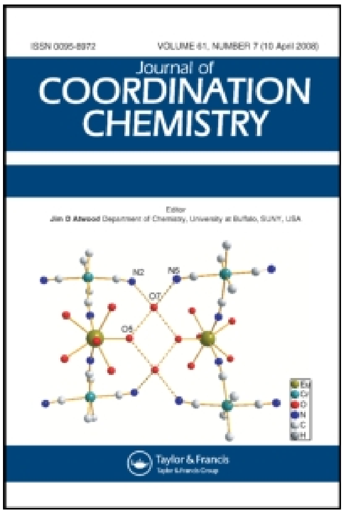

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SHORT COMMUNICATION
Metal-ligand Coordinate Bond Energy Terms in Complexes of Ammonia and 1,2-Diaminoethane

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Metal–ligand coordinate bond energy terms have been calculated for ammonia complexes of : Li^+, Mg^{+2}, Co^{+2}, Co^{+3}, Ni^{+2}, Cu^+, Cu^{+2}, Ag^+, Zn^{+2}, Cd^{+2}, Hg^{+2}; and for 1,2-diaminoethane complexes of: Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}. Bond energy terms $B(M^{+z} - OH_2)$, $B(M^{+z} - NH_3)$ and $B(M^{+z} - en/2)$ all increase monotonically across the 3d series: bond energy terms are larger for a 3d metal than for its 4d analogue, thus $B(Zn^{+2} - L) > B(Cd^{+2} - L)$ and $B(Cu^+ - L) > B(Ag^+ - L)$.

KEY WORDS: Bond energies; complexes, bond energies; coordinate bond energies.

INTRODUCTION

In a previous paper[1] on metal–water coordinate bond energy terms, $B(M^{+z} - OH_2)$, a brief allusion to metal–ammonia bond energy terms was made. The purpose of this paper is to present the determination of metal–ligand coordinate bond energy terms for complexes of ammonia and 1,2-diaminoethane.

DATA SOURCES

Except as specifically stated otherwise, reaction enthalpies are taken from the collection of Christensen and Izatt:[2] crystal field stabilisation energies were calculated from the data given by Jørgensen.[3] Hydration enthalpies were estimated using the Born equation,[4] which for water at 298 K is

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

The enthalpy of vaporisation of water is taken as 44.0 kJ mol^{-1} and the enthalpy of aquation of ammonia as -35.4 kJ mol^{-1}:[5] from the enthalpies of vaporisation, +44.0 kJ mol^{-1}, and of solution in water, -31.8 kJ mol^{-1} of 1,2-diaminoethane,[5] the enthalpy of aquation of the gaseous ligand was found to be -75.8 kJ mol^{-1}. From the crystal structures of $Cr(NH_3)_6(ClO_4)_3$[6] and $Co(NH_3)_6I_3$,[7] radii for the ions $Cr(NH_3)_6^{+3}$ and $Co(NH_3)_6^{+3}$ of 2.63 Å and 2.55 Å respectively were derived: a radius of 2.74 Å was determined for the ion $Coen_3^{+3}$ (en = 1,2-diaminoethane) from the crystal structure[8] of $(Coen_3)Cl_3.3H_2O)$. All other radii of complex ions were derived from these, assuming that $r(M_1L_n^{+z_1}) - r(M_2L_n^{+z_2}) = r(M_1^{+z_1}) - r(M_2^{+z_2})$, by use of Pauling's ionic radii. Hydration enthalpies of gaseous metal ions were derived from the same sources as in ref. 1.

RESULTS

For the reaction of ammonia molecules in solution with an aquo-ion

$$M(H_2O)_{p(aq)}^{+z} + n\,NH_{3\,(aq)} \longrightarrow [M(H_2O)_{p-n}(NH_3)_n^{+z}]_{(aq)} + n\,H_2O_{(l)}$$

the observed enthalpy of reaction $(\Delta H^{\ominus})^{obs}$ may be written

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

where the terms $(\Delta H^{\ominus})^{aq}_{X}$ represent aquation enthalpies of X: this is conveniently rearranged to read

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

TABLE I
Bond energy terms for metal-ammonia bonds (/kJ mol^{-1})

M^{+z}	Step	*p*	$(\Delta H^\ominus)^{obs}$	$-\Delta(CFSE)$	$-n[(\Delta H^\ominus)^{aq}_{NH_3}$	$-(\Delta H^\ominus)^{vap}_{H_2O}] = n\Delta B$	ΔB	$B(M^{+z} - NH_3)$
Li^+	n = 0 → 3	6	−2.1	0	+25.8	+23.7	+7.9	77.3
Mg^{+2}	n = 0 → 6	6	−0.4	0	+51.6	+51.2	+8.5	176.8
Co^{+2}	n = 0 → 3	6	−22.0	+11.3	+25.8	+15.1	+5.0	
	n = 0 → 6	6	−54.4[a]	+22.5	+51.6	+19.7	+3.3	186.4
Co^{+3}	n = 0 → 6	6	−237.7	+156.9	+51.6	−29.2	−4.9	389.3
Ni^{+2}	n = 0 → 6	6	−87.9	+33.2	+51.6	−3.0	−0.5	197.3
Cu^+	n = 0 → 2	6	−66.9[b]	0	+17.2	−49.7	−24.8	128.0
Cu^{+2}	n = 0 → 4	(4 + 2)	−83.7	+15.0	+34.4	−34.3	−8.6	213.5
Ag^+	n = 0 → 2	?6	−56.1	0	+17.2	−38.9	−19.5	106.6
Zn^{+2}	n = 0 → 1	6	−10.9	0	+8.6	−2.3	−2.3	
	1 → 2	6	−13.0	0	+8.6	−4.4	−4.4	
	2 → 3	6	−16.3	0	+8.6	−7.7	−7.7	
	3 → 4	6	−21.8	0	+8.6	−13.2	−13.2	
	0 → 4	6	−62.0	0	+34.4	−27.6	−6.9	218.9
Cd^{+2}	0 → 1	6	−14.6	0	+8.6	−6.0	−6.0	
	1 → 2	6	−15.1	0	+8.6	−6.5	−6.5	
	2 → 4	6	−23.4	0	+17.2	−6.2	−3.1	
	4 → 6	6	−34.8	0	+17.2	−17.6	−8.8	
	0 → 6	6	−87.9	0	+51.6	−36.3	−6.1	191.7

[a] Ref. 12
[b] Ref. 13

taking the radii and therefore the hydration enthalpies of $M(H_2O)_p^{+z}$ and $M(H_2O)_{p-n}(NH_3)_n^{+z}$ to be equal.

In Table I are set out calculations for $B(M^{+z} - NH_3)$ for a number of metal ions. Values of $B(M^{+z} - OH_2)$ are taken from ref. 1, except for Cu^{+2} and Ag^+ for which mean values of B, based on a coordination number of six, can be calculated as 204.9 kJ mol^{-1} and 87.1 kJ mol^{-1} respectively. It should be noted that these values are mean values for bonds of different lengths in Cu^{+2} and possibly also in heavy d^{10} Ag^+. (The value for the CFSE of $Co(H_2O)_6^{+2}$ was incorrectly given[1] earlier as −56.5 kJ mol^{-1}: the correct value is −90.0 kJ mol^{-1} so that $B(Co^{+2} - OH_2)$ becomes 189.7 kJ mol^{-1}).

In a similar way, the complexation reactions of 1,2-diaminoethane can be written

$$M(H_2O)^{+z}_{p(aq)} + n(en)_{(aq)} \longrightarrow [M(H_2O)_{p-2n}(en)_n^{+z}]_{(aq)} + 2nH_2O_{(l)}$$

so that

$$\begin{aligned}(\Delta H^\ominus)^{obs} = {} & [(\Delta H^\ominus)^{aq}_{M(H_2O)_p + z} \\ & - (\Delta H^\ominus)^{aq}_{M(H_2O)_{p-2n}(en)_n + z}] \\ & + \Delta(CFSE) + n[(\Delta H^\ominus)^{aq}_{en} \\ & \qquad -2(\Delta H^\ominus)^{vap}_{H_2O}] \\ & + 2n[B(M^{+z} - OH_2) \\ & \qquad - B(M^{+z} - en/2)]\end{aligned}$$

or

$$\begin{aligned}2n\Delta B = {} & (\Delta H^\ominus)^{obs} - \Delta(CFSE) \\ & - n[(\Delta H^\ominus)^{aq}_{en} - 2(\Delta H^\ominus)^{vap}_{H_2O}] \\ & - [(\Delta H^\ominus)^{aq}_{M(H_2O)_p + z} \\ & \qquad - (\Delta H^\ominus)^{aq}_{M(H_2O)_{p-2n}(en)_n + z}]\end{aligned}$$

Table II contains calculations of $B(M^{+z} - en/2)$ for

TABLE II
Bond energy terms (/kJ mol^{-1}) in 1,2-diaminoethane complexes

M	*n*	$(\Delta H^\ominus)^{obs}$	$-\Delta(CFSE)$	$-n[(\Delta H^\ominus)^{aq}_{en} - 2(\Delta H^\ominus)^{vap}_{H_2O}]$	$-\Delta$(hydration)	$2n\Delta B$	ΔB	$B(M^{+z} - en/2)$
Mn^{+2}	3	−46.2	0	+36.6	−71.7	−81.3	−13.6	186.1
Fe^{+2}	3	−66.3	+13.9	+36.6	−77.4	−93.2	−15.5	200.9
Co^{+2}	3	−92.7	+25.2	+36.6	−70.5	−101.4	−16.9	206.6
Ni^{+2}	3	−114.6	+43.3	+36.6	−67.7	−102.4	−17.1	213.9
Zn^{+2}	3	−86.6	0	+36.6	−56.8	−106.8	−17.8	229.8
Cd^{+2}	3	−77.8	0	+36.6	−50.1	−91.3	−15.2	200.8

TABLE III
Bond energy terms for water, ammonia and 1,2-diaminoethane complexes of d metals (/kJ mol^{-1})

M^{+Z}	Cu^+	Ag^+	Mn^{+2}	Fe^{+2}	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}	Cd^{+2}	Co^{+3}
$B(M^{+Z} - OH_2)$	103.2	87.1	182.5	185.4	189.7	196.8	204.9	212.0	185.6	384.4
$B(M^{+Z} - NH_3)$	128.0	106.6			186.4	197.3	213.5	218.9	191.7	389.3
$B(M^{+Z} - en/2)$			186.1	200.9	206.6	213.9		219.8	200.8	

some M^{+2} species: although enthalpy data are available[2] for stepwise substitution of pairs of water molecules by en, the non-spherical nature of the intermediate complexes renders the estimation of effective ionic radii somewhat hazardous, and it was not felt to be worthwhile to attempt this. However, the essentially equal stepwise complexation enthalpies suggest that no significant changes, either of metal–ligand bond energy or of coordination polyhedron, are occurring. Enthalpies of complex formation

$$M(H_2O)_p^{+3} + en \longrightarrow M(H_2O)_q en^{+3}$$

where M^{+3} is a lanthanide ion are known, and all are very similar ranging from −72.4 kJ mol^{-1} for lanthanum to −83.7 kJ mol^{-1} for lutetium. However neither p nor q is defined, so that the radii of the complexes in solution are unknown; for these metal ions even $B(M^{+3} - OH_2)$ is undetermined.

DISCUSSION

Table III summarises for convenience values of $B(M^{+z} - OH_2)$, $B(M^{+z} - NH_3)$ and $B(M^{+z} - en/2)$ for those metals of the d-series (including zinc and cadmium) for which at least two values are known. From the data available, it appears that each of these three bond energy terms experiences a monotonic increase on traversing the 3d series. It is the increase in bond energies, together with the fall in radii of the complex ions and hence increase in solvation enthalpy on traversing the 3d series which accounts for the underlying increase in $-(\Delta H^{\ominus})^{obs}$ for complexation reactions, upon which is superimposed the influence of CFSE to give overall the Irving–Williams order. As might be expected from results on aquo complexes[1], on descent from a 3d to the analogous 4d ion, the bond energy term decreases, thus $B(Zn^{+2} - L) > B(Cd^{+2} - K)$ and $B(Cu^{+} - L) > B(Ag^{+} - L)$. It is unfortunate that no ion hydration data are available for Ru^{+2}, Ru^{+3} and Rh^{+3} all of which form octahedral aquo-ions, nor does it appear that there yet exist enthalpy data for $Ru(NH_3)_6^{+2}$, $Ru(NH_3)_6^{+3}$ or $Rh(NH_3)_6^{+3}$: all such data would provide valuable comparison of metal-ligand bonds involving 3d and 4d metal ions.

That successive substitution processes are essentially similar in character is shown by the data for the ammonia complexes of Co^{+2}, and particularly of Zn^{+2} and Cd^{+2}, for which ΔB, and $(\Delta H^{\ominus})^{obs}$ are essentially independent of the substitution step. The zinc data also provide evidence for the view that in solution the tetra-ammine complex is octahedral $Zn(NH_3)_4(OH_2)_2^{+2}$ rather than tetrahedral $Zn(NH_3)_4^{+2}$: octahedral six-coordinate zinc in known in the solid state in $Zn(H_2O)_6(BrO_3)_2$[9] and in $Zn(NH_3)_6Br_2$[10] and $Zn(NH_3)_6I_2$[10], and there is no reason to suppose that this coordination geometry cannot persist in solution. If a change in coordination number occurred on complexation, then the enthalpy change expected (assuming that the effective radii of $Zn(H_2O)_6^{+2}$ and $Zn(NH_3)_6^{+2}$ are the same) for the process

$$Zn(H_2O)^{+2}_{6(aq)} + 4\ NH_{3(aq)} \longrightarrow Zn(NH_3)^{+2}_{4(aq)} + 6\ H_2O_{(l)}$$

is calculated to be

$$\begin{aligned}\Delta H^{\ominus} &= +6B(Zn^{+2} - OH_2) - 4B(Zn^{+2} - NH_3) \\ &\quad + 4(\Delta H^{\ominus})^{aq}_{NH_3} - 6(\Delta H^{\ominus})^{vap}_{H_2O} \\ &= +\,224.8\ \text{kJ mol}^{-1}\end{aligned}$$

This value is much greater than the observed value of −62.0 kJ mol^{-1}; the only plausible rationalisations are either, that *no* change in coordination number occurs, *i.e.* that the tetra-ammine exists in solution as $Zn(NH_3)_4(OH_2)_2^{+}$, or, that $B(Zn^{+2} - NH_3)$ changes markedly on successive substitutions, which seems very unlikely in view of the observed $\Delta H^{\ominus}$ values for Co^{+2} and Cd^{+2} (Table 1).

Complexes such as $Zn(NH_3)_5OH_2^{+2}$ and $Zn(NH_3)_6^{+2}$ probably do not exist in appreciable concentrations in aqueous solution because a_{H_2O}/a_{NH_3} is so high: they may exist in liquid ammonia where a_{NH_3} is higher.

It seems probable that in the majority of examples, a dominant factor influencing the adoption of a particular coordination number in molecular complexes is the sum of bond energy terms, offset against ligand solvation enthalpies, with factors such as CFSE playing only a subordinate role. Certainly, it has been demonstrated[11] that CFSE plays only a minor role in determining octahedral or tetrahedral site occupancy in spinels AB_2X_4 (X = 0, S, Se, Te): in these species, the change in lattice energy on inversion is much bigger than the corresponding change in CFSE.

An anomaly is found in the complexation of Hg^{+2} by ammonia: for formation of $Hg(NH_3)_2(H_2O)_p^{+2}$, $\Delta H^{\ominus} = -103.3$ kJ mol^{-1}, while for substitution of the next two ammonia molecules the stepwise $\Delta Hs^{\ominus}$ are -13.8 kJ mol^{-1} and -15.1 kJ mol^{-1} respectively. These latter two values are typical of those found for substitution by ammonia at Zn^{+2} and Cd^{+2}, while the initial $\Delta H^{\ominus}$ is almost an order of magnitude greater. Several explanations are possible. Those most plausible seem to be, either; the mercury ion undergoes an increase of coordination number on complexing of the first two ammonias, or; the coordination polyhedron of the mercury (II) ion in solution contains two tightly bound water molecules in a linear arrangement, with perhaps four less tightly bound equatorial waters, with the $\Delta H^{\ominus}$ data reflecting this difference in bond character. For the first possibility, we may write

$$2NH_{3(aq)} + Hg(H_2O)^{+2}_{q(aq)} \longrightarrow Hg(NH_3)_2(H_2O)^{+2}_{p(aq)} + (q-p)H_2O_{(l)}$$

$$\Delta H^{\ominus}/\text{kJ mol}^{-1} = (q-p)\bar{B}(Hg^{+2}-OH_2) - 2\bar{B}(Hg^{+2}-NH_3) + 2 \times 35.4 - (q-p) \times 44.0 = 103.3$$

Until an estimate for $\bar{B}(Hg^{+2} - OH_2)$ is available, this equation is insoluble: however, insertion of educated guesses for the $\bar{B}$ terms yields $(q - p) \cong 1$.

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