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Bond Energy Terms in Complex Ions

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Bond Energy Terms B(M–L) are calculated from experimental data for a number of metal complexes having H_2O, NH_3, CN^- and F^- as ligands.

Introduction

The energetics of ionic solids can be understood both qualitatively and quantitatively in terms of the Lattice Energy[1]: the energetics of covalent molecules, although less well understood, are well described by means of Bond Dissociation Energies, D, for diatomic molecules and Bond Energy Terms, B, for polyatomic molecules[2]. For coordination compounds, the energetics are in general neither defined nor understood. For the *d*-block elements, the problem has generally been approached in terms of Crystal Field Stabilisation Energy (CFSE): however this method describes only a small proportion of the energy of the interaction between a metal ion and a group of ligands, and can be applied to few elements other than the 3*d* metals.

In this paper, values of the coordinate bond energy terms for metal–ligand bonds, B(M–L) are derived for a wide range of aquo ions and for a few complexes of NH_3, CN^- and F^-. The derivation of these values makes no assumptions about the nature of the metal–ligand bonds. Only homogeneous complexes $ML_n{}^{+z}$ where the L are identical are considered: for mixed complexes the reliable estimation of hydration enthalpies and of crystal field stabilisation energies is difficult.

Results

Bond Energy Terms for M^{+z}–OH_2 Bonds

Bond energy terms for M^{+z}–OH_2 bonds can be derived from the hydration enthalpies of M^{+z} by means of the following cycle

$$\begin{tikzcd}[column sep=huge, row sep=large]
nH_2O_{(l)} + M^{+z}{}_{(g)} \arrow[r, "(\Delta H^\ominus)^{obs}"] \arrow[d, "+n(\Delta H^\ominus)^{vap}{}_{H_2O}"'] & M(H_2O)_n{}^{+z}{}_{(aq)} \\
nH_2O_{(g)} + M^{+z}{}_{(g)} \arrow[r, "-nB(M^{+z}\text{–}OH_2)", "-CFSE"'] & M(H_2O)_n{}^{+z}{}_{(g)} \arrow[u, "-(\Delta H^\ominus)^{aq}"']
\end{tikzcd}$$

$$(\Delta H^\ominus)^{obs} = +n(\Delta H^\ominus)^{vap}{}_{H_2O} - nB(M^{+z} - OH_2)_2 - CFSE - (\Delta H^\ominus)^{aq}$$

where $(\Delta H^\ominus)^{obs}$ = experimental hydration enthalpy of M^{+z}, $(\Delta H^\ominus)^{vap}$ = enthalpy of vaporisation of H_2O, $(\Delta H^\ominus)^{aq}$ = enthalpy of hydration of $M(H_2O)_n{}^{+z}$, and $B(M^{+z}\text{–}OH_2)$ is the bond energy term in question.

Absolute hydration enthalpies[2,3,4,5] were adjusted to the value[3] for the absolute hydration enthalpy of H^+ = -1091 kJ mol^{-1}.

There seems little doubt that ions of the 3*d* series form complexes in aqueous solution of the form $M(H_2O)_6{}^{+2}$ for z = 2 and 3. Al^{+3}, Sc^{+3} and Ga^{+3} all similarly form[6,7,8] ions $M(H_2O)_6{}^{+3}$: the same is probably true also of In^{+3} and Tl^{+3}, although the suggestion has been made[9] that Tl^{+3}, in common with a number of other heavy d^{10} ions, may bind two of its ligands rather more strongly than the remainder; for Y^{+3}, n is probably[8] 8. For Be^{+2} and Mg^{+2}, n has been shown to take the values 4 and 6 respectively[10]. The nature of the remaining Group II ions, Ca^{+2}, Sr^{+2} and Ba^{+2}, in aqueous solution is obscure, as is the behaviour of the Group I ions: there is some evidence to suggest[8] that for Group I ions n = 6 and that for Group II ions n = 8. Both zinc and cadmium form hexaquo ions in the solid state[11,12] and it does not seem unreasonable to suppose that these will persist in aqueous solution.

Hydration enthalpies of the complex ions $M(H_2O)_n{}^{+z}$ were estimated using the Born equation[13]:

$$\Delta H^\ominus = -\frac{Ne^2z^2}{2r}\left(1-\frac{1}{D}\right) + \frac{TNe^2z^2}{2DR}\,\frac{\partial \ln D}{\partial T}$$

where r = radius of the ion, D = electric constant of the solvent.

Inserting constants, this becomes at 298° K

$$\Delta H^\ominus = -689.5\,\frac{z^2}{r}\ \text{kJ mol}^{-1}$$

so that $\Delta H^\ominus$ can be determined provided that r is known. Radii of aquo ions have usually been estimated by adding to Pauling's ionic radii[14] the diameter of the water molecule, taken to be 2.76 Å. This value seems to be chosen as it represents the shortest distance between oxygen atoms in ice[15]: however in ice the oxygen atoms have tetrahedral symmetry, due to the statistical distribution of the hydrogen atoms, so that this value for the diameter of water may not be very appropriate for a water molecule in a complex ion where the local symmetry about oxygen is far from tetrahedral. In this work, the radii of a number of aquo ions have been derived from the structures of crystalline hydrates; application of Pauling's radii has enabled the radii of further aquo ions to be estimated.

By use of the radius of the $SiF_6{}^{-2}$ ion, 2.19 Å derived from the structures[16] of caesium, potassium and rubidium fluorosilicates, radii were derived for the hexaquo ions of Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2} and Zn^{+2} from the structures of their fluorosilicates[11, 17]; the values were 2.68 Å, 2.63 Å, 2.62 Å and 2.66 Å respectively. Values of 2.63 Å and 2.55 Å respectively were adopted for $Cr(H_2O)_6{}^{+3}$ and $Co(H_2O)_6{}^{+3}$: these are the radii found for the corresponding hexammino cations in $Cr(NH_3)_6(ClO_4)_3$[18] and $Co(NH_3)_6I_3$[19].

A radius of 2.44 Å was derived for $Al(H_2O)_6{}^{+3}$ from the structure of $Al(H_2O)_6Cl_3$[20]. Other radii for complex ions were derived from these values by use of Pauling's radii, assuming that $r(M_1{}^{+z_1}) - r(M_2{}^{+z_2}) = r[M_1(H_2O)_n{}^{+z_1}] - r[M_2(H_2O)_n{}^{+z_2}]$.

Crystal-field stabilisation energies were derived from the values of Δ and B given by Jørgensen[21], adopting the usual relationship between the Racah parameters, C = 4B. The enthalpy of vaporisation of water was taken to be[2] 44.0_2 kJ mol^{-1}.

Tables I–IV present bond-energy data for the *3d* ions $M(H_2O)_6{}^{+2}$ and $M(H_2O)_6{}^{+3}$ and for the Group II ions $M(H_2O)_n{}^{+2}$ and the Group III ions $M(H_2O)_6{}^{+3}$ respectively. Table V presents values for the alkali metal ions, calculated for various values of n.

Bond Energy for M^{+z}–NH_3 Bonds

The bond energy terms $B(M^{+z}-OH_2)$ and $B(M^{+z}-NH_3)$ can be related using the thermochemical cycle:

$$\begin{tikzcd}
\mathrm{M(H_2O)_n{}^{+z}{}_{(aq)}} + \arrow[d, "+(\Delta H^{\ominus})^{aq}_{M(H_2O)_n{}^{+z}}"] & \mathrm{nNH_{3(aq)}} \arrow[r, "(\Delta H^{\ominus})^{obs}"] \arrow[dd, "+n(\Delta H^{\ominus})^{aq}{}_{NH_3}"] & \mathrm{M(NH_3)_n{}^{+z}{}_{(aq)}} + & \mathrm{nH_2O_{(l)}} \\
\mathrm{M(H_2O)_n{}^{+z}{}_{(g)}} \arrow[d, "+nB(M^{+z}-OH_2) \\ +(CFSE)_{H_2O}"] & & & \\
\mathrm{M^{+z}{}_{(g)} + nH_2O_{(g)}} + & \mathrm{nNH_{3(g)}} \arrow[r, "-nB(M^{+z}-NH_3)", "-(CFSE)_{NH_3}"'] & \mathrm{M(NH_3)_n{}^{+z}{}_{(g)}} + \arrow[uu, "-(\Delta H^{\ominus})^{aq}_{M(NH_3)_n{}^{+z}}"] & \mathrm{nH_2O_{(g)}} \arrow[uu, "-n(\Delta H^{\ominus})^{vap}{}_{H_2O}"]
\end{tikzcd}$$

$$(\Delta H^{\ominus})^{obs} = [(\Delta H^{\ominus})^{aq}_{M(H_2O)_n{}^{+z}} - (\Delta H^{\ominus})^{aq}_{M(NH_3)_n{}^{+z}}] + n[B(M^{+z}-OH_2) - B(M^{+z}-NH_3)]$$
$$+ [(CFSE)_{H_2O} - (CFSE)_{NH_3}] + n[(\Delta H^{\ominus})^{aq}{}_{NH_3} - (\Delta H^{\ominus})^{vap}{}_{H_2O}]$$

where $(\Delta H^{\ominus})^{aq}{}_{NH_3}$ is the enthalpy of solution of ammonia and $(CFSE)_{H_2O}$ and $(CFSE)_{NH_3}$ are the crystal field stabilisation energies of $M(H_2O)_n{}^{+z}$ and $M(NH_3)_n{}^{+z}$ respectively.

If the radii, and hence the hydration enthalpies of $M(H_2O)_n{}^{+z}$ and $M(NH_3)_n{}^{+z}$ are taken to be equal, then this equation becomes

$$n\Delta B = (\Delta H^{\ominus})^{obs} - [(CFSE)_{H_2O} - (CFSE)_{NH_3}] - n[(\Delta H^{\ominus})^{aq}{}_{NH_3} - (\Delta H^{\ominus})^{vap}{}_{H_2O}]$$

where now $\Delta B = B(M^{+z}-OH_2) - B(M^{+z}-NH_3)$. The enthalpy of solution of ammonia is taken[22] as –35.4 kJ mol^{-1}. Rather few reliable enthalpy data are available; these are collected in Table VI.

TABLE I. Bond Energy Terms (kJ mol^{-1}) for *3d* Ions $M(H_2O)_6{}^{+2}$.

M	n	r(Å)	$+n(\Delta H^{\ominus})^{vap}{}_{H_2O}$	$-(\Delta H^{\ominus})^{aq}$	$-(\Delta H^{\ominus})^{obs}$	–CFSE	nB	B
V^{+2}	6	2.75	+264.1	–1002.9	+1887.0	–177.8	970.4	161.7
Cr^{+2}	6	2.71	+264.1	–1017.5	+1907.5	–99.6	1054.5	175.8
Mn^{+2}	6	2.68	+264.1	–1029.3	+1860.2	–0.0	1095.0	182.5
Fe^{+2}	6	2.63	+264.1	–1048.5	+1946.4	–49.8	1112.2	185.4
Co^{+2}	6	2.63	+264.1	–1048.5	+2012.5	–56.5	1171.6	195.3
Ni^{+2}	6	2.62	+264.1	–1052.7	+2091.2	–121.8	1180.8	196.8
Zn^{+2}	6	2.66	+264.1	–1036.8	+2044.7	–0.0	1272.0	212.0

TABLE II. Bond Energy Terms (kJ mol^{-1}) for 3*d* Ions $M(H_2O)_6^{+3}$.

M	n	r(Å)	$+n(\Delta H^{\ominus})^{vap}_{H_2O}$	$-(\Delta H^{\ominus})^{aq}$	$-(\Delta H^{\ominus})^{obs}$	−CFSE	nB	B
Sc^{+3}	6	2.74	+264.1	−2264.8	+3903.3	−0.0	1902.6	317.1
Ti^{+3}	6	2.69	+264.1	−2307.1	+4287.4	−97.1	2147.3	357.9
V^{+3}	6	2.67	+264.1	−2324.2	+4396.1	−176.1	2159.9	360.0
Cr^{+3}	6	2.63	+264.1	−2359.8	+4613.7	−249.8	2268.2	378.0
Mn^{+3}	6	2.60	+264.1	−2387.0	+4584.4	−98.3	2363.2	393.9
Fe^{+3}	6	2.55	+264.1	−2433.4	+4475.6	−0.0	2306.3	384.4
Co^{+3}	6	2.55	+264.1	−2433.4	+4701.6	−225.9	2306.4	384.4

TABLE III. Bond Energy Terms (kJ mol^{-1}) for Group II Ions $M(H_2O)_n^{+2}$.

M	n	r(Å)	$+n(\Delta H^{\ominus})^{vap}_{H_2O}$	$-(\Delta H^{\ominus})^{aq}$	$-(\Delta H^{\ominus})^{obs}$	nB	B
Be^{+2}	4	2.20	+176.1	−1253.5	+2487.0	1409.6	352.4
Mg^{+2}	6	2.57	+264.1	−1073.2	+1920.9	1111.8	185.3
Ca^{+2}	8	2.91	+352.2	−947.8	+1576.5	980.9	122.6
Zn^{+2}	6	2.66	+264.1	−1036.8	+2044.7	1272.0	212.0
Cd^{+2}	6	2.89	+264.1	−954.4	+1804.1	1113.8	185.6

TABLE IV. Bond Energy Terms (kJ mol^{-1}) for Group III Ions $M(H_2O)_6^{+3}$.

M	n	r(Å)	$+n(\Delta H^{\ominus})^{vap}_{H_2O}$	$-(\Delta H^{\ominus})^{aq}$	$-(\Delta H^{\ominus})^{obs}$	nB	B
Al^{+3}	6	2.44	+264.1	−2543.3	+4669.3	2390.1	398.4
Sc^{+3}	6	2.74	+264.1	−2264.8	+3903.3	1902.6	317.1
Y^{+3}	8	2.86	+352.2	−2169.4	+3589.0	1771.8	221.5
Ga^{+3}	6	2.54	+264.1	−2443.0	+4684.8	2505.9	417.7
In^{+3}	6	2.73	+264.1	−2273.2	+4108.7	2099.6	350.0
Tl^{+3}	6	2.87	+264.1	−2162.3	+4184.0	2285.8	381.0

Bond Energy Terms for M^{+z}–CN Bonds

The bond energy terms ($M^{+z}-OH_2$) and (M^{+z}–CN) can be related by the cycle

$$\begin{tikzcd}
M(H_2O)_n{}^{+z}{}_{aq} \arrow[d] & {}+ nCN^-_{(aq)} \arrow[r, "(\Delta H^{\ominus})^{obs}"] \arrow[dd, "+n(\Delta H^{\ominus})^{aq}_{CN^-}"] & M(CN)^{+(z-n)}_{n(aq)} & {}+ nH_2O_{(l)} \\
M(H_2O)_n{}^{+z}{}_{(g)} \arrow[d, "{+nB(M^{+z}-OH_2) \atop +(CSFE)_{H_2O}}"'] & & & \\
M^{+z}{}_{(g)} + nH_2O_{(g)} & {}+ nCN^-_{(g)} \arrow[r, "-nB(M^{+z}-CN)", "-(CFSE)_{CN}"'] & M(CN)_{n(g)}{}^{+(z-n)} \arrow[uu, "-(\Delta H^{\ominus})^{aq}_{M(CN)_n{}^{+(z-n)}}"] & {}+ nH_2O_{(g)} \arrow[uu, "-n(\Delta H^{\ominus})^{vap}_{H_2O}"']
\end{tikzcd}$$

$$(\Delta H^{\ominus})^{obs} = [(\Delta H^{\ominus})^{aq}_{M(H_2O)_n{}^{+z}} - (\Delta H^{\ominus})^{aq}_{M(CN)_n{}^{+(z-n)}}] + n[B(M^{+z}-OH_2) - B(M^{+z}-CN)]$$
$$+ [(CFSE)_{H_2O} - (CFSE)_{CN^-}] + n[(\Delta H^{\ominus})^{aq} \quad (\Delta H^{\ominus})^{vap}{}_{H_2O}]$$

where $(\Delta H^{\ominus})^{aq}{}_{CN^-}$ is the aquation enthalpy of the cyanide ion.

Crystal field stabilisation energies for hexacyanides were calculated using values of Δ, B and C given[27] by Chadwick and Sharpe: the hydration enthalpy of the cyanide ion was taken to be[3] -342.3 kJ mol^{-1}.

TABLE V. Bond Energy Terms (kJ mol^{-1}) for Group I Ions $M(H_2O)_n^+$.

M	n = 4	n = 6	n = 8
Li^+	105.8	85.2	74.9
Na^+	85.4	71.6	64.7
K^+	71.6	62.4	57.8
Rb^+	68.5	60.3	56.3
Cs^+	65.4	58.3	54.7

TABLE VI. Values of $B(M^{+z}-OH_2)-B(M^{+z}-NH_3)$ (kJ mol^{-1}).

M	$(\Delta H^\ominus)^{obs}$	$-[(CFSE)_{H_2O}-(CFSE)_{NH_3}]$	$-n[(\Delta H^\ominus)^{aq}_{NH_3}-(\Delta H^\ominus)^{vap}_{H_2O}]$	$n\Delta B$	B
Co^{+3}	-237.7[a]	$+156.9$	$+51.7$	-29.1	-4.8
Co^{+2}	-54.4[b]	$+9.5$	$+51.7$	$+6.8$	$+1.1$
Ni^{+2}	-87.9[c]	$+29.7$	$+51.7$	-6.5	-1.1
Cd^{+2}	-29.8[d]	–	$+17.2$	-12.6	-6.3
	-53.1	–	$+34.5$	-18.6	-4.7

[a] Ref. 23. [b] Ref. 24. [c] Ref. 25. [d] Ref. 26. Data refer to reactions $Cd(H_2O)_6^{+2} + 2NH_3 \rightarrow Cd(H_2O)_4(NH_3)_2^{+2} + 2H_2O$ and $Cd(H_2O)_6^{+2} + 4NH_3 \rightarrow Cd(H_2O)_2(NH_3)_4^{+2} + 4H_2O$ respectively.

TABLE VII. Values of $B(M^{+z}-CN)-B(M^{+z}-OH_2)$ (kJ mol^{-1}).

M	$[(\Delta H^\ominus)^{aq}_{M(H_2O)_6^{+z}}-(\Delta H^\ominus)^{aq}_{M(CN)_6^{+(z-6)}}]$	$+[(CFSE)_{H_2O}-(CFSE)_{CN}]$	$+6[(\Delta H^\ominus)^{vap}_{H_2O}-(\Delta H^\ominus)^{aq}_{CN^-}]$	$-(\Delta H^\ominus)^{obs}$	$6\Delta B$	B
V^{II}	-1649.0	-180.7	$+1789.4$	$+196.6$[a]	$+156.3$	$+26.1$
Cr^{II}	-1659.7	-163.6	$+1789.4$	$+264.4$[a]	$+256.6$	$+42.8$
Mn^{II}	-1675.2	-18.4	$+1789.4$	$+144.3$[a]	$+210.1$	$+40.0$
Fe^{II}	-1709.4	-574.0	$+1789.4$	$+358.9$[b]	-135.1	-22.5
Co^{II}	-1709.4	-331.0	$+1789.4$	$+311.3$[a]	$+60.3$	$+10.1$
Fe^{III}	$+851.2$	-315.1	$+1789.4$	$+293.5$[b]	$+2619.0$	$+436.5$

[a] Ref. 31. [b] Ref. 32.

Hexacyanometallate ions are markedly non-spherical: the effective radius of the $Fe^{II}(CN)_6^{-4}$ ion in the direction Fe–C–N is[28] 4.34 Å in a number of hexacyanoferrate(II) derivatives, while in a direction normal to a face of the coordination octahedron the effective radius is 3.66 Å: a mean radius of 4.00 Å was adopted. Comparison of the structures of $Cu_2Cr(CN)_6$[29], $Cu_2Mn(CN)_6$[30] and $Cu_2Fe(CN)_6$[28] led to estimated mean radii of 4.12 Å and 4.08 Å for the chromium and manganese species. Calculations for $\Delta B = B(M^{+z}-CN)-B(M^{+z}-OH_2)$ are set out in Table VII; these lead to bond energy terms for $M^{+z}-CN$ bonds in hexacyano ions as follows: V^{II}, 188.7 kJ; Cr^{II}, 218.6 kJ; Mn^{I}, 222.5 kJ; Fe^{II}, 162.9 kJ; Co^{II}, 205.4 kJ; Fe^{III} 820.9 kJ.

The cycle employed to relate the bond energy terms $B(M^{+z}-OH_2)$ and $B(M^{+z}-CN)$ will be apt for any uninegative anionic ligand. Enthalpy data are available for the formation of both BeF_4^{-2} and AlF_6^{-3} from the corresponding aquo ions, -9.4 kJ mol^{-1} [33] and $+0.4$ kJ mol^{-1} [34] respectively: the radius of AlF_6^{-3} is taken as 2.37 Å, and that of BeF_4^{-2} as 2.13 Å. Hence $B(Be^{+2}-F)-B(Be^{+2}-OH_2) = 453.7$ kJ mol^{-1} or $B(Be^{+2}-F) = 805.1$ kJ mol^{-1}, and $B(Al^{+3}-F)-B(Al^{+3}-OH_2) = 448.8$ kJ mol^{-1}, so that $B(Al^{+3}-F) = 847.2$ kJ mol^{-1}.

Discussion

Comparison of the results for $M^{+z}-OH_2$ bond energy terms presented in Tables I–V reveals some general trends. Firstly, bond energy terms for similar elements increase with the charge Z: this is apparent both in the M^{+2} and M^{+3} ions of the 3rd series, and in series such as Na^+, Mg^{+2}, Al^{+3}, and probably reflects the increased polarising power of the multiply-charged metal ions. Secondly across the *3d* series from Ca^{+2} to Zn^{+2} for the M^{+2} ions, and from Sc^{+3} to Ga^{+3} for the M^{+3} ions, there is generally an increase in B; this may reflect both the decrease in M–O distance, and an increase in covalence on traversing the series. Thirdly on descending vertical groups the bond energy term decreases: while this may merely reflect an increase in the M–O distance, it may also be associated with the decrease in polarising power of the cations, leading to bonds of lower covalence at the foot of the periodic table. At any rate, this decrease in bond energy is typical of the behaviour of covalent bonds.

Turning to the individual values, the only anomalies appear to be Mn^{+3} and Tl^{+3}: Mn^{+3} is subject to Jahn–Teller distortions while Tl^{+3} may[9] be subject to the distortions characteristic of heavy d^{10} ions[36], and in each of the ions $Mn(H_2O)_6^{+3}$ and $Tl(H_2O_6)^{+3}$ it is possible that some of the ligands are tighter bound than the remainder. The value for Be^{+2}, 352.4 kJ mol^{-1}, is similar in magnitude to the bond energies found for tripositive ions: however this value is by no means unreasonable in view of B(B–O) of approximately[37] 525 kJ mol^{-1}.

So far as the rather limited data are available, it seems that M^{+2}–NH_3 bond energy terms are identical, within experimental uncertainty, to the corresponding M^{+2}–OH_2 energies (Table VI). This similarity in M–NH_3 and M–OH_2 is manifested also in the very similar ligand field parameters of NH_3 and H_2O.

In the cyanide species, $B(M^{+2}–CN)$ is somewhat larger than $B(M^{+2}–OH_2)$ except in the case of Fe^{+2}: the apparent discrepancy in this example may be real, in which case no convincing interpretation can be offered, or it may arise from an overestimate of the CFSE of the $Fe(CN)_6^{-4}$ ion. The value of Δ employed[27], 34.7 kK, is much larger than for other M ions: reduction of this to 25 kK would lead to an Fe^{+2}–CN bond energy term of 207.3 kJ. This may underline a weakness of this type of calculation in the case of ligands such as cyanide where the crystal field model may not be a good representation and where the parameters are not easy to extract from the observed spectra. It would be of interest to have available more enthalpy data for formation of hexacyano complexes of tripositive metal ions, since the value of Fe^{+3} indicates that $B(M^{+z}–CN)–B(M^{+z}–OH_2)$ is much greater for Z = 3 than Z = 2. If this difference were substantiated for other metals, this would presumably indicate a much bigger increase in covalence in going from $M(H_2O)_6^{+3}$ to $M(CN)_6^{-3}$ than in going from $M(H_2O)_6^{+2}$ to $M(CN)_6^{-4}$. Similarly, more enthalpy data for formation of fluoride complexes are needed before any discussion of the results for Be^{+2} and Al^{+3} becomes worthwhile.

The data in Tables I and II indicate that for simple aquo ions of the 3*d* series, the CFSE rarely amounts to more than 10% of the metal–ligand bond energy. Attempts are made[38] from time to time to correlate $\Delta H^{\ominus}$ values for redox reactions with CFSE values, and surprise expressed when these attempts are only partially successful. By means of the cycles below for neutral and uninegative ligands the conditions under which such correlations may be expected to be successful can be defined.

For a neutral ligand, L:

$$\begin{tikzcd}
ML_n{}^{+(z+1)}{}_{(aq)} + \arrow[d, "+(\Delta H^{\ominus})^{aq}_{ML_n{}^{+(z+1)}}"'] & e^-{}_{(aq)} \arrow[r, "(\Delta H^{\ominus})^{obs}{}_L"] \arrow[dd, "+(\Delta H^{\ominus})^{aq}_{e}"] & ML_n{}^{+z}{}_{(aq)} \\
ML_n{}^{+(z+1)}{}_{(g)} \arrow[d, "\substack{+nB(M^{+(z+1)}-L)\\ +(CFSE)_{z+1}}"'] & & ML_{n(g)}{}^{+z} \arrow[u, "-(\Delta H^{\ominus})^{aq}_{ML_n{}^{+z}}"'] \\
M^{+(z+1)}{}_{(g)} + nL_{(g)} + & e^-{}_{(g)} \arrow[r, "-I_{z+1}"] & M^{+z}{}_{(g)} + nL_{(g)} \arrow[u, "\substack{-nB(M^{+z}-L)\\ -(CFSE)_z}"']
\end{tikzcd}$$

where

$$(\Delta H^{\ominus})^{obs}{}_L = (\Delta H^{\ominus})^{aq}_{e^-} - I_{z+1} + [(\Delta H^{\ominus})^{aq}_{ML_n{}^{+(z+1)}} - (\Delta H^{\ominus})^{aq}_{ML_n{}^{+z}}] + n[B(M^{+(z+1)}-L) - B(M^{+z}-L)]$$
$$+ [(CFSE)_{ML_n{}^{+(z+1)}} - (CFSE)_{ML^{+z}}]$$

which may be written as

$$(\Delta H^{\ominus})^{obs}{}_L = \text{Constant} - \frac{A}{r_L}(2z+1) + n\Delta B_L + \Delta(CFSE)_L$$

where $\Delta B = B(M^{+(z+1)}-L) - B(M^{+z}-L)$, $(\Delta H^{\ominus})^{aq}{}_{e^-} - I_{z+1}$ is constant for a given metal and the term $-\frac{A}{r_L}(2z+1)$ represents the difference in hydration enthalpies (for a mean ionic radius r_L).

For a uninegative ligand, X^-:

$$MX_n{}^{+(z+1-n)}{}_{(aq)} + e^-{}_{(aq)} \xrightarrow{(\Delta H^{\ominus})^{obs}_{X^-}} MX_n{}^{+(z-n)}{}_{aq}$$

so that following the above

$$(\Delta H^{\ominus})^{obs}_{X^-} = (\Delta H^{\ominus})^{aq}_{e^-} - I_{z+1} + [(\Delta H^{\ominus})^{aq}_{MX_n^{+(z+1-n)}} - (\Delta H^{\ominus})^{aq}_{MX_n^{+(z-n)}}] + n[B(M^{+(z-1)}-X) - B(M^{+z}-X)] + [(CFSE)_{MX_n^{+(z+1-n)}} - (CFSE)_{MX_n^{+(z-n)}}]$$

which may be written as

$$(\Delta H^{\ominus})^{obs}_{X^-} = \text{Constant} - \frac{A}{r_{X-}}(2z+1-2n) + n\Delta B_{X^-} + \Delta(CFSE)_{X^-}$$

For neutral ligands, the difference in hydration enthalpy is proportional to $(2z + 1)$, while for uninegative ligands this difference is proportional to $(2z+1-2n)$ so that only species having the same type (neutral or uninegative, *etc.*) of ligand can be compared. Within such series of complexes of a common metal, a linear relationship between $(\Delta H^{\ominus})^{obs}$ and $\Delta(CFSE)$ will be expected if (i) the coordination number n is the same throughout, (ii) the radii of the complexes are closely similar, (iii) B is the same for each ligand considered.

The conditions are adequately fulfilled by complexes of water and ammonia (and probably also by complexes of other amines such as ethylene diamine). Conditions (ii) and (iii) are probably not fulfilled by complexes of fluoride and cyanide; if these are compared with complexes of chloride, condition (i) is also broken. In particular cyano complexes cannot be compared in this manner with aquo and ammino species. Overall therefore, there is little to be gained from attempted correlations of CFSE with $\Delta H^{\ominus}$ for redox processes: the CFSE term represents only a small part of the energy, the remainder of which varies in a complex but definable manner with both metal and ligand.

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