CALCULATION OF BINDING ENERGIES OF Fe^{3+}-$(H_2O)_n$ (n = 1 and 6)

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ABSTRACT

The binding energies of one and six water ligands to ferric ion are determined by dipole electrostatic interaction. A slow increase is observed in the Fe^{3+}-$(H_2O)_n$ binding energy from one to six water ligands similar to what is observed for Fe^{+}-$(H_2O)_n$ complexes. This trend is ascribed to ligand-ligand repulsion and ligand to metal charge donation. The large Fe^{3+}-$(H_2O)_n$ binding energies computed suggest that the bonding in these complexes is mainly electrostatic through dipole interactions.

INTRODUCTION

Although the calculation of the crystal field splitting energy of the first row transition metal ion complexes has received considerable attention[1], it is only at the beginning of this decade that the calculation of their binding energies emerged[2-5]. Even then, most of the calculations were limited to one or two H_2O and NH_3 ligands bound to unipositive transition metals ions. To date, Cu^+ is apparently the only first row transition metal ion whose binding energy calculation with more than two ligands is available[4]. In these publications, the binding energies of the M^+-$(H_2O)_n$ and M^+-$(NH_3)_n$ (n = 1 and 2) first row transition metal complexes computed were in good agreement with experiment and the calculations showed that the metal – ligand bond is electrostatic in origin.

However, such study on these metals in other oxidation states, especially the tripositive octahedral complexes of water ligands, M^{3+}-$(H_2O)_6$, is not yet readily available. In this communication we consider the interaction of ferric ion with one and six water molecules.

Since calculations have shown the bonding in M^+-$(H_2O)_n$ (n = 1 and 2) complexes of the first row unipositive transition metals ions to be electrostatic in origin, the M^{3+}-$(H_2O)_n$ complexes of these metals are expected to be similar. An electrostatic approach recently yielded an excellent agreement between theory and experiment for the binding energy of the H....OH_2 and H....NH_3 hydrogen bonds; similar calculations on the water ligands are expected to give a quantitative understanding of the bonding as well as yielding reliable prediction of the binding energy of the Fe^{3+}-$(H_2O)_n$ complexes. The large binding energies (BE) of the Fe^{3+}-$(H_2O)_n$ (n = 1 and 6) high spin complexes computed suggest that the ferric ion – water bond is also primarily electrostatic in nature as in the M^+-$(H_2O)_n$ (n = 1 and 2) first row transition metal complexes (Table 1). Further, the calculations indicate that the bond energy of subsequent H_2O ligands is substantially decreased due to ligand – ligand repulsion and ligand to metal charge donation effects.

EXPERIMENTAL

In our study, electrostatic interaction in the Fe^{3+}-$(H_2O)_n$ complex is simulated by a

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$Fe^{3+}....(H_2O)_n$ van der Waals (vdW) molecule. Then, for n = 6 the water ligands in the vdW molecule are assumed to have a regular octahedral structure about the Fe^{3+}. Further, near the vdW energy surface of the complex and large Fe^{3+}-H_2O separations, we consider the electrons of the ferric ion to 'view' the water ligands as point multipolar bodies. The equivalence of this approximation to the vdW molecule in electrostatic language is an Fe^{3+}-(dipole + quadrupole + octopole + hexadecapole + ...)$_n$ model. The main contribution to the electrostatic binding energy of the vdw molecule comes from dipole interactions.

In dipole approximation, the general electrostatic model above reduces to Fe^{3+}-(dipole)$_n$ electrostatic molecule representation of the Fe^{3+}-$(H_2O)_n$ complex. The potential energy of the Fe^{3+}-(dipole)$_n$ entity is partitioned into two components:

$$U=\sum_{i-1}^{n} U_i+\sum_{i}\sum_{<j} U_{ij} \quad \ldots\ldots (1)$$

where U_i and U_{ij} stand for the potential energy of interaction between the valence electrons of the ferric ion and the point dipole of the ith water ligand and that between the point dipoles of the ith and jth water ligands (i.e. ligand – ligand interactions), respectively. The derivation of U_i for the case of a dipolar ligand that binds to a metal ion with its negative end to the metal was reported in our earlier communication[6]. For U_{ij}, use has been made of the dipole – dipole interaction potential energy derived by Hirschfelder et al.[7]. Finally, the computations were performed over the $^6A_{1g}$ ground electronic state of the Fe^{3+}-$(H_2O)_n$ complex using SZ + 3d basis set on a Pentium 266 machine.

RESULTS AND DISCUSSION

The results of the calculations are summarized in Table 1. At the level of this calculation, consistent with an electrostatic interaction model, the geometry and the equilibrium charge distribution of the H_2O ligands do not change; the H_2O ligand does not need to rearrange in order to bond. The bonding is simply due to the net attraction of the ferric ion for the H_2O equilibrium dipolar charge distribution. The Fe^{3+} also retains the $3d^5$ occupation as in the free ion and the $^6A_{1g}$ ground electronic state of the Fe^{3+}-$(H_2O)_n$ is derived from it. Thus neither the H_2O ligand nor the Fe^{3+} lost its identity by this interaction.

The binding energies (BE) of the Fe^{3+}-$(H_2O)_n$ complexes computed are consistent with the experimental observation[8-11] that the binding energy of the first row unipositive transition metal ion bound to H_2O and NH_3 ligands increases slowly as n increases from 1 to 4. The Fe^{3+}-$(H_2O)_n$ binding energy for the first water is about 3 kcal/mol more than half of the binding energy of all the six water ligands. The computed BEs are 23.7083 and 40.7127 kcal/mol for one and six water ligands. However, one of the factors that lead to the slow increase of the binding energy for the six water ligands in Fe^{3+}-$(H_2O)_n$ is ligand – ligand repulsion energy (LLRE). The reduction can also be due to any ligand to metal charge donation; the subsequent waters see a smaller charge on the ferric ion and therefore the electrostatic interaction is smaller. This is clearly visible if we compare the ferric ion – water ligand interaction energies (FLIE) for the two complexes. Thus subsequent water ligands are bound less than the first. Although experimental binding energies are not yet available for the iron group tripositive transition metals bound to water ligands, the magnitude of our ligand binding energies is consistent with that found for Fe^{+}-$(H_2O)_n$ (n = 1 and 2) systems[2,3].

The ferric ion – water bond lengths in the Fe^{3+}-$(H_2O)_n$ (n = 1 and 6) ions are 2.381 and 2.375Å for one and six water ligands, respectively. The $R_e(Fe^{3+}$-$H_2O)$ distance in Fe^{3+}-H_2O is slightly (0.006Å) longer than in Fe^{3+}-$(H_2O)_6$. Our R_e(M - H_2O) bond distances are similar to those obtained by Rosi and Bauschlicher[2,3] for the Fe^{+}-$(H_2O)_n$ (n = 1 and

Table 1. Summary of the Fe^{3+} -$(H_2O)_n$ (n = 1 and 6) results.

Complex	BE	FLIE	LLRE	$R_e(Fe^{3+}-H_2O)$	$R_e(H_2O - H_2O)$
		kcal mol^{-1}			
Fe^{3+}-(H_2O)	23.7083	23.7083	-	2.381Å	-
Fe^{3+} -$(H_2O)_6$	40.7127	48.5087	-7.7960	2.375Å	3.359Å

2) systems. They also found $R_e(Fe^{+}-H_2O)$ distance in Fe^{+}-H_2O to be (0.124Å) longer than in Fe^{+}-$(H_2O)_2$ complex. However, their $R_e(M-H_2O)$ bond lengths, 2.114 and 1.990Å for Fe^{+}-H_2O and Fe^{+}-$(H_2O)_2$ systems respectively, are slightly shorter than ours. Lastly, an $R_e(H_2O - H_2O)$ equilibrium separation of 3.359Å was obtained in this work. The water ligands are very far apart compared to their proximity to the ferric ion in the complexes.

CONCLUSION

The calculations confirm, as observed for first row unipositive transition metal ions, that subsequent water ligands are bound less than the first. The slow increase of the binding energy is shown to be due to ligand – ligand repulsion and ligand to metal charge donation. The large Fe^{3+}-$(H_2O)_n$ binding energies determined suggest that the bonding in these complexes is primarily electrostatic through dipole interactions.

ACKNOWLEDGEMENT

The authors wish to thank the Ahmadu Bello University, Zaria, for funding this research.

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accepted 4/6/99

received 26/5/99