Ligand Field Stabilization Energies of the Hexaaqua 3+ Complexes of the First Transition Series

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An analysis of the ligand field stabilization energy which makes allowance for the nephelauxetic effect is shown to give satisfactory results when applied to the hydration enthalpies of the hexaaqua 3+ complexes of the first transition series. The contribution from the nephelauxetic effect is substantial, and the baseline for zero ligand field stabilization energy is displaced below the d^0 point. In these respects, the complexes show a closer resemblance to the hexafluorometalates(III) than to the hexaaqua 2+ ions. In the course of the analysis, the electronic spectra of the cesium alums of vanadium(III), manganese(III), and cobalt(III) are reexamined, and thermodynamic properties of particular complexes are calculated. These include $\Delta H_f^{\ominus}(\text{Ti}^{3+},\text{aq})$, $E^{\ominus}(\text{Ti}^{3+}|\text{Ti}^{2+})$, and the relative stabilities of the high- and low-spin states of $\text{Co}^{3+}(\text{aq})$, $\text{Mn}^{3+}(\text{aq})$, and $\text{Cr}^{2+}(\text{aq})$. The general influence of ligand field stabilization energies on redox potentials is also discussed.

In their classical review of inner orbital splittings, George and McClure[1] showed that d-orbital splitting energies derived from electronic spectra may sometimes differ substantially from thermodynamic values of the ligand field stabilization. We have shown[2] that, for the hexafluorometalates(III) of the first-row transition elements, the discrepancy is particularly large and that it can be explained by previously unrecognized contributions from the nephelauxetic effect. By contrast,[3] for the hexaaqua 2+ complexes, the discrepancy is small because the nephelauxetic effect is weak. Our theory suggests that the hexaaqua 3+ complexes should resemble the hexafluorometalates(III) rather than the hexaaqua 2+ complexes because the common 3+ oxidation state should ensure a large nephelauxetic effect which is little affected by the small difference in the positions of the water and fluoride ligands in the nephelauxetic series. In this paper, we put this prediction to the test. Finally, a study of the hexaqua 3+ complexes, when combined with our existing treatment of the 2+ series, gives us the opportunity to apply our theory to the redox potentials $E^{\ominus}(\text{M}^{3+}|\text{M}^{2+})$ of the first-row transition metals; it also allows an assessment of the relative stabilities of high- and low-spin states in both oxidation states.

Our investigation coincides with a renewed interest in these complexes. Their energies have been the subject of ab initio SCF calculations,[4,5] and there have been several studies of the mutual interactions between the complexes and their environment in the alkali metal and ammonium alums.[6,7] The SCF calculations, however, were only able to reproduce 40−70% of the observed ligand field stabilization energies.[5]

At the outset, it was clear that our analysis would benefit from some enlargement of the available ligand field parameters for the hexaaqua 3+ complexes. We have therefore recorded or reexamined the electronic spectra of the cesium alums of vanadium(III), manganese(III), and cobalt(III), and this aspect is dealt with first.

Experimental Section

The cesium alums of vanadium, chromium, and manganese were prepared as previously described.[8] Reflectance spectra of the alums were determined at both room temperature and 80 K by using a Beckman DK-2 spectrometer.

Absorption Spectra of the Cesium Alums of Vanadium(III), Manganese(III), and Cobalt(III)

Previous investigations[9] of the electronic spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ in its alums have been confined to the region $14000-34000$ cm^{-1}. Here we report the absorption spectrum of $\text{CsV}(\text{SO}_4)_2\cdot12\text{H}_2\text{O}$ over a wider range. In the cesium alum, vanadium in $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ experiences an octahedral field with an additional trigonal component.[10] Figure 1 shows the spectrum which is dominated by two broad, asymmetric bands with maxima at 17 800 and 26 000 cm^{-1}. Table 1 contains the interpretation using an energy level scheme in a trigonal field.[11]

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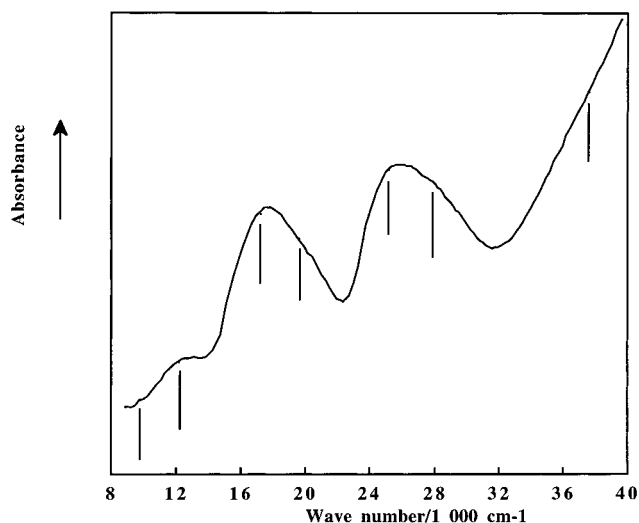(11) Pryce, M. H. L.; Runciman, W. A. *Discuss. Faraday Soc.* **1958,** *26,* 34.

Figure 1. Absorption spectrum of CsV(SO$_4$)$_2$·12H$_2$O at 80 K. The vertical lines show the positions of the peaks identified by Gaussian analysis (Table 1).

Table 1. Bands Observed in the Absorption Spectrum of Cesium Vanadium(III) Alum, Together with the Proposed Assignment

band max/cm^{-1}	assgnt
1 940^a	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3E_g(^3T_{1g},F)$
9 850	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^1E_g(^1T_{2g},D)$
12 200	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^1A_{1g}(^1T_{2g},D)$
17 200	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3A_{1g}(^3T_{2g},F)$
19 600	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3E_g(^3T_{2g},F)$
25 200	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3A_{2g}(^3T_{1g},P)$
27 900	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3E_g(^3T_{1g},P)$
37 600	$^3A_{2g}(^3T_{1g},F) \rightarrow {}^3A_{2g}(^3A_{2g},F)$

^{a} Raman spectrum, ref 10.

The band maxima were obtained by a Gaussian analysis. There is a $^3A_{2g}$ ground state, and a transition at 1940 cm^{-1} to the upper ^3E_g component of what, in octahedral symmetry, would be a $^3T_{1g}$ ground state has been determined by Raman spectroscopy.[10] Hitchman[9] studied the absorption spectrum of the ammonium alum between 14 000 and 34 000 cm^{-1}, and in this range, our energies and assignments are very similar to his. Above 9300 cm^{-1}, there is a region of increasing absorption, not present in the chromium alum, which terminates with a fairly weak peak at 12 200 cm^{-1}. This is where spin-forbidden transitions are expected,[11,12] and we identify the terminal peak as the upper $^1A_{1g}$ component of the split $^1T_{2g}$ state. There is a much weaker peak at about 9850 cm^{-1} which we assign to the lower ^1E_g component, but this assignment is tentative, because there is slight absorption in this region in the chromium alum, although this is weaker. However, the value of C obtained from this band is in line with other values (cf. Table 3). The energies of the transitions in octahedral symmetry were calculated from the weighted averages of split components and interpreted in the intermediate field approximation,[13a] spin–orbit coupling being neglected. From the bands up to 30 000 cm^{-1}, $\Delta = 18\,800$ cm^{-1}, $B = 635$ cm^{-1}, and $C = 2605$ cm^{-1}. The previously unobserved two-electron transition is then predicted at 37 600 cm^{-1} and occurs where expected as a discernible intrusion on the charge-transfer band in the ultraviolet.

The spectrum of cesium manganese(III) alum at 80 K contains an intense band with an absorption maximum at 21 050 cm^{-1}

Table 2. Calculation of $\Delta H^\ominus(1)^a$

	$\Delta H_f^\ominus(M^{3+},g)$	$\Delta H_f^\ominus(M^{3+},aq)$	$\Delta H^\ominus(1)$
Sc	4652	−647	−5299
Ti	5112		
V	5426	−285	−5711
Cr	5648	−233	−5881
Mn	5779	−104	−5883
Fe	5715	−49.0	−5764
Co	6084	77	−6007
Ga	5812	−216	−6028

^{a} For sources, see text. All values in units of kJ mol^{-1}.

Table 3. Values of Δ, the Splitting of the d Orbitals, and of the Racah Parameters B and C for the Complexes [M(H$_2$O)$_6$]$^{3+}$ in a Regular Octahedral Ligand Field

complex	Δ/cm^{-1}	B/cm^{-1}	C/cm^{-1}	ref
[Ti(H$_2$O)$_6$]$^{3+}$	18 800			28
[V(H$_2$O)$_6$]$^{3+}$	18 400	632	2593	see text
[Cr(H$_2$O)$_6$]$^{3+}$	17 400	720	3055	29
[Mn(H$_2$O)$_6$]$^{3+}$	15 800	(629)	(3530)	see text
[Fe(H$_2$O)$_6$]$^{3+}$	14 000	780	3340	30
[Co(H$_2$O)$_6$]$^{3+}$	16 750	660	3650	see text

and a moderately strong one at 10 500 cm^{-1}. These energies are little different from those given by Davis et al.[14] for both the cesium and a mixed Mn–Al alum. The combination is characteristic of the tetragonally distorted octahedral complex which is expected for a d^4 system subject to the Jahn–Teller effect: in regular octahedral symmetry, the energy of the first band is equal to Δ but should be smaller than observed, and the second band should be absent. We assign the low energy band in D_{4h} symmetry to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition and take the high energy one to be the envelope of the transitions to the $^5B_{2g}$ and ^5E_g states. This gives $\Delta = 15\,800$ cm^{-1} for the regular octahedral complex, a much more reasonable value. A possible objection to such an assignment is that an X-ray study gives equal Mn–O bond lengths in the compound.[15] However, this is almost certainly because the distortion is dynamic (the work was carried out at 295 K). The thermal parameter for the oxygen atom of Mn–O in the direction of the bond is 20% higher than in the corresponding vanadium salt ($^3T_{1g}$ in O_h) and 40–70% higher than in the chromium ($^4A_{2g}$), iron ($^6A_{1g}$), cobalt ($^1A_{1g}$), and gallium ($^1A_{1g}$) salts.[15a] Similar evidence has been presented for dynamic distortion in a manganese(III)–urea complex.[16]

Ligand field parameters for [Co(H$_2$O)$_6$]$^{3+}$ have previously been calculated from four bands in the absorption spectrum of CsCo(SO$_4$)$_2$·12H$_2$O by using the strong field approximation.[8] However, the spectra described here show that the low-energy peak at 8100 cm^{-1} is very similar to one observed in those of both the vanadium and chromium alums and may therefore be a vibrational overtone or combination band. The parameters have therefore been recalculated from the three other bands at 12 500, 16 500, and 24 700 cm^{-1}, the assignment being unchanged. Also, our more comprehensive work on first-row complexes[2,3] suggests that, in general, the intermediate, rather than the strong field approximation, provides the better fit. We have therefore used the intermediate field approximation of ref 13a, except that the terms in B^2/Δ, which are numerically large for the states arising from the d^6 configuration, were algebraically reexpressed by eliminating the simplifying assumption that $C = 4B$. This gives $\Delta = 16\,750$ cm^{-1}, $B = 660$ cm^{-1}, and $C = 3650$ cm^{-1},

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the value of Δ now being more in line with those of the other $[M(H_2O)_6]^{3+}$ complexes. The spin-forbidden transition $^1A_{1g} \rightarrow {}^3T_{1g}$ is predicted at 8200 cm^{-1} where it presumably contributes to the observed band at 8100 cm^{-1}. The two-electron transition $^1A_{1g} \rightarrow {}^5T_{2g}$ is predicted at $\{2\Delta - 5B - 8C + [12B^2 + 3(2B + C)^2]/\Delta\}$ or 5740 cm^{-1}.

Analysis of Ligand Field Stabilization Energies of $[M(H_2O)_6]^{3+}$

The hydration enthalpy that we shall study is the one used by George and McClure:[1]

$$M^{3+}(g) + 3H^+(aq) + 3e^-(g) = M^{3+}(aq) + {}^3/_2H_2(g) \quad (1)$$
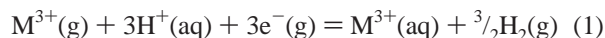
The standard enthalpy changes at 298.15 K, $\Delta H^{\ominus}$,[17] are given by

$$\Delta H^{\ominus}(1) = \Delta H_f^{\ominus}(M^{3+},aq) - \Delta H_f^{\ominus}(M^{3+},g) \quad (2)$$

In the absence of competing ligands, there is strong evidence[18,19] that, in all cases except scandium,[20] the M^{3+} ion in aqueous solution is octahedrally coordinated by water molecules within its primary coordination sphere. We shall treat 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 appropriate points are considered later.

Our analysis of $\Delta H^{\ominus}(1)$ is very similar to the one used for the hexafluorometalates(III).[2] We calculate a residual, $\Delta H_{res}^{\ominus}(1)$, from the equation

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

Here, ΔE_{orb} is the orbital-stabilization energy of the complex, ΔE_{rlx} is the relaxation energy induced by contraction of the metal–ligand distance in the ligand field, ΔE_{so} is the energy change due to changes in spin–orbit coupling, and $\Delta E_{rep}(irreg)$ is the change 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. If the theory is sound, $\Delta H_{res}^{\ominus}(1)$ for the series of d^n complexes 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.

Values of $\Delta H^{\ominus}(1)$

These were calculated from eq 2, and the results are shown in Table 2. Values of $\Delta H_f^{\ominus}(M^{3+},g)$ are from ref 2. Those of $\Delta H_f^{\ominus}(M^{3+},aq)$ are essentially from ref 21, but modifications have been made, mainly to take account of recent work. Thus the vanadium value has been calculated using revised values of $\Delta G_f^{\ominus}(VO^{2+},aq)$[22] and $\Delta H_f^{\ominus}(V_2O_5,s)$.[23] The data given for Cr^{3+}-(aq), Fe^{3+}(aq), and Co^{3+}(aq) have been altered to be consistent with a recent review[24] of the thermochemistry of iron and also,

in the case of chromium, with the data on the hydrogen chromate and dichromate ions proposed in ref 25. For $\Delta H_f^{\ominus}(Ga^{3+},aq)$, we have used the average of two independent literature values.[26,27]

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 $\Delta H_f^{\ominus}(M,g)$, the ionization energies, and $\Delta H_f^{\ominus}(M^{3+},aq)$. We estimate those in the latter quantity to be, in kJ mol^{-1}, ± 2 (Fe), ± 6 (Sc), ± 7 (Co, Ga), ± 10 (V, Cr), and ± 12 (Mn). Putting the assessments for the three contributions together, the uncertainties in the *variation* in $\Delta H^{\ominus}(1)$ become, in kJ mol^{-1}, ± 3 (Fe), ± 8 (Sc, Ga), ± 11 (Cr), ± 12 (V, Co), and ± 13 (Mn).

Values of ΔE_{orb}

These were calculated from parameters which were obtained by assigning bands in the absorption spectra of $[M(H_2O)_6]^{3+}$ complexes and by fitting the band maxima to formulas provided by the intermediate field approximation.[13a] The calculated parameters are shown in Table 3. As we are dealing with the thermodynamics of formation of aqueous ions, solution spectra in an acidic perchlorate medium were used when this was possible, but for manganese and cobalt, the spectra of solid alums allowed better identification of peaks and detection of spin-forbidden transitions. For $[V(H_2O)_6]^{3+}$, the spectrum in aqueous perchlorate solution[31] provides little evidence of trigonal field splitting, and the two band maxima at 17 100 and 25 250 cm^{-1} occur at significantly lower energies than in the cesium alum. They were therefore assigned in O_h symmetry and used to obtain Δ and B. A value of C was then calculated using the C/B ratio derived from the alum spectrum.

Values of ΔE_{orb} were calculated from the data in Table 3 following the methods of ref 2. For the reasons cited in the previous paragraph, any trigonal field splitting of V^{3+}(aq) was ignored. In the case of the manganese complex, the value of $3\Delta/5$ must be supplemented by the stabilization, E_{JT}, brought about by the Jahn–Teller distortion of the regular octahedral coordination. As theoretical calculations[4] on $[Mn(H_2O)_6]^{3+}$ imply an a/E_{JT} value of only 0.2, a being the difference between the potential energy minima of the axially compressed and axially elongated states of the octahedron, E_{JT} was taken to be $\Delta E/4$ (cf. ref 3), where ΔE is the energy of the d–d transition at 10 500 cm^{-1}.

For $[Co(H_2O)_6]^{3+}$, the value of ΔE_{orb} must be supplemented by the stabilization of the low-spin complex with respect to the high-spin state. This is the energy of the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition, calculated from the parameters of Table 3, less the vibrational energy in the excited state. This vibrational energy, calculated as before[21] but using new auxiliary data quoted later in this paper, comes to 26 kJ mol^{-1}. The resulting stabilization of the low-spin state is 43 kJ mol^{-1}. The complete set of ΔE_{orb} values is shown in Table 6.

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(28) Reference 13b; Δ is the average value of the two bands at 20 100 and 17 400 cm^{-1}.
(29) Calculated from the four bands in the solution spectrum of Elving and Zemel (Elving, P. J.; Zemel, B. *J. Am. Chem. Soc.* **1957**, *79*, 1281) using the assignment of ref 13c, the lowest-energy band being assigned to the $^4A_{2g} \rightarrow {}^2E_g$ transition.
(30) The solution spectrum and assignment of Jørgensen (Jørgensen, C. K. *Acta Chem. Scand.* **1954**, *8*, 1502), the four bands being fitted by using the ratio $C/B = 4.3$, a value suggested by the vanadium and chromium spectra.
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Table 4. Data Used in the Calculation of $\Delta E_{rep}(irreg)^a$

	B_g	C_g	B'_g	C'_g	b	c	$-\Delta B$	$-\Delta C$	$-\Delta F_2$	$-\Delta F_4$
$[Ti(H_2O)_6]^{3+}$									(300)	(17)
$[V(H_2O)_6]^{3+}$	881	3364	862	3114	0.733	0.833	235	562	315	16.1
$[Cr(H_2O)_6]^{3+}$	929	3705	917	3677	0.785	0.831	200	626	289	17.9
$[Mn(H_2O)_6]^{3+}$	829	4414	828	4412	(0.760)	(0.800)	(199)	(882)	(325)	(25.2)
$[Fe(H_2O)_6]^{3+}$	1047	4245	1067	4322	0.731	0.773	282	964	420	27.5
$[Co(H_2O)_6]^{3+}$	982	4835	988	4862	0.668	0.751	326	1204	498	34.4

^{a} For sources, see text. All values in cm^{-1} except for b and c.

Table 5. Data Used in the Estimation of ΔE_{rlx}

complex^a	$r(M-OH_2)$/ pm	$r_{spher}(M-OH_2)$/ pm	Δr/ pm	ΔE_{rlx}/ kJ mol^{-1}
$[Sc(H_2O)_6]^{3+}$	$(211.7)^b$	211.7	0	0
$[Ti(H_2O)_6]^{3+}$	202.8	208.7	5.9	17
$[V(H_2O)_6]^{3+}$	199.2	206.0	6.8	24
$[Cr(H_2O)_6]^{3+}$	195.9	203.5	7.6	30
$[Mn(H_2O)_6]^{3+}$	199.1	201.4	2.3	3
$[Fe(H_2O)_6]^{3+}$	199.5	199.5	0	0
$[Co(H_2O)_6]^{3+}$	$(194.5)^b$	197.9	3.4	6
$[Ga(H_2O)_6]^{3+}$	194.4	194.4	0	0

^{a} O_h symmetry, high spin. ^{b} Estimated; see text.

Table 6. Calculation of the Residual $\Delta H_{res}^{\ominus}(1)$ by Using Eq 3^a

M	$\Delta H^{\ominus}(1)$	ΔE_{orb}	$\Delta E_{rep}(irreg)$	ΔE_{rlx}	ΔE_{so}	$\Delta H_{res}^{\ominus}(1)$
Sc	−5299	0	0	0	0	−5299
Ti	(−5548)	−90	(−38)	17	2	(−5439)
V	−5711	−160	−51	24	3	−5527
Cr	−5881	−250	−46	30	5	−5620
Mn	−5883	−145	−46	3	4	−5699
Fe	−5764	0	0	0	0	−5764
Co	−6007	−123	−68	6	7	−5829
Ga	−6028	0	0	0	0	−6028

^{a} All in units of kJ mol^{-1}.

Values of $\Delta E_{rep}(irreg)$

The methods of calculation, the symbolism, and the sources of data for the gaseous ions have already been described,[2] and the parameters used in the calculation are given in Table 4. The values of B_g and C_g are identical with those given in ref 2, except at manganese and cobalt where our need for fuller analyses of the gaseous ion spectra has added to or improved the data. The values of B'_g and C'_g depend on the transitions observed in the spectra of the complexes, and this explains the changes at iron and cobalt. The observed transitions for iron arise from the ^6S and ^4G levels of the gaseous ion; those for cobalt from ^1I and ^3H. Two levels are insufficient to separate B'_g and C'_g, so, in these cases, values were obtained by assuming that their ratio is the same as that between the corresponding values of B_g and C_g. As in the case of the hexafluorometalates(III),[2] the values of ΔF_2 and ΔF_4 increase significantly across the series. Estimated figures for manganese are given in parentheses and were obtained by interpolation of $\Delta B/B'_g$ and $\Delta C/C'_g$. Those for titanium are the average of the vanadium and chromium values. The values of $\Delta E_{rep}(irreg)$ to which the data in Tables 3 and 4 give rise are shown in Table 6.

Values of ΔE_{rlx}

As before,[2] we use the valence force field approximation in the following form:

$$\Delta E_{rlx} = 12\pi^2\nu^2 m(H_2O)(\Delta r)^2 \qquad (4)$$

Values of ν have been determined in both the cesium[32] and rubidium[6] alums of titanium, vanadium, and chromium and in

cesium cobalt alum in which the hexaaqua complex is low spin.[33] To obtain figures for the manganese(III) and high-spin cobalt(III) alums, we must first estimate the internuclear distance in their hexaaqua complexes. For manganese we use the experimental M−O distance of 199.1 pm,[15] but the value for high-spin cobalt(III) must be obtained by estimating the difference in the equilibrium internuclear distance (δr) for the high- and low-spin states. Shannon[34] derived the radius of the high-spin ion in six-coordination (60.5 pm) from the Co−F distance[35] in CoF$_3$. He also obtained a radius for the low-spin ion (54.5 pm) from various cobalt(III) compounds. His δr value is therefore 6.0 pm. Beattie et al.[15] estimated $\delta r = 7$ pm; we have repeated their calculation using more recent data[3] for the metal−oxygen distances in the Tutton salts of manganese(II) and iron(II) and corrected for an assumed linear drift in the difference in bond lengths of the isoelectronic +2 and +3 complexes between d^5 and d^{10}. This yields 7.6 pm. The insertion of the Co−F distance[35] in high-spin CoF$_3$ into a linear plot of the internuclear distances of trifluorides[35−37] versus those of the cesium alums[15] for titanium, vanadium, chromium, iron, and gallium gives $\delta r = 7.7$ pm. Finally, we used Hitchman's relationship[38] with $\nu(M-O) = 530$ cm^{-1} for low-spin [Co-(H$_2$O)$_6$]$^{3+}$ in aqueous solution and $n = 3.70$. This value of n brings the values of δr calculated for [Co(NH$_3$)$_6$]$^{3+}$ by his method and by spectroscopy[38] into agreement. It gives $\delta r = 7.3$ pm. By averaging these different methods, we take $\delta r = 7.2 \pm 1.5$ pm which, when combined with data on the low-spin alum,[15] gives 194.5 pm for the internuclear distance in high-spin [Co(H$_2$O)$_6$]$^{3+}$.

Values of ν in the manganese(III) and high-spin cobalt(III) alums can now be estimated from the inverse correlation with internuclear distance.[32] The value of ν for [Cr(H$_2$O)$_6$]$^{3+}$ in aqueous solution is 522 cm^{-1}, and in general, the solution values appear to be about 15−20 cm^{-1} less than those in the alums.[32,33] This suggests the following values (in cm^{-1}): titanium (505); vanadium (515); chromium (522); manganese (510); cobalt (515). To estimate the values of Δr in eq 4, we have assumed that, in aqueous solutions of the complexes, the M−OH$_2$ distances are identical with those in the cesium alums.[15] These are shown in column 2 of Table 5. For cobalt, we use the value calculated in the preceding paragraph for the high-spin state. The M−OH$_2$ distances in the hypothetical spherical-ion complexes are in column 3. They were estimated from a parabolic baseline through the values for scandium, iron, and gallium. A figure of 211.7 pm was used for the scandium complex. This

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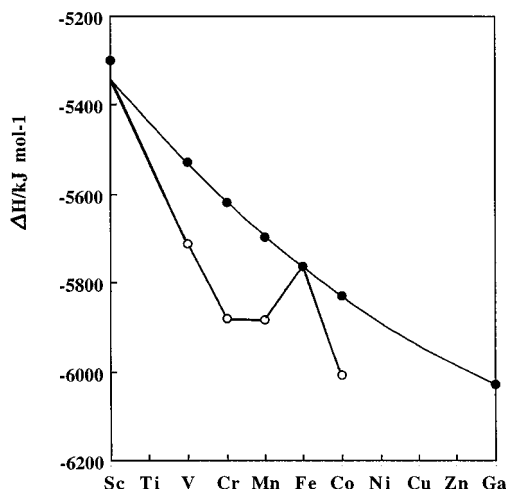(38) Hitchman, M. A. *Inorg. Chem.* **1982**, *21*, 821.

Figure 2. 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, $\Delta H^{\ominus}_{\mathrm{res}}(1)$ (filled circles).

was obtained by assuming a linear correlation between the ionic radii in six coordination[34] and the M–OH$_2$ distances. 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 4.

Values of ΔE_{so}

These were calculated by using the methods and gaseous ion data of ref 2, a procedure which yielded λ values of 122 and 85 cm^{-1} for [Ti(H$_2$O)$_6$]$^{3+}$ and [V(H$_2$O)$_6$]$^{3+}$, respectively. The resulting values of ΔE_{so} are shown in Table 6.

Discussion

In Table 6, the residual, $\Delta H^{\ominus}_{\mathrm{res}}(1)$, has been calculated from eq 3 by removing ΔE_{orb}, $\Delta E_{\mathrm{rep}}(\mathrm{irreg})$, ΔE_{rlx}, and ΔE_{so} from $\Delta H^{\ominus}(1)$. Figure 2 shows how this eliminates the cusp at iron and leaves values that, except for scandium, lie very close to a smoothly curved baseline. This baseline can be fitted to a parabolic equation of the type

$$\Delta H^{\ominus}_{\mathrm{res}}(1)/\mathrm{kJ\ mol}^{-1} = a + bn + cn^2 \qquad (5)$$

Here, n is the number of d electrons in the tripositive ion, $a = -5340.9$, $b = -101.57$, and $c = 3.2933$. The correlation factor is then $R^2 = 1.000$, and all points lie within 5 kJ mol^{-1} of the baseline to an extent which, in each case, is less than the experimental uncertainty in $\Delta H^{\ominus}(1)$.

In general, the values of $\Delta E_{\mathrm{rep}}(\mathrm{irreg})$ in Table 6 are similar to, but slightly larger than, those calculated for the corresponding hexafluorometalates(III).[2] This is consistent with the nephelauxetic series[13d] which shows that water has a slightly greater nephelauxetic effect than fluoride. Table 6 also shows that $\Delta E_{\mathrm{rep}}(\mathrm{irreg})$ is some 20–50% of ΔE_{orb}, a percentage similar to that observed for the hexafluorometalates(III). The expectation raised in our introduction is therefore fulfilled: the hexaaqua +3 complexes resemble the hexafluorometalates(III) rather than the hexaaqua +2 complexes; for [M(H$_2$O)$_6$]$^{2+}$ the values of $\Delta E_{\mathrm{rep}}(\mathrm{irreg})$ are only 10–35% of ΔE_{orb}[3] and well under 40% of the values for the [M(H$_2$O)$_6$]$^{3+}$ complex with the same d-electron configuration. The ligand field stabilization energies of both K$_3$MF$_6$ and [M(H$_2$O)$_6$]$^{3+}$ fit the traditional explanation given by ligand field theory very poorly: in both series they are substantially larger than the orbital stabilization energies. In the case of the [M(H$_2$O)$_6$]$^{3+}$ complexes, this was noted many years

ago by George and McClure,[1a] who were unable to explain it. We now provide the explanation through the substantial contributions made by $\Delta E_{\mathrm{rep}}(\mathrm{irreg})$.

Figure 2 reveals another resemblance between the [M(H$_2$O)$_6$]$^{3+}$ and K$_3$MF$_6$ series: removal of the ligand field stabilization energies from the binding energies clearly separates scandium from the members of the d^1–d^{10} transition series. The projected baseline falls below the experimental scandium point by 42 kJ mol^{-1}. This displacement is less than that observed in the hexafluorometalate(III) series but for understandable reasons: in the K$_3$MF$_6$ compounds, scandium assumes the common octahedral coordination of the other transition metal ions; in the M^{3+}(aq) series it does not.[20] Consequently, the value of $\Delta H^{\ominus}$-(1) for octahedral Sc^{3+}(aq) should be less negative than the scandium point in Figure 2, so that in both the [M(H$_2$O)$_6$]$^{3+}$ and K$_3$MF$_6$ series, the scandium point lies well above the projected baseline. Despite the assumption made in traditional analyses, there is no reason why the spherical-complex values for the d^1–d^{10} series should be continuous with the so-called d^0 system with its p^6 inert-gas configuration. The discontinuity seems to be most marked in series such as [M(H$_2$O)$_6$]$^{3+}$, K$_3$MF$_6$, and MI$_2$,[39] when the nephelauxetic effect is substantial, and least noticeable when it is weak as with MF$_2$[39] and [M(H$_2$O)$_6$]$^{2+}$.[3]

Because factors other than just ΔE_{orb} contribute to the ligand field stabilization energies, the estimation of thermodynamic quantities using ligand field theory is a more complex matter than was previously thought. Nevertheless, this recognition leads to improvements. Thus, for [Ti(H$_2$O)$_6$]$^{3+}$, the value of $\Delta H^{\ominus}(1)$ in Table 6 was estimated by adding the 4 components of the ligand field stabilization energy to a $\Delta H^{\ominus}_{\mathrm{res}}(1)$ value obtained from the extrapolated baseline. This gives $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{Ti}^{3+},\mathrm{aq}) = -436$ kJ mol^{-1}.

Some support for this value can be obtained from experimental thermodynamic data[40] and estimated entropies, if the predominant species present in dilute acid solutions of titanium-(IV) is taken to be TiO^{2+}(aq). This assumption has been used[40] to derive $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{TiO}^{2+},\mathrm{aq}) = -689.9$ kJ mol^{-1}. Evidence for the existence of this ion in such solutions has been obtained by Raman spectroscopy,[41] and stability constant data[42] show that, at low concentrations, oligomerization is negligible. Equating the titanium(IV)–titanium(III) formal potential in chloride solution (0.033 V)[43] to $E^{\ominus}(\mathrm{TiO}^{2+}|\mathrm{Ti}^{3+})$, and $S^{\ominus}(\mathrm{TiO}^{2+},\mathrm{aq})$ to $S^{\ominus}(\mathrm{VO}^{2+},\mathrm{aq})$,[40] yields $\Delta G^{\ominus}_{\mathrm{f}}(\mathrm{Ti}^{3+},\mathrm{aq}) = -415$ kJ mol^{-1}. With the estimated entropy $S^{\ominus}(\mathrm{Ti}^{3+},\mathrm{aq}) = -292$ J K^{-1} mol^{-1} (vide infra), $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{Ti}^{3+},\mathrm{aq}) = -453$ kJ mol^{-1}, in fair agreement with the value calculated from ligand field theory. A discrepancy is to be expected if TiO^{2+}(aq) is not overwhelmingly preponderant in dilute acid solutions of titanium(IV). [Ti(OH)$_2$]$^{2+}$(aq) is a possible rival species.[42]

We now turn to $E^{\ominus}(\mathrm{Ti}^{3+}|\mathrm{Ti}^{2+})$. Our use of ligand field theory to estimate enthalpies of formation can also be applied to Ti^{2+}-(aq) (Table 7) by using the data of ref 3. Here Δ for [Ti(H$_2$O)$_6$]$^{2+}$ is taken to be identical with the value for [V(H$_2$O)$_6$]$^{2+}$, and the metal–ligand distance is assumed to be 3.5 pm greater than in [V(H$_2$O)$_6$]$^{2+}$, a difference calculated from the internuclear distances in VI$_2$ and TiI$_2$, the latter of which, unlike TiCl$_2$ and TiBr$_2$, is not metallic.[39,44] This yields $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{Ti}^{2+},\mathrm{aq}) = -238$

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Table 7. Estimated Contributions to the Hydration Enthalpies of Ti^{2+} and Ti^{3+} [a]

	$\Delta H^{\ominus}_{res}(1)$	ΔE_{orb}	ΔE_{rep}(irreg)	ΔE_{rlx}	ΔE_{so}	$\Delta H^{\ominus}(1)$
Ti^{2+}	−2592	−105	−20	24	1	−2692
Ti^{3+}	−5439	−90	−38	17	2	−5548

[a] All in units of kJ mol^{-1}.

$kJ\ mol^{-1}$. The entropies of $Ti^{2+}(aq)$ and $Ti^{3+}(aq)$ were obtained by using the methods and estimated magnetic entropies of ref 21. First, the estimated magnetic entropies were removed from the experimental values[21,24,40] of the entropies of first-row transition metal aqueous ions. Values of $S^{\ominus}(Ti^{2+},aq)$ and $S^{\ominus}$-(Ti^{3+},aq) were then obtained from linear plots of the resulting values for d^n dipositive or tripositive ions against those of d^{n+5} dipositive ions ($n = 0 \rightarrow 5$). Finally, the magnetic entropies were restored. The resulting figures are $S^{\ominus}(Ti^{2+},aq) = -91$ J $K^{-1}\ mol^{-1}$ and $S^{\ominus}(Ti^{3+},aq) = -292$ J K^{-1} mol^{-1}; whence, $E^{\ominus}$-$(Ti^{2+}|Ti) = -1.25$ V, $E^{\ominus}(Ti^{3+}|Ti^{2+}) = -1.63$ V, and $Ti^{2+}(aq)$ is predicted to be highly unstable with respect to disproportionation. This estimate of $E^{\ominus}(Ti^{3+}|Ti^{2+})$ is about 0.4 V more negative than those obtained from more traditional analyses,[45] a change caused mainly by recognition of the need to detach the tripositive ion baseline from the scandium point. It is more in accord with the experimental work of Olver and Ross,[46] who found the $Ti^{3+}|Ti^{2+}$ half-wave potential in acetonitrile at −1.06 V on the hydrogen electrode scale. Differences between the half-wave potentials of $M^{3+}|M^{2+}$ systems in acetonitrile and their standard redox potentials in water are in the region of 0.6−0.8 V[47] and suggest that $E^{\ominus}(Ti^{3+}|Ti^{2+})$ is −1.6 to −1.9 V. The frequently quoted value estimated by George and McClure (−2.3 V)[1] is almost certainly too negative. It was obtained by assuming a constant difference between the baselines derived by subtracting ligand field stabilization energies from the hydration enthalpies of the M^{2+} and M^{3+} ions. Our values of $\Delta H^{\ominus}_{res}(1)$ cited here for M^{3+}, and elsewhere[3] for M^{2+}, show that the difference increases by about 250 kJ mol^{-1} between scandium and zinc. This drift is in qualitative agreement with the Born equation[48a] in which it arises mainly from the charge difference between the ions. George and McClure's assumption therefore gives too negative estimates of $E^{\ominus}(M^{3+}|M^{2+})$ at the beginning of the series and too positive values at the end.

As Figure 3 shows, as one moves across the series, the variations in $E^{\ominus}(M^{3+}|M^{2+})$ resemble those in the third ionization energy of the metal but only in a strongly attenuated form. That attenuation is due to the ligand field stabilization energies of the aqueous ions. For example, the relatively small drop in $E^{\ominus}$-$(M^{3+}|M^{2+})$ between manganese and iron is caused by zero values of such energies for ions with d^5 configurations, those for $Mn^{3+}(aq)$ and $Fe^{2+}(aq)$ being substantial. Removal of our ligand field stabilization energies for both $M^{2+}(aq)$[3] and M^{3+}-(aq) ions from the redox potentials $E^{\ominus}(M^{3+}|M^{2+})$ generates a lanthanide-like near-parallelism between the latter quantity and the corresponding ionization energy (Figure 3), the expected result for a redox process when ligand field effects are negligible.[48b,49] As explained above, the values of $E^{\ominus}(M^{3+}|M^{2+})$ estimated by George and McClure[1] were obtained by assuming that the parallelism is exact, whereas there is a drift of about 25 kJ mol^{-1} per element across the series. Were it not for the ligand field stabilization energies, $Cr^{3+}(aq)$ would be a strong

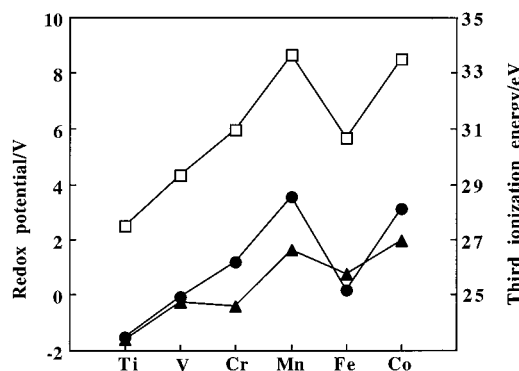**Figure 3.** Variations in $E^{\ominus}(M^{3+}|M^{2+})$ for the first-row transition metals (filled triangles) showing the influence of those in the third ionization energies (open squares) but in a strongly attenuated form. Removal of the ligand field stabilization energies of aqueous $[M(H_2O)_6]^{2+}$ and $[M(H_2O)_6]^{3+}$ from $E^{\ominus}(M^{3+}|M^{2+})$ gives values (filled circles) which closely parallel the ionization energy variations.

oxidizing agent, $Mn^{3+}(aq)$ would probably be unknown, Fe^{2+}-(aq) would be a more powerful reducing agent than it is, and, beyond iron, proven existence of tripositive aqueous ions would be unlikely.

Cases in which the d-electron configuration can assume either a high- or low-spin state deserve special comment, because SCF calculations tend to underestimate the binding energy of low-spin complexes. For example, the states of $Co^{3+}(aq)$, $Ru^{2+}(aq)$ and $Ru^{3+}(aq)$ predicted by such methods were all high spin.[5] The case of $Co^{3+}(aq)$ is of particular interest because its stabilization with respect to the high-spin state has a crucial bearing on competing explanations of the anomalous rates of its electron-transfer and ligand-exchange reactions.[18,50−53] The unexpectedly high rates are sometimes explained by a small stabilization, typically less than 20 kJ mol^{-1}.[54] Our calculations give a figure of over 40 kJ mol^{-1}, and in Figure 2, the small deviation of the $\Delta H^{\ominus}_{res}(1)$ point for cobalt from the baseline curve corroborates our value. We have previously estimated the stabilization[21] by both spectroscopic calculations and empirical thermodynamic methods akin to those of Hisham and Benson.[55] The first approach gave 36 kJ mol^{-1}, and the second 56 kJ mol^{-1} leading to a preferred value of 46 ± 20 kJ mol^{-1}. However, as noted earlier, the application of the intermediate field approximation to the electronic spectrum of $[Co(H_2O)_6]^{3+}$ revises the spectroscopic estimate of the energy of the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition, and the procedure of ref 21, using our difference in internuclear distance of 7.2 pm for the high- and low-spin states, then yields a stabilization of 43 kJ mol^{-1}, a figure in better agreement with the empirical thermodynamic one. The revised preferred value is 50 ± 15 kJ mol^{-1}.

In Table 8, the thermodynamic properties of $Co^{3+}(aq)$, given in ref 21 for both spin states, have been recalculated using both

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Table 8. Thermodynamic Properties of High- and Low-Spin $Co^{3+}(aq)$

	$\Delta H_f^{\ominus}/kJ\ mol^{-1}$	$\Delta G_f^{\ominus}/kJ\ mol^{-1}$	$S^{\ominus}/kJ\ mol^{-1}$
Co^{3+}(aq,low-spin)	77 ± 7	131 ± 4	-346 ± 25
Co^{3+}(aq,high spin)	127 ± 17	169 ± 17	-306 ± 30

the new estimated stabilization and revised iron thermochemistry.[24] For the reaction

$$Co^{3+}(aq,\text{low-spin}) \rightarrow Co^{3+}(aq,\text{high-spin}) \qquad (6)$$
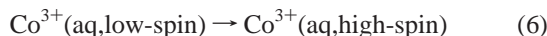
$\Delta S^{\ominus}(6)$ is positive because of the increase in both bond length and magnetic entropy, an effect which is qualitatively consistent with empirical equations for the entropies of ions.[56-58] The data give $\Delta G^{\ominus}(6) = 38 \pm 16$ kJ mol^{-1}, a figure corresponding to an equilibrium constant of 2×10^{-7} at 298.15 K and consistent with the NMR measurements of Navon,[59] who concluded that $\Delta G^{\ominus}(6) > 23$ kJ mol^{-1}.

In contrast to $[Co(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{3+}$ exists in the high-spin state.[60] To see if our analysis is consistent with this, we have used our interpolated values of B and C (Tables 3 and 4) in the regular octahedral state. As C/B is nearly 6, reflecting the unusually high value for d^4 gaseous ions, we avoid the assumption $C = 4B$. When this simplification is removed, the intermediate field approximation[13a] gives $\{-1.6\Delta + 6B + 5C - [28B^2 + (2B + C)^2]/\Delta\}$ for the energy of the $^3T_{1g}$ state of t_{2g}^4. The $^5E_g \rightarrow {}^3T_{1g}$ transition is thus predicted at 3470 cm^{-1}. The difference in bond lengths for high- and low-spin manganese(III) is 6−7 pm,[34] suggesting an a_{1g} stretching frequency of about 520 cm^{-1} for the low-spin state. The a_{1g} vibrational energy in the excited $^3T_{1g}$ state at the internuclear distance in the ground state is then 22 kJ mol^{-1} (1830 cm^{-1}, eq 4) implying that, of the two regular octahedra, the high-spin state is the lower in energy by about 1640 cm^{-1}. This stabilization is further enhanced by a Jahn−Teller distortion of the ground state to 4300 cm^{-1} (51 kJ mol^{-1}).

From an X-ray study of $CrSiF_6 \cdot 6H_2O$, Cotton et al. concluded that the $[Cr(H_2O)_6]^{2+}$ octahedron is regular, with an unusually short bond length.[61,62] This prompted the interesting suggestion that the chromium(II) complex might be in the low-spin state.[5]

But if $[Mn(H_2O)_6]^{3+}$ is highly unstable in a low-spin state, then $[Cr(H_2O)_6]^{2+}$, with its smaller orbital splitting, should be even more so. For this complex, the data and sources of ref 3 give $B_g = 723$ cm^{-1} and $C_g = 3480$ cm^{-1}, and interpolation of ΔB and ΔC then leads to $\Delta = 9250$ cm^{-1}, $B = 614$ cm^{-1}, and $C = 3352$ cm^{-1}, putting the $^5E_g \rightarrow {}^3T_{1g}$ transition in the regular octahedral state at about 7800 cm^{-1}. With a bond length difference of 7 pm[34] and a vibrational frequency of 380 cm^{-1}, the vibrational energy of the excited state is 1100 cm^{-1} (eq 4) implying that, with respect to the low-spin state, $[Cr(H_2O)_6]^{2+}$ is stable by about 6700 cm^{-1} (80 kJ mol^{-1}) if regular octahedral and by about 9100 cm^{-1} (109 kJ mol^{-1}) if distorted.

This degree of instability of the low-spin state makes its existence in $CrSiF_6 \cdot 6H_2O$ unlikely. The observed bond length is 6.1 pm shorter than the average internuclear distance in the distorted octahedron in the Tutton salt,[62] corresponding to a destabilization of about 9 kJ mol^{-1} (eq 4). This is not enough to make the low-spin state more stable. Reexamination of the thermal parameters in the X-ray study of $CrSiF_6 \cdot 6H_2O$ has indicated[63] that there is a disordered Jahn−Teller effect in this salt; moreover, its color is blue[61] like other compounds and solutions containing high-spin $[Cr(H_2O)_6]^{2+}$. Retention of the high-spin state with compression is therefore more likely than a low-spin state. Magnetic measurements would settle the question.

Note Added in Proof. A new electronic spectrum of the rubidium vanadium alum at 16 K (Tregenna-Piggott, P. L. W.; Best, S. P.; Gudel, H. U.; Weihe, H.; Wilson, C. C. *J. Solid State Chem.* **1999**, *145*, 460) is very similar to our results for the cesium alum, except that a band centered at about 10 500 cm^{-1} is assigned to the $^3A_{2g} \rightarrow {}^1E_g$ transition. If this change is made to Table 1, then for the alum, $C = 2819$ cm^{-1}, in Table 3, $C = 2805$ cm^{-1}, and for vanadium in Table 6, $\Delta H_{res}^{\ominus}(1) = -5539$ kJ mol^{-1}. This further improves the baseline fit in Figure 2. The titanium estimates become $\Delta H_f^{\ominus}(Ti^{3+},aq) = -446$ kJ mol^{-1} and $E^{\ominus}(Ti^{3+}|Ti^{2+}) = -1.73$ V. For other elements, any changes are very small.

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