

ASSESSMENT OF BINDING ENERGIES AND LIGAND - LIGAND REPULSION OF ONE TO SIX WATER LIGANDS BOUND TO FERRIC ION

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ABSTRACT

The successive binding energies of up to six water ligands to ferric ion and the reduction in the gross binding energies by ligand - ligand repulsion are determined by electrostatic interaction. The gross binding energy is found to be both geometry and coordination number dependent: whereas it increases with number of ligands for $Fe^{3+}-(H_2O)_n$ ($n = 1(C_{\infty}), 2(C_{2h}), 4(D_{4h}), 5(C_{3h})$ and $6(O_h)$) geometries, a decrease with increasing n is observed for $Fe^{3+}-(H_2O)_n$ ($n = 3(D_{3h}), 4(T_d)$ and $5(C_{4v})$) ions. These trends are ascribed to metal - ligand repulsion which grows much faster with increase in coordination number in the latter geometries than in the former. This effect also accounts for up to about 18 - 20 kcal mol⁻¹ difference in stability between $Fe^{3+}-(H_2O)_n$ ($n = 4(D_{4h})$ and $5(C_{3h})$) and ($n = 4(T_d)$ and $5(C_{4v})$) geometries.

INTRODUCTION

The determination of successive ligand (L) binding energies in metal (M) containing $M^{k+}-L_n$ ions can yield insight into how the metal - ligand bonding changes with number of ligands. It can also provide us with the information about the energy required to add or remove individual ligands, perhaps in a particular sequence¹. An example of the importance of individual fragment binding energies is in the study of the dynamics of

$M^{k+} + 6L = \dots\dots\dots$ or $ML_6^{k+} = \dots\dots$;
 ML_4^{k+} (tetrahedral) = ML_4^{k+} (square planar), etc.)

reactions. The progress of these reactions can be accurately modeled given accurate binding energies of the individual $M^{k+}-L_n$ ($n = 1 - 6$) fragments. However, experiments² indicate that the binding energies of H_2O with alkali ions slowly decrease with the number of ligands. For example, the experimental binding energies of $Na^+-(H_2O)_n$ are 23.4, 19.2, 15.2 and 13.2 kcal/mol for $n = 1 - 4$, respectively. In contrast, experimental studies³⁻⁶ on the first

row unipositive transition metal ions bound to either H_2O or NH_3 ligands indicate that the first two ligand binding energies are comparable and much larger than the subsequent ligand binding energies. Thus the relative ligand binding energies for unipositive transition metal ions differ substantially from those for the alkali ions. In spite of the importance of these physical quantities, it is only at the beginning of this decade that their calculations emerged⁷⁻¹⁰ for the transition metal ions. Even then, most of the calculations were limited to one or two H_2O and NH_3 ligands bound to first row unipositive transition metal ions. For this class of metals, Cu^+ is apparently the only ion whose binding energies of the $M^{k+}-L_n$ fragments with more than two ligands and the assessment of ligand - ligand repulsion in reducing the binding energy is available¹⁰. While for Fe both theoretical and experimental binding energies of $Fe^+-(H_2O)_n$ ($n = 1$ and 2) have been reported³⁻⁶, such data is not yet readily available for $Fe^{3+}-(H_2O)_n$ ($n = 1 - 6$). But, quantum calculations can provide a valuable alternative source for such quantities. In addition the calculations provide insight into the bonding mechanism which is not readily obtained from experimental data. We have previously reported¹¹ the calculations

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of one and six water ligand binding energies to Fe^{3+} . In the present work, the results of the calculations of metal – ligand binding energies of three to five water molecules bound to the same metal ion, together with the already published one and six water ligands results for completeness, are presented. This then gives the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) series. Since calculations have shown the bonding in $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1$ and 2) systems to be electrostatic in origin^{7,8}, the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) ions are expected to be similar. An electrostatic approach recently¹² yielded an excellent agreement between theory and experiment for the binding energy of the $\text{H}\dots\text{OH}_2$ and $\text{H}\dots\text{NH}_3$ hydrogen bonds; similar calculations on the water ligands are expected to give a quantitative understanding of the bonding as well as yield reliable prediction of the binding energies of the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) complexes and the assessment of ligand – ligand repulsion as water molecules are added to the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ion one at a time. The results computed are similar to what is observed for $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ systems. Further, the calculations indicate a large decrease in the binding energy for the third and subsequent water ligands to be caused primarily by metal – ligand repulsion than ligand – ligand correlation.

EXPERIMENTAL

The electrostatic interaction in the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) systems is modeled by an $\text{Fe}^{3+}\dots(\text{H}_2\text{O})_n$ van der Waals (vdW) molecule. The detail of the model is reported in our earlier work¹¹. For $\text{Fe}^{3+}-(\text{H}_2\text{O})_2$ a linear C_{2h} geometry is assumed, triangular planar D_{3h} for $\text{Fe}^{3+}-(\text{H}_2\text{O})_3$ and octahedral O_h for $\text{Fe}^{3+}-(\text{H}_2\text{O})_6$, respectively. In the case of $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ and $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ ions, two possible structures are calculated for each: square planar D_{4h} and tetrahedral T_d geometries for the former and square pyramidal C_{4v} and triangular bipyramidal C_{3h} geometries for the latter. The geometry of the H_2O molecule is fixed and binds to the ferric ion by the negative end. The Fe^{3+} ion retains the high spin $3d^5$ occupation as in the free ion and the ground

electronic states of the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ions are derived from it. Finally, the computations were performed over the ground electronic states of the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ systems using SZ + 3d basis set on a Pentium 266 machine.

RESULTS AND DISCUSSION

The binding energies (BE) of the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) series are given, together with other quantities, in Table 1. The $\text{Fe}^{3+}-\text{H}_2\text{O}$ and $\text{Fe}^{3+}-(\text{H}_2\text{O})_2$ ions have the same M-L distances. The first ligand binding energy is about 23.7083 kcal mol⁻¹. The second binding energy is slightly (0.9108 kcal mol⁻¹) smaller than the first because the ligand – ligand repulsion energy (LLRE) is not significantly increased as both ligands approach Fe^{3+} from opposite sides. The binding energies of the one and two water ligands are similar to those of Rosi and Bauschlicher⁷ and the results of Curtiss and Jurgens⁹ for $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1$ and 2) systems.

For $\text{Fe}^{3+}-(\text{H}_2\text{O})_3$, the three H_2O ligands were taken to be equivalent and have a D_{3h} symmetry about the ferric ion. The M-L distance is (0.064Å) shorter than in either $\text{Fe}^{3+}-\text{H}_2\text{O}$ or $\text{Fe}^{3+}-(\text{H}_2\text{O})_2$. The binding energy, however, drops significantly to about 36.5021 kcal mol⁻¹ on adding the third water molecule. Also, the ligand – ligand repulsion energy (LLRE) sharply increased in magnitude from 0.9118 to 2.8565 kcal mol⁻¹. The reduction in the binding energy from two to three ligands is caused by the change in the L-M-L bond angle, being a parameter in the calculations, which translates to more than -8.0590 kcal mol⁻¹ (in magnitude) metal – ligand and -1.9447 kcal mol⁻¹ ligand – ligand repulsions, respectively.

The $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ ion is represented by two possible optimal geometries: the four water ligands may have either tetrahedral (T_d) or square planar (D_{4h}) structures about the Fe. The M-L distance of the tetrahedral geometry is (0.026Å) shorter than that of the square planar. The LLRE drops by about 0.2579 kcal mol⁻¹ on adding the fourth water ligand for the

Table 1. Summary of $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$) results.

Complex	Geometry	Symmetry	GBE	LLRE		BE	Distance (Å)	
				(kcal mol ⁻¹)			M-L	L-L
$\text{Fe}^{3+}-\text{H}_2\text{O}$	Linear	C_∞	23.7083			23.7083	2.381	-
$\text{Fe}^{3+}-(\text{H}_2\text{O})_2$	Linear	C_{2h}	47.4176	-0.9118		46.5058	2.381	4.762
$\text{Fe}^{3+}-(\text{H}_2\text{O})_3$	Triangular	D_{3h}	39.3586	-2.8565		36.5021	2.317	4.013
$\text{Fe}^{3+}-(\text{H}_2\text{O})_4$	Square planar	D_{4h}	47.9631	-2.5986		45.3645	2.375	3.359
	Tetrahedral	T_d	30.3075	-5.0237		25.2838	2.349	3.702
$\text{Fe}^{3+}-(\text{H}_2\text{O})_5$	Triangular bipyramidal	C_{3h}	48.2359	-6.5503		41.6856	2.375	3.359
	Square pyramidal	C_{4v}	24.8061	-5.2303		19.5758	2.370	3.352
$\text{Fe}^{3+}-(\text{H}_2\text{O})_6$	Octahedral	O_h	48.5087	-7.7960		40.7127	2.375	3.359

square planar geometry, whereas an increase of about 2.1672 kcal mol⁻¹ is obtained for the tetrahedral case. The binding energies of the $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ ion are 45.3645 and 25.2838 kcal mol⁻¹, respectively, for the square planar and tetrahedral geometries. Comparing the gross binding energies (GBE) for the two geometries, the (17.6556 kcal mol⁻¹) difference in the binding energy is primarily accounted by metal – ligand repulsion since the T_d and D_{4h} geometries have almost the same LLREs.

The $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ ion is also represented by two possible symmetric geometries; the five water molecules are equivalent and have either square pyramidal or triangular bipyramidal arrangements about Fe with C_{4v} and C_{3h} symmetries. Their M-L distance is almost the same – only 0.005 Å difference. The triangular bipyramidal geometry is about 22.1098 kcal mol⁻¹ more stable than the square pyramidal. Again comparing their gross binding energies,

metal – ligand repulsion accounts up to 23.4298 kcal mol⁻¹ energy difference. The triangular bipyramidal has 1.3200 kcal mol⁻¹ (in magnitude) more ligand – ligand repulsion than the square pyramidal. The binding energies are 41.6856 and 19.5758 kcal mol⁻¹ for the latter and the former geometries, respectively.

A regular octahedral geometry was computed for the $\text{Fe}^{3+}-(\text{H}_2\text{O})_6$ ion. It has the same M-L distance with square planar $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ and triangular bipyramidal $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ ions. The GBE is increased by only about 0.4728 kcal mol⁻¹ on adding one water ligand to the triangular bipyramidal $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ which is outweighed by a -1.2457 kcal mol⁻¹ increased ligand – ligand repulsion. The BE is about 40.7127 kcal mol⁻¹. This is 0.9729 and 4.6518 kcal mol⁻¹ lower than the binding energies of triangular bipyramidal (C_{3h}) $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ and square planar (D_{4h}) $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ ions, respectively. The $\text{Fe}^{3+}-(\text{H}_2\text{O})_6$ ion has the

highest LLRE in agreement with common prejudices.

Although experimental binding energies are not yet available for $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1 - 6$), the magnitude of our first and second ligand binding energies is consistent with $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ ($n = 1$ and 2) systems^{7,8}, which supports the consistency of our binding energies for the third, fourth, fifth and sixth water ligands. Further, the gross metal - ligand binding energy generally increases with number of ligands though reduced to (net) binding energy by ligand - ligand correlation. Our analysis also shows that large differences in $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ binding energies arise primarily from metal - ligand repulsion effects rather than ligand - ligand correlation. For example, the GBEs of square pyramidal (C_{4v}) and triangular bipyramidal (C_{3h}) $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ ion are 24.8061 and 48.2359 kcal mol⁻¹, respectively. Their total ligand - ligand repulsion energies (LLRE) are also -5.2303 and -6.5503 kcal mol⁻¹, respectively. Combining the GBEs and LLREs gives the BEs of the two geometries as 19.5758 and 41.6856 kcal mol⁻¹. This indicates clearly that the difference in the BEs of the two geometries is primarily due to metal - ligand repulsion since they have comparable total ligand - ligand repulsion energies. On the other hand, small differences in the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ binding energies arise mainly from ligand - ligand correlations. For instance, $\text{Fe}^{3+}-(\text{H}_2\text{O})_4$ (D_{4h}), $\text{Fe}^{3+}-(\text{H}_2\text{O})_5$ (C_{3h}) and $\text{Fe}^{3+}-(\text{H}_2\text{O})_6$ (O_h) have 47.9631, 48.2359 and 48.5087 kcal mol⁻¹ as their GBEs, respectively. These are, however, reduced to 45.3645, 41.6856 and 40.7127 kcal mol⁻¹ BEs of the ions by their -2.5986, -6.5503 and -7.7860 kcal mol⁻¹ respective ligand - ligand repulsion energies. Lastly, the C_{∞} and C_{2h} geometries have the longest equilibrium M-L distance, and C_{2h} the longest L-L distance.

CONCLUSION

The metal - ligand binding energies computed are consistent with what is observed for Fe^{3+} -

$(\text{H}_2\text{O})_n$ ($n = 1$ and 2) complexes. The gross binding energy of the second water ligand is comparable to the first and drastically reduced for subsequent ligands. Whereas metal - ligand repulsion plays a major role in determining large differences in the $\text{Fe}^{3+}-(\text{H}_2\text{O})_n$ binding energies, small differences are determined by ligand - ligand correlation. Lastly for coordination numbers $n = 4$ and 5 , the calculations suggest that the square planar (D_{4h}) and triangular bipyramidal (C_{3h}) geometries are more stable than tetrahedral (T_d) and square pyramidal (C_{4v}).

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