligand field stabilization energies. In the case of the hexafluorometalates(III), these contributions can be as much as 75−90% of those made by orbital splittings in the octahedral field which, in traditional treatments,[7] are regarded as the source of ligand field stabilization energies.

Table 1. Calculation of $\Delta H^\ominus(1)$

	$\Delta H_f^\ominus(M^{2+},g)$/ kJ mol^{-1}	$\Delta H_f^\ominus(M^{2+},aq)$/ kJ mol^{-1}	$\Delta H^\ominus(1)$/ kJ mol^{-1}
Ca	1925.5	−542.8	−2468
V	2592.7	−221	−2814
Cr	2655.5	−143.5	−2799
Mn	2522.0	−220.8	−2743
Fe	2752.2	−91.2	−2843
Co	2845.7	−58.2	−2904
Ni	2931.8	−54.0	−2986
Cu	3053.4	64.8	−2989
Zn	2782.5	−153.9	−2936

The reasons for these irregularities in interelectronic repulsion lie in the exchange interactions between pairs of electrons with parallel spins in the ground states of the d^n configurations.[6] The number of such pairs does not increase smoothly with n: relative to a linear variation through the numbers at the d^0, d^5, and d^{10} configurations, there is a deficiency of two at d^1, d^4, d^6, and d^9, and of three at d^2, d^3, d^7, and d^8. 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 when the

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complex ion is formed, amounts to a contribution to the ligand field stabilization energy. Although these contributions may, as we have seen, be substantial, they are nothing like as great as they would be if, as was suggested in a recent qualitative discussion of the problem,[8] exchange interactions between electrons in different d orbitals were eliminated when the degeneracy of those orbitals is removed by the ligand field.

The hydration energies of the dipositive ions of the first row transition metals are a crucial test of this new method of analysis. Not only were they used to establish the traditional approach,[9,10] but they also frequently appear in inorganic chemistry textbooks as a proof of its worth. There is no doubt that removal of the orbital stabilization energies, caused by the octahedral field in $[M(H_2O)_6]^{2+}$, from the double-bowl-shaped variation in the hydration energies of the M^{2+} ions, does leave something close to a smooth curve through the ions with d^0, d^5, and d^{10} configurations. We must therefore establish that this is a special case, in which the additional contributions to ligand field stabilization energies, which we introduced in our new treatment, are either negligible or largely cancel one another out.

Our approach is very similar to the one used for the hexafluoro metalates(III).[6] The hydration reaction that we shall study is the one used by George and McClure:[7]

$$M^{2+}(g) + 2H^+(aq) + 2e^-(g) = M^{2+}(aq) + H_2(g) \quad (1)$$

The standard enthalpy changes at 298.15K, $\Delta H^\ominus(1)$[11] can be established by purely experimental means, and are given by

$$\Delta H^\ominus(1) = \Delta H^\ominus_f(M^{2+},aq) - \Delta H^\ominus_f(M^{2+},g) \quad (2)$$

In the absence of competing ligands, there is strong evidence[12,13] that, in all cases except calcium, the M^{2+} ion in aqueous solution is octahedrally coordinated by water molecules within its primary coordination sphere. We shall therefore regard reaction 1 as a process in which the gaseous ions enter into octahedral coordination, and become subject to an octahedral ligand field in a high-spin configuration; deviations at calcium are considered later.

According to our theory,[6] the departures of the standard enthalpy change of reaction 1, $\Delta H^\ominus(1)$, from a smooth variation have four components:

1. The orbital stabilization energy of the complex, ΔE_{orb}, caused by d orbital splitting in the octahedral ligand field.
2. The relaxation energy, ΔE_{rlx}, introduced by the contraction of the metal−ligand distance in the octahedral ligand field.
3. The energy change ΔE_{so} induced by the change in the stabilization of the ground state by spin−orbit coupling when the gaseous ion forms the complex.
4. The change ΔE_{rep}(irreg) in the excess interelectronic repulsion energy of the d^n shell, relative to a smooth variation through the values for the d^0, d^5, and d^{10} configurations.

George and McClure[7] made allowances for components 1 and 3, noting that these did not fully eliminate the irregularities in the $\Delta H^\ominus$ variation for equation 1, and other similar reactions. They also remarked that inclusion of component 2 would worsen this discrepancy between thermodynamic and spectroscopic values of the ligand field stabilization energies, saying, "we will leave it to some future investigation to determine a more exact relationship between them." By including component 4, this paper tries to fulfil that role. We calculate a residual, $\Delta H^\ominus_{res}(1)$, by subtracting the four components from $\Delta H^\ominus(1)$:

$$\Delta H^\ominus_{res}(1) = \Delta H^\ominus(1) - \Delta E_{orb} - \Delta E_{rlx} - \Delta E_{so} - \Delta E_{rep}(\text{irreg}) \quad (3)$$

In this equation, ΔE_{orb} and ΔE_{rep}(irreg) are negative; ΔE_{rlx} and ΔE_{so} are positive. If the theory is sound, $\Delta H^\ominus_{res}(1)$ 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 eq 3.

The Values of $\Delta H^\ominus$(1)

These were calculated from eq 2, and the results are shown in Table 1. Values of $\Delta H^\ominus_f(M^{2+},g)$ were obtained from the equation

$$\Delta H^\ominus_f(M^{2+},g) = \Delta H^\ominus_f(M,g) + I_1 + I_2 + [H^\ominus_{298} - H^\ominus_0](M^{2+},g) + 2[H^\ominus_{298} - H^\ominus_0](e^-,g) - [H^\ominus_{298} - H^\ominus_0](M,g) \quad (4)$$

Ionization energies, I_n, were from ref 14 and 15, except for those of zinc.[16] Enthalpies of atomization of the metals,[17] and $[H^\ominus_{298} - H^\ominus_0]$ values,[16] were taken from standard compilations. $\Delta H^\ominus_f(M^{2+},aq)$ values were from ref 16, except for those of iron and cobalt[18] and those of vanadium, where the figure was obtained by combining $\Delta G^\ominus_f(V^{3+},aq)$[18] with $E^\ominus(V^{3+}|V^{2+})$,[19] $S^\ominus_m(V,s)$,[16] and the value $S^\ominus_m(V^{2+},aq) = -114$ J K^{-1} mol^{-1} estimated by the method of ref 18.

In this paper, it is the *relative* values of $\Delta H^\ominus(1)$ that are important, and their uncertainties can be obtained from those in $\Delta H^\ominus_f(M,g)$,[17,20] the ionization energies,[21] and $\Delta H^\ominus_f(M^{2+},aq)$. We estimate those in the latter quantity to be, in kJ mol^{-1}, ±1 (Cu, Zn), ±2 (Ca, Mn, Fe, Co, Ni), and ±10 (V, Cr). Putting the assessments for the three contributions together, the uncertainties in the *variation* in $\Delta H^\ominus(1)$ become, in kJ mol^{-1}, ±1(Zn), ±2 (Cu), ±3 (Ca, Fe, Ni), ±5 (Mn), ±6 (Co) and ±12 (V, Cr).

The Values of ΔE_{orb}

These were calculated from parameters which were obtained by assigning bands in the absorption spectra of $[M(H_2O)_6]^{2+}$ complexes, and by fitting the band maxima to formulas provided by the intermediate field approximation.[22a] The calculated parameters are shown in Table 2. As we are dealing with the

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Table 2. Values of Δ, the Splitting of the d Orbitals in a Regular Octahedral Ligand Field, and of the Racah Parameters *B* and *C* for the Complexes $[M(H_2O)_6]^{2+}$

complex	Δ/cm^{-1}	*B*/cm^{-1}	*C*/cm^{-1}	ref
$[V(H_2O)_6]^{2+}$	12 300	633	2728	23
$[Cr(H_2O)_6]^{2+}$	9 250			24
$[Mn(H_2O)_6]^{2+}$		687	3626	25
$[Fe(H_2O)_6]^{2+}$	9350			26
$[Co(H_2O)_6]^{2+}$	8400	855	4020	27
$[Ni(H_2O)_6]^{2+}$	8600	940	3702	28
$[Cu(H_2O)_6]^{2+}$	7850			see text

thermodynamics of formation of aqueous ions, solution spectra were used wherever possible. The one case where this caused difficulties was that of $[Cu(H_2O)_6]^{2+}$: the solution spectrum[29] covers the region above 9000 cm^{-1} and includes two bands, but the reflectance spectra of solids containing this complex[30] have three, there being an additional band in the 6000−8000 cm^{-1} range. As the positions of the two high energy bands in the reflectance spectrum of $K_2Cu(ZrF_6)_2{\cdot}6H_2O$ match those of the aqueous ion most closely, we have used the spectrum of this solid[30] to calculate Δ for the aqueous ion by assuming a tetragonal distortion and assigning the bands at 7800, 9760, and 12 740 cm^{-1} to transitions from the ground state, $^2B_{1g}$, to the excited states $^2A_{1g}$, $^2B_{2g}$, and ^2E_g, respectively. We then estimate Δ = 7850 cm^{-1} for the regular octahedral complex with the method previously used[31] for MnF_6^{3-}.

Values of ΔE_{orb} can now be calculated from the data in Table 2. For the vanadium, manganese, iron, and nickel complexes, these are $-6\Delta/5$, 0, $-2\Delta/5$ and $-6\Delta/5$, respectively. For the cobalt complex the intermediate field approximation gives:[6]

$$\Delta E_{orb} = 7^1/_2 B - {}^3/_{10}\Delta - {}^1/_2(225B^2 + 18B\Delta + \Delta^2)^{1/2} \quad (5)$$

In the case of the chromium and copper complexes, the values of $-3\Delta/5$ must be supplemented by the stabilization, E_{JT}, brought about by the Jahn−Teller distortion of the regular octahedral coordination. Usually,[32−34] E_{JT} is taken to be $\Delta E/4$ where ΔE is the energy of the longest-wavelength d−d transition which occurs at 9500 and 7800 cm^{-1} in $[Cr(H_2O)_6]^{2+}$, and $[Cu(H_2O)_6]^{2+}$ respectively. As we have remarked elsewhere,[6] this gives a lower limit which corresponds to the case where there is no difference between the potential energy minima of the axially compressed and axially elongated states of the octahedron. An upper limit of $\Delta E/2$ is reached when the energy difference, *a*, between the two minima is equal to E_{JT}. Theoretical calculations on the chromium and copper complexes[3] imply a/E_{JT} values of 0.1−0.3 and suggest the lower limit is much the more appropriate. The value $\Delta E/4$ has therefore been used in our calculations. The complete set of ΔE_{orb} values is shown in Table 5.

The Values of ΔE_{rep}(irreg)

The method of calculation has already been described,[6] and the results are given in Table 3 where the symbols have the meanings specified in ref 6. Data on the energy levels of the gaseous ions were taken from references 14 and 15. The important differences from the results obtained in reference 6 are that the values of ΔF_2 and ΔF_4 are less than half those calculated for MF_6^{3-} and that they show no significant variation across the series. The estimated figures for the chromium, iron and copper complexes were therefore obtained by averaging those for the other complexes in the table. The values of ΔE_{rep}(irreg) to which the data in Table 3 give rise are shown in Table 5. The interpolation procedure for the d^7 complex was described in ref 6.

The Values of ΔE_{rlx}

As before,[6] we use the valence force field approximation in the following form:

$$\Delta E_{rlx} = 12\pi^2\nu^2 m(H_2O)(\Delta r)^2 \quad (6)$$

Here, Δr is the contraction in the metal−ligand distance when the spherical ion complex is converted to the real complex, and $m(H_2O)$ is the mass of the ligand. The frequency ν is that of the A_{1g} stretching vibration in the regular octahedral complex. Values for the aqueous ions[35] suggest that it is about 360 cm^{-1} in the first half of the series and 380 cm^{-1} in the second. Equation 6 then becomes

$$\Delta E_{rlx}/\text{kJ mol}^{-1} = K(\Delta r/\text{pm})^2 \quad (7)$$

where *K* takes the values 0.2485 and 0.2769 respectively.

To estimate values of Δr, we have assumed that in aqueous solutions of the complexes, the $M{-}OH_2$ distances are identical with the average of those in the octahedra of water molecules surrounding the metal ion in the ammonium Tutton salts. Although the hexafluorosilicates also provide a carefully studied isostructural series containing the hexaaqua complexes, we have not used this because of the suggestion[1,36] that, in these compounds, the metal−oxygen distances may be significantly affected by crystal forces. Support for the suggestion is provided by measurements of metal−oxygen distances in aqueous solution; although these have larger uncertainties, their variation between manganese and zinc[37,38] is more like that seen in the Tutton salts than in the hexafluorosilicates. The chosen values in column 2 of Table 4 are therefore the averages of those obtained from accurate published determinations[1,39−47] of the crystal structures of the ammonium Tutton salts at room temperature.

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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}
$[V(H_2O)_6]^{2+}$	762	2906	755	2910	0.838	0.937	123	183	149	5.2
$[Cr(H_2O)_6]^{2+}$									(143)	(5.1)
$[Mn(H_2O)_6]^{2+}$	873	3515	787	3796	0.873	0.955	111	158	134	4.5
$[Fe(H_2O)_6]^{2+}$									(143)	(5.1)
$[Co(H_2O)_6]^{2+}$	978	4156	971	4209	0.880	0.955	117	187	144	5.3
$[Ni(H_2O)_6]^{2+}$	1080	4150	1056	3880	0.890	0.954	119	191	146	5.5
$[Cu(H_2O)_6]^{2+}$									(143)	(5.1)

Table 4. Data Used in the Estimation of ΔE_{rlx}

	$r(M-OH_2)$/ pm	$r_{spher}(M-OH_2)$/ pm	Δr/ pm	ΔE_{rlx}/ kJ mol^{-1}
$[V(H_2O)_6]^{2+}$	213.7	223.5	9.8	24
$[Cr(H_2O)_6]^{2+}$	216.7	220.5	3.8	4
$[Mn(H_2O)_6]^{2+}$	217.8	217.8	0	0
$[Fe(H_2O)_6]^{2+}$	212.6	215.5	2.9	2
$[Co(H_2O)_6]^{2+}$	209.3	213.5	4.2	5
$[Ni(H_2O)_6]^{2+}$	206.0	211.9	5.9	10
$[Cu(H_2O)_6]^{2+}$	208.7	210.6	1.9	1
$[Zn(H_2O)_6]^{2+}$	209.7	209.7	0	0

The M-OH$_2$ distances in the hypothetical spherical-ion complexes are in column 3 of Table 4. They were estimated from a parabolic baseline through the values for calcium, manganese and zinc. A figure of 235 pm was used for the calcium complex. This was obtained by adding the difference in the ionic radii of Ca^{2+} and Mn^{2+} in six coordination,[48] to the manganese value in Table 4, and it matches the distances observed in some of the few crystal structures in which calcium is surrounded by six water molecules.[49] Δr is then the difference between columns 2 and 3, and it yields the values of ΔE_{rlx} shown in column 5 when substituted in eq 7.

The Values of ΔE_{so}

These were taken to be equal to the stabilization of the ground state of the gaseous M^{2+} ion with respect to the baricenter 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.[14,15] Spin–orbit splittings in the complexes were calculated from the formulas of Figgis.[50] For $[Co(H_2O)_6]^{2+}$, the coupling parameter was calculated from the empirical formula of Reedijk[27] which gives $\lambda = 136$ cm^{-1}. Both this value and that for the corresponding nickel complex[28] are about four-fifths of the free ion values. That ratio was therefore used to estimate $\lambda = 84$ cm^{-1} for $[Fe(H_2O)_6]^{2+}$. The factor A for the d^7 ion was interpolated between 1.5 (weak-field limit) and 1.0 (strong-field limit) by using the formula

$$A = 3 + \frac{5\Delta E_{orb}}{2\Delta} \tag{8}$$

This yields $A = 1.31$. The resulting values of ΔE_{so} are shown in Table 5.

Table 5. Calculation of the Residual $\Delta H^{\ominus}_{res}(1)$ by Using Eq 3

M	$\Delta H^{\ominus}(1)$/ kJ mol^{-1}	ΔE_{orb}/ kJ mol^{-1}	ΔE_{rep}(irreg)/ kJ mol^{-1}	ΔE_{rlx}/ kJ mol^{-1}	ΔE_{so}/ kJ mol^{-1}	$\Delta H^{\ominus}_{res}(1)$/ kJ mol^{-1}
Ca	−2468	0	0	0	0	−2468
V	−2814	−177	−18	24	2	−2645
Cr	−2799	−95	−16	4	2	−2694
Mn	−2743	0	0	0	0	−2743
Fe	−2843	−45	−16	2	3	−2787
Co	−2904	−68	−19	5	6	−2828
Ni	−2986	−123	−18	10	12	−2867
Cu	−2989	−80	−16	1	10	−2904
Zn	−2936	0	0	0	0	−2936

Discussion

In Table 5, the residual, $\Delta H^{\ominus}_{res}(1)$, has been calculated from eq 3 by removing ΔE_{orb}, ΔE_{rep}(irreg), ΔE_{rlx} and ΔE_{so} from $\Delta H^{\ominus}(1)$ for the elements vanadium to zinc inclusive. Figure 1 shows how this eliminates the cusp at manganese and leaves values which lie very close to a smoothly curved baseline. This baseline can be fitted to a parabolic equation of the type:

$$\Delta H^{\ominus}_{res}(1)/\text{kJ mol}^{-1} = a + bn + cn^2 \tag{9}$$

Here, n is the number of d electrons in the dipositive ion, $a = -2476.8$, $b = -60.238$, and $c = 1.4286$. The correlation factor is then $R^2 = 1.000$ to three decimal places, and the greatest deviation of any point from the baseline is <2 kJ mol^{-1}. Thus, within the experimental uncertainties in the $\Delta H^{\ominus}(1)$ variation which we estimated earlier, $\Delta H^{\ominus}_{res}(1)$ changes smoothly with n. The projected baseline misses the experimental calcium point by 9 kJ mol^{-1}, and the deviation will be even greater if Ca^{2+}(aq) is not octahedral, since the value of $\Delta H^{\ominus}(1)$ for octahedral Ca^{2+}(aq) should then be less negative. This is quite acceptable, however, because as our work on the hexafluorometalate(III) compounds has shown,[6] there is no reason why spherical-ion values for the d^0 system, with its p^6 configuration, should be perfectly continuous with corresponding data for the d^1–d^{10} transition series. The fit to the smooth curve in Figure 1 is better than that obtained by the usual method of subtracting ΔE_{orb} values alone: if this is done using the values of ΔE_{orb} in Table 5, the deviations are, in kJ mol^{-1}, 1 (Co, Zn), 3 (Cu), 4 (Mn), 5 (V, Fe), 8 (Cr), and 10 (Ni), and $R^2 = 0.997$.

These deviations are, however, close to the experimental uncertainties in the variation in $\Delta H^{\ominus}(1)$. A more telling sign of the superiority of our approach is provided by a comparison with the analysis of George and McClure[7] who allowed for spin–orbit coupling by subtracting both ΔE_{orb} and ΔE_{so} from $\Delta H^{\ominus}(1)$ and then compared the result with a baseline constructed from the calcium, manganese, and zinc points. We have repeated this exercise using the data in Table 5, and all points between d^0, d^5, and d^{10}, except that for vanadium, lie more than 5 kJ mol^{-1} from, and *below*, a parabolic baseline, the depres-

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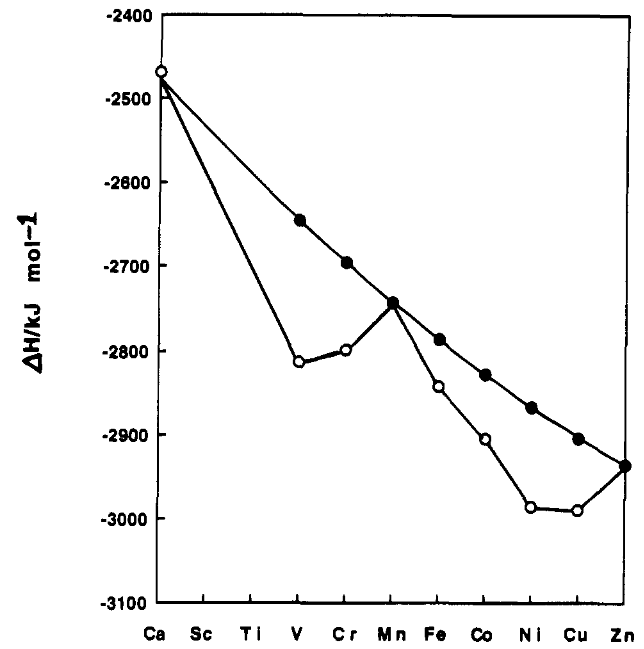

Figure 1. Subtraction of the four components of the ligand field stabilization energy from the values of $\Delta H^{\ominus}(1)$ (open circles) leaving a smooth curve, $\Delta H^{\ominus}_{\text{res}}(1)$ (filled circles).

sions being 11 (Cr), 13 (Fe), 12 (Co), 6 (Ni), and 15 (Cu). George and McClure also pointed out that their analysis could be refined by subtracting ΔE_{rlx} as well as ΔE_{orb} and ΔE_{so} from $\Delta H^{\ominus}(1)$. This refinement can also be performed with our data, and *all* points between d^0, d^5, and d^{10} then lie below the baseline by 15−20 kJ mol^{-1}. So, in agreement with the findings of George and McClure,[7] the discrepancies obtained using traditional analyses are not random; they exceed the experimental uncertainties in the variation in $\Delta H^{\ominus}(1)$, and indicate the presence of a systematic error which is answered by $\Delta E_{\text{rep}}(\text{irreg})$. Thus the approach used here is an improvement upon an existing theory whose success in explaining the hydration energy variation has been described[8] as "a splendid vindication of ligand-field theory at large."

If the hexaaqua +2 ions are compared with the hexafluorometalates(III),[6] our treatment reveals marked differences between corresponding contributions to the ligand field stabilization energies. In the case of the dipositive ions, the orbital stabilization energies are 60−75% of those of the hexafluorometalates(III), a difference attributable to lower values of Δ in the +2 oxidation state. However, the values of $\Delta E_{\text{rep}}(\text{irreg})$ are as little as 10−20% of their hexafluorometalate(III) counterparts, thereby showing the lesser importance of energy contributions from the nephelauxetic effect within the hexaaqua 2+ ions. Another striking feature is the near constancy of $-\Delta F_2$ and $-\Delta F_4$ in Table 3; in the hexafluorometalates(III), these values increase steadily as one moves into, and across, the second half of the series. The result of the smaller, and less variant influence of the nephelauxetic effect in the hexaaqua +2 series is that the terms $\Delta E_{\text{rep}}(\text{irreg})$ and $(\Delta E_{\text{rlx}} + \Delta E_{\text{so}})$ are of opposite sign and similar magnitude, so they largely cancel each other out: the difference between them is <12 kJ mol^{-1}. This explains why a theory which ignores these terms is quite successful in this particular case.

The ideas elaborated here are relevant to explanations of the variations in the stability constants of complex ions of the elements Mn → Zn in the +2 oxidation state and high-spin configuration. These usually follow the stability sequence suggested by the Irving−Williams rule,[51] Mn < Fe < Co < (Ni, Cu) > Zn. Consider first the case in which an octahedral, high-spin complex is formed with a ligand, L:

$$[M(H_2O)_6]^{2+}(aq) + 6L(aq) = [ML_6]^{2+}(aq) + 6H_2O(l) \qquad (10)$$

When reaction 10 is thermodynamically favorable, it seems to be almost always the case that the complex of zinc is more stable than that of manganese. This trend was attributed by Williams to an increase in radial or spherically symmetrical polarization,[52] and if the increase were smooth, then it alone would give the stability sequence Mn < Fe < Co < Ni < Cu < Zn and generate the Irving−Williams order in all but the last step. The solitary discrepancy between (Ni, Cu) and Zn can then be eliminated if one can identify a supplementary stabilization in the formation of the nickel, copper, cobalt, and iron complexes, $[ML_6]^{2+}$, relative to the manganese and zinc ones. Such a supplement can be supplied by d-orbital stabilization energies: if L is a stronger field ligand than H_2O, then ΔE_{orb} will be more negative for $[ML_6]^{2+}$ than for $[M(H_2O)_6]^{2+}$ at the $d^6 \rightarrow d^9$ points. This is the conventional textbook explanation of the Irving−Williams rule.[53]

Objections to this explanation have been raised by Williams himself. First, the orbital stabilization energies are symmetry dependent, but the Irving−Williams order seems largely unaffected by changes from regular to irregular octahedral coordination in the complex ion which is formed.[54] However, such changes do not usually affect the ligand field around the complex ion very much, and since the orbital stabilization energies will often have only to supplement the overall increase in stability from manganese to zinc in the $d^6 \rightarrow d^9$ cases, the fulfilment of this rather broad condition should not be very sensitive to them.

More telling is the objection that the Irving−Williams order is sometimes observed when the incoming ligand has a weaker ligand field strength than water.[52,55] A typical spectrochemical series[22b] implies that oxalate and hydroxide are two such ligands, yet the log K_1 data for the formation of their complexes follow the Irving−Williams order,[55] the values for Fe → Cu being significantly greater than those implied by a linear variation of log K_1 between manganese and zinc. This is inconsistent with explanations based upon orbital stabilization energies and the spectrochemical series; the Irving−Williams order seems, in general, to be more persistent than these explanations imply.

The irregularities in interelectronic repulsion that have been discussed in this paper can account for such discrepancies. A typical nephelauxetic series[22b] shows that only fluoride has a weaker nephelauxetic effect than water. This then implies that, for complexing reactions *in aqueous solution* with ligands other than fluoride, the nephelauxetic effect will *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. This effect should not be much influenced by symmetry and may either supplement or oppose the irregularities introduced by orbital stabilization energies. In the great majority of cases open to quantitative study, the incoming ligand is of higher field strength than water, there is supplementation, and *both* effects work to encourage the emergence of an Irving−Williams order. When, as in the case of oxalate or hydroxide, the incoming ligand has a lower field strength than water, there is opposition, and the Irving−Williams order marks the dominance of the nephelauxetic effect over the lesser irregularities introduced by orbital stabilization energies.

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Table 6. Estimated Contributions of d-Orbital Splitting Energies (Column 4) and the Nephelauxetic Effect (column 5) to $\Delta H^{\ominus}(11)$ Where Removal of Both Contributions Leaves the Residual $\Delta H^{\ominus}_{\mathrm{res}}(11)$

	$\Delta H^{\ominus}(11)$[60]/ kJ mol^{-1}	$\Delta\Delta$/cm^{-1}	$\Delta E_{\mathrm{orb}}(11)$/ kJ mol^{-1}	ΔE_{rep}(irreg)/ kJ mol^{-1}	$\Delta H^{\ominus}_{\mathrm{res}}(11)$/ kJ mol^{-1}
Mn	−46.2		0	0	−46.2
Fe	−66.3	1000	−4.8	−8.9	−52.6
Co	−92.7	2200	−19.6[a]	−11.0	−62.1
Ni	−116.7	2900	−41.6	−9.9	−65.2
Zn	−77.2		0	0	−77.2

[a] Calculated as described in the text.

Both this interpretation and the conventional explanation of the Irving–Williams order are very hard to test quantitatively. The effects at issue appear as irregularities in the enthalpies of complexing reactions. Because the irregularities are small, we require accurate thermodynamic data for a set of such reactions, in which something close to a regular octahedral ligand field is retained in all of the cases M = Mn → Zn inclusive, and where the appropriate spectroscopic parameters are available for the complexes that are formed. One of the very few cases where these conditions come close to being fulfilled is the reaction

$$[M(H_2O)_6]^{2+}(aq) + 3en(aq) = [M(en)_3]^{2+}(aq) + 6H_2O(l) \qquad (11)$$

Thermodynamic data for this reaction indicate that the variations in $\Delta G^{\ominus}$ are mainly determined by those in $\Delta H^{\ominus}$.[56] A previous test[57,58] subtracted, from $\Delta H^{\ominus}$, the effects of orbital stabilization energies alone and found residual irregularities which, with hindsight, appear close to those expected from the nephelauxetic effect. Table 6 repeats the analysis, but includes some more recent data; copper has been omitted because of the absence of data on $[Cu(en)_3]^{2+}(aq)$. $\Delta E_{\mathrm{orb}}(11)$ is the contribution of the d orbital stabilization energies to $\Delta H^{\ominus}(11)$. At M = Fe and M = Ni, it is $-{}^2/_5\Delta\Delta$ and $-{}^6/_5\Delta\Delta$ respectively, where $\Delta\Delta$ is the change in the d orbital splitting. In the case of iron, we use the difference in the high-energy components[26,58] of the split $^5T_{2g} \rightarrow {}^5E_g$ band because the low-energy component seems not to have been observed in $[Fe(en)_3]^{2+}$. Our $\Delta\Delta$ value is then identical with Ciampolini's.[58] For nickel, we use the Δ values of Reedijk[28]. With cobalt, the spectra of the two complexes[27,59] were analyzed using Reedijk's two-band scheme,[27] and, in each case, a value of ΔE_{orb} was obtained from Δ and B using eq 5; the difference appears in Table 6.

When the $\Delta E_{\mathrm{orb}}(11)$ contributions are removed from $\Delta H^{\ominus}(11)$, the irregularities do not wholly disappear. Indeed, as the filled square plot in Figure 2 shows, an Irving–Williams order still persists in attenuated form. If we consider which of the terms ΔE_{rep}(irreg), ΔE_{rlx}, and ΔE_{so} might be responsible for this, the last can be dismissed: differences in stabilizations due to spin–orbit coupling will be far too small. A comprehensive set of M–L bond lengths for the complexes $[M(en)_3]^{2+}$ is not available, so ΔE_{rlx} contributions cannot be calculated. However, the breathing frequency of the M–N$_6$ octahedron seems to be about 400 cm^{-1}, close to our value for the hexaaqua complexes,[61] and the crystal structures of solids containing the nickel[62] and zinc[63] ethylenediamine complexes reveal a difference in metal–ligand distance similar to that in the corresponding aqua complexes. The assumption that ΔE_{rlx} contributions to reaction 11 are very small is therefore a reasonable one. This leaves ΔE_{rep}(irreg), and the residual bowl has just the shape that might be produced by ΔE_{rep}(irreg) terms. Because small differences in interelectronic repulsion parameters are involved, and because these are sensitive to quite small variations in individual spectra and to the way in which spectra are analyzed,[64] precise calculation is unwarranted. However, if we take $\Delta C/\Delta B = 1.6$ from the cobalt and nickel values in Table 3, and use the average of the strong and weak field limits for cobalt(II), then the ΔE_{rep}(irreg) values for iron, cobalt and nickel become 11.5ΔB, 14.2ΔB, and 12.7ΔB respectively. For ΔB in reaction 11, the most reliable figure is the nickel value[28] of $\Delta B = -65$ cm^{-1}. Subtraction of the ΔE_{rep}(irreg)(11) values and $\Delta E_{\mathrm{orb}}(11)$ values from $\Delta H^{\ominus}(11)$ then leaves the quantity $\Delta H^{\ominus}_{\mathrm{res}}(11)$, which appears in Table 6 and has been plotted with filled circles in Figure 2. Something close to a straight line is obtained. This instance therefore provides considerable support for the belief that the Irving–Williams rule has part of its origin in the nephelauxetic effect.

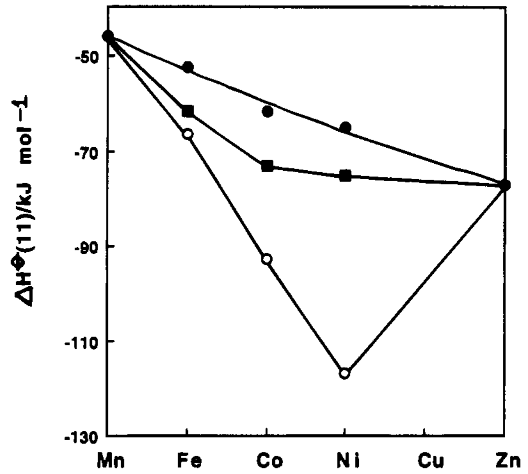

Figure 2. Subtraction of the contribution of the orbital stabilization energies from $\Delta H^{\ominus}(11)$ (open circles) leaving values (filled squares) which still display a distinct bowl-shaped pattern. If estimated contributions from ΔE_{rep}(irreg) are removed as well, the resulting values (filled circles) lie close to a straight line.

Our theoretical discussion, and calculations on the ethylenediamine complexes, justify Williams' long-standing unease[52,54,55] about the conventional explanation of the Irving–Williams rule. The nephelauxetic effect corresponds, to some extent, to his ideas about the importance of radial or spherically-symmetrical polarization, except that the energy changes affected by this polarization do not vary smoothly between d^5 and d^{10}. Our physical explanation[6] attributes this to the fact that the ground states of d^6 → d^9 configurations have fewer pairs of parallel spins and lower exchange energies than the d^5 → d^{10} baseline implies and are therefore relatively destabilized by increased interelectronic repulsion within the d shell. This destabilization generates a corresponding stabilization in a process such as reaction 11, when the enhanced nephelauxetic effect of the ethylenediamine ligand relieves the excess repulsion.

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