Bond Energies in Transition Metal Complexes

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The feasibility of calculating the heat of formation of a gaseous complex ion, $\text{MX}_{\text{p(g)}}^{+\text{m}-\text{px}}$, from $\text{M}_{\text{(g)}}^{+\text{m}}$ and $\text{pX}_{\text{(g)}}^{-\text{x}}$ and hence the total bond energy by a procedure similar to the Born-Haber cycle is examined critically. It is concluded that at least in some cases the procedure has merit and application is made to some hexammines of divalent first transition series ions. Some implications of the results with regard to theories of the bonding in such complex ions are noted.

There have been three general theoretical approaches to the problem of bonding in transition metal complexes, *viz.*, the valence bond theory, the crystal field (ligand field) theory, and the molecular orbital theory. The valence bond approach as formulated by Pauling ¹ makes the approximation that the energy of the process

as well as other properties of the resulting complex can be accounted for by the formation of *x* directed bonds, more or less covalent. While this theory has had considerable qualitative success in accounting for stereochemistry and bulk magnetic properties it is not completely satisfactory even in these respects and fails seriously in dealing with detailed magnetic properties and spectra. The ligand field theory (a term proposed ² to replace the term "crystal field theory" when the concepts of the latter are applied to complex ions) while saying nothing explicitly about the overall process (and energy) of complex ion formation focuses attention on the effects of an electrostatic field of given symmetry upon the partially filled *d*-shell of the metal ion. It is thus able to account for the spectral and magnetic properties in some cases quantitatively, in general semiquantitatively. It is also successful in explaining the stereochemistry of the complexes, sometimes more reliably than valence bond theory. These successes of ligand field theory for a time led to the suggestion that perhaps, where transition metal complexes were concerned, the valence bond theory was wholly inappropriate, or at least that the formation of directed covalent bonds was a negligible part of the problem. However, there are a

number of points on which a *purely electrostatic* ligand field model is not satisfactory, and it now seems that a molecular orbital theory in which both directed covalent bonding and ligand field effects upon the metal *d*-shell may be simultaneously recognized and their interrelations formulated is the best conceptual approach to the problem *.

With these considerations in mind the various energy terms involved in the overall process (1) are of considerable interest and we may enquire whether the total energy or any of the contributing energies may be calculated from experimental data. It is well known ² that the energy contribution resulting from ligand field stabilization of the partially filled *d*-shell of the metal ion can be computed from spectroscopic data. It is the purpose of this note to suggest and utilize a simple method for estimating the total energy of the process.

METHOD OF CALCULATION

In principle the total energy, *Q*, of process (1) for the hexammine of a divalent metal ion may be calculated from the following thermodynamic cycle analogous to the Born-Haber cycle for simple ionic crystals.

$$Q = -\Delta H_f^\circ + 6\Delta H_f^\circ NH_3 + D_{X_2} + 2A_X + \Delta H_v^{X_2} + (I_1 + I_2) + \Delta H_v^M - E_L \quad (2b)$$

The symbols have their customary meanings **. It is clear that the energies of all of the steps in this cycle can be evaluated with considerable accuracy from known experimental data with the exception of E_L . The validity of the computed value of *Q* will thus depend upon the reliability of the method used to evaluate the pseudo-lattice energy, E_L . We have adopted the approximation that the hexammine ion, $M(NH_3)_6^{+2}$, can be regarded as a large, spherical, monatomic cation whose interactions with other ions in the lattice is essentially coulombic as is that of Na^+ in the NaCl lattice for example.

If this assumption were strictly correct then we might anticipate calculating E_L with the usual accuracy of the Born approximation, $\pm 3\%$. The two effects which will most appreciably detract from the validity of this approximation

* A good general discussion of these points will be found in Ref. ², parts b and c.

** For information concerning this general type of calculation see Ref. ⁴.

are the high polarizability of the large complex ion and the possible existence of other non-central coulombic interactions, especially hydrogen bonding to the halide ions. That these two effects are probably not large in the compounds to be treated below may be inferred from the following facts. (a) Each ion is centrosymmetrically coordinated by a large number of other ions thus tending to balance out polarization effects by symmetry; (b) the lattice does not provide geometry especially suitable for the formation of $N-H \cdots X$ bonds *; and (c) it has been observed that in crystals similar to those treated here various types of free or nearly free rotation occur at room temperature which requires that hindering energies are so small as to be negligible compared to the total lattice energy. Murray and Waugh ³ have found rotation ($\sim 5\,000$ cps) of the ammonia ligands about the metal-ligand axis in several salts of $Co(NH_3)_6^{+3}$ and also rotation *even of the BF_4^- ion* in $Co(NH_3)_6(BF_4)_3$. Finally it may be noted that application of the Born equation to lattices containing polyatomic ions has been made before. Sherman ⁴ used this method to compute the lattice energies of the ammonium halides from which he derived the energy of protonation of ammonia. It is interesting to note that Stephenson ⁵ has recently concluded that rotation of the NH_4^+ ion may occur in crystalline NH_4I thus lending further confidence to Sherman's calculation. The possible sources of uncertainty in calculating E_L which have been discussed are such as to make the estimate too low, and hence, in view of eqn. (2b), to make the estimated value of Q too high.

One further point requires consideration, namely, the form to be assumed for the repulsive potential. The Born-Mayer equation using an exponential repulsive potential, while fundamentally the most correct, will not be used because of the difficulty of evaluating the constant ρ ⁴ in the present case. Instead we shall use the original Born equation

$$E_L = \frac{Az^2e^2}{R} \left(1 - \frac{1}{n}\right) \quad (3)$$

in which the repulsive potential is of the form $1/R^n$. Rather than merely assuming n to be equal to 9, an attempt has been made to adjust it to the nature of the ions concerned in this case, and using the usual empirical relation of n to ion size ⁶ the following values were chosen:

$M(NH_3)_6Cl_2$	8.70
$M(NH_3)_6Br_2$	8.73
$M(NH_3)_6I_2$	8.80

While the number of hexammino, hexaquo (or even hexahalo) salts for which the calculation might be made is large, there are actually very few indeed for which all necessary data are available. It is necessary to know, *inter alia*, the appropriate ionization potential of the metal ion, the heat of formation of the solid salt, the crystal structure of the solid and the Madelung constant for that structure. (Approximations might be made for some of these but it seems undesirable to add unnecessary approximations to an already

* It may also be remarked that hydrogen bonds to Cl are generally only very weak, while hydrogen bonding to Br and I is considered to be negligible.

Table 1.

Values of Q calculated for $M(NH_3)_6^{++}$ ions

Compound M	X	Lattice Constant a_0 in Å	E_L kcal	$-\Delta H_f^{(b)}$ kcal	$\Delta H_V^M^{(c)}$ kcal	$I_1 + I_2^{(d)}$ kcal	Q kcal	Average Q for metal M	
Ca	Br	10.71	315.2	310.5	46.0	414.3	414.3	281.1	282
	I	11.24	302.5	289.0	46.0	414.3	414.3	283.0	
Mn	Cl	10.20	329.6	268.9	68.3	533.3	533.3	356.9	357
	Br	10.52	326.4	256.1	68.3	533.3	533.3	356.6	
	I	11.04	308.2	232.7	68.3	533.3	533.3	362.2	
Fe	Cl	10.15	331.2	246.6	96.7	554.7	554.7	382.8	376
	Br	10.47	322.2	219.8	96.7	554.7	554.7	370.3	
	I	10.97	310.2	288.9	96.7	554.7	554.7	375.3	
Co	Cl	10.10	332.8	239.0	105.0	580.0	580.0	407.2	406
	Br	10.39	324.6	230.	105.0	580.0	580.0	411.7	
	I	10.91	311.8	188.6	105.0	580.0	580.0	398.0	
Ni	Cl	10.06	334.3	239.1	101.6	595.6	595.6	418.0	415
	Br	10.34	326.2	221.7	101.6	595.6	595.6	414.0	
	I	10.88	312.8	191.2	101.6	595.6	595.6	411.9	
Zn	Br	10.46	322.6	246.7	31.2	629.1	629.1	405.7	401
	I	10.96	310.3	209.8	31.2	629.1	629.1	396.0	

(a) The lattices are of the fluorite type for which the Madelung constant to be used in conjunction with a_0 , the length of the unit cube edge, is 11.637. The a_0 values are from Böttker-Naess, G. and Hassel, O. *Z. physik. Chem.* B22 (1933) 471.

(b) All taken from Bichowsky, F. R. and Rossini, F. D. *The Thermochemistry of the Chemical Substances*, Reinhold Publishing Corp., New York 1936. The value they list for $Mn(NH_3)_6I_2$ (201.8) is in error and the above value was recalculated from the supplementary data also listed.

(c) All taken from *Handbook of Chemistry and Physics*, 32nd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio 1954.

(d) All taken from Moore, C. E. *Atomic Energy Levels*, Natl. Bur. Standards, Circular 467, Vols. I, II, 1952.

The quantities $D_x + 2A_x + 6\Delta H_f^{NH_3} + \Delta H_V^X$ computed from data in *Handbook of Chemistry and Physics*, 32nd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio 1954 and using "best values" of A_x given by Pritchard, H. O. *Chem. Rev.* 52 (1953) 554 for $X = Cl, Br, I$, respectively, are -184.0, -182.0 and -178.8 kcal.

long list of unavoidable ones.) For the series of salts $M(NH_3)_6X_2$ where $M = Ca, Mn, Fe, Co, Ni$ and Zn and $X = Cl, Br$ and I sufficient data are at hand. The various parameters used and the results of the calculation for this group of compounds are summarized in Table 1.

DISCUSSION

The calculated values of the Q 's, the total heats of dissociation of the complex ions, require comment in three respects. It is first to be clearly realized that these are and ought to be lower than the heats of solution of the gaseous

Fig. 1. Energy in kcal/mole of the gas phase dissociation of $M(\text{NH}_3)_6^{++}$ ions. Calculated points, O; --- values predicted by adding ligand field stabilization energies to points on solid curve.

divalent metal ions of the first transition series as quoted by Orgel⁷. The latter values are the sum of an association energy analogous to that calculated here with water instead of ammonia as ligand (and probably not too different in magnitude) plus the heat of solution of the resulting complex ion. The $-Q$'s are about 100 kcal. less than the total heats of solution which is a reasonable magnitude for the heat of solution on an ion of the size and charge of these hexammine cations. Secondly, the mean deviation of the Q values averaged for the several halides of a given hexammine run from 1 to 8 kcal., or 1 to 3 %. While in terms of kilocalories these deviations are rather large, the percentages are less than the expected absolute errors of perhaps 3 to 5 %. It will be observed that the calculated Q 's for a given metal ammine vary randomly with the halide ion. This indicates the absence of any important special energy contributions such as hydrogen bonding in the case of the chlorides. Finally, it has been noted by Orgel⁷ that when the hydration energies of the divalent cations from Ca^{++} to Zn^{++} are plotted *versus* atomic number and a smooth curve drawn through the points for Ca^{++} , Mn^{++} and Zn^{++} , the ions for which no ligand field stabilization occurs, then the (positive) deviations of the other ions follow very closely the ligand field stabilization energies calculated from spectroscopic data. If the calculated Q 's are at least not erratic (which of course indicates little about their *absolute* accuracy) they should show similar behavior. In Fig. 1 the Q 's are plotted *versus* atomic number. The dotted line represents the calculated curve through Ca^{++} , Mn^{++} and Zn^{++} . The agreement is seen to be satisfactory. The ligand field stabilization energies were computed from the data summarized by Klixbüll-Jørgensen^{2a}.

It may also be noted that although the ligand field stabilization energies play a critical role in determining the detailed chemistry of the transition metal

ions, they actually constitute a rather small fraction of the total bond energy. Also the mean ligand-metal bond energies are 60 to 70 kcal. This might be taken to mean that the reactions of the more labile complex ions which have activation energies of 20 to 30 kcal. do not proceed by a simple S_N-1 mechanism in which the activation energy is simply that required to break one metal-ligand bond without some other compensatory action.

Acknowledgement. Thanks are due to Prof. Sv. Å. Schou of Danmarks Farmaceutiske Højskole for the hospitality of his laboratories and to the *John Simon Guggenheim Memorial Foundation* for a Fellowship during the course of this work. Additional support by the *United States Atomic Energy Commission* is acknowledged.

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ADDENDUM ADDED IN PROOF

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It was felt that the results of a calculation of the type described above applied to $\text{Co}(\text{NH}_3)_6^{+3}$ might be of interest. This was not done previously because there were no salts of this ion with crystal structures for which the Madelung constant was known. It was found however that $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ and the isomorphous $[\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}]\text{I}_3$ crystallize in a cubic structure¹ in which the units to be considered ($[\text{Co}(\text{NH}_3)_6]^{+3}$, $[\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}]^{+3}$, I^-) occur at lattice positions having coordinates which are integral multiples of $1/12$ of the unit cell edge. (This structure is the *anti* form of that found by Pauling² for $(\text{NH}_4)_3\text{AlF}_6$ and $(\text{NH}_4)_3\text{FeF}_6$). The Madelung constant for such a structure may be computed relatively simply from the table compiled by Emersleben³. For this structure we have calculated A_{∞} (i.e., Madelung constant to be used with lattice parameter a_0 , the length of the unit cell edge) to be 22.12196. The third ionization potential of Co was taken from C. E. Moore's table. The heats of formation of the above salts were taken as -201.6 and -240.9 kcal/mole respectively⁴. Using these and other data from sources cited above we have obtained for $[\text{Co}(\text{NH}_3)_6]\text{I}_3$, $E_L = 593.8$ kcal/mole and $Q = 854.7$ kcal/mole and for $[\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}]\text{I}_3$, $E_L = 597.6$ kcal/mole and $Q = 843.3$ kcal/mole. Thus the mean ligand metal bond energies in these complexes of Co^{+3} are about 140 kcal. The ~10 kcal difference accords with the expectation that water would be less strongly bound than ammonia, but is of no quantitative significance in view of the possible errors (perhaps as much as 5-10 kcal/mole).

It has also been found that although no data on $\text{Cu}(\text{NH}_3)_6\text{X}_2$ compounds are given in the general reference for lattice parameters consulted previously, such data are available for $\text{Cu}(\text{NH}_3)_6\text{Br}_2$ ⁵. The compound has the fluorite structure with $a_0 = 10.30$ Å and the heat of formation (Bichowsky and Rossini) is -193.2 kcal/mole. From these data $E_L = 327.3$ kcal/mole and $Q = 420.6$ kcal/mole were computed. The use of this crystallographic data requires comment since they were previously criticized on the logical ground that while the structure is given as cubic, the crystals are also said to be *slightly* dichroic. This is not necessarily inconsistent because Jahn-Teller distortion, which would of course occur in $\text{Cu}(\text{NH}_3)_6^{+2}$, could conceivably give rise to a noticeable spectral effect without causing sufficient steric distortion to be observed in X-ray studies of moderate accuracy.

Thanks are due to Professor R. G. Pearson who read the manuscript and caught a potentially disastrous numerical error.

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Received August 9, 1956.