

DFT Study of the interaction between the [Zn(H₂O)₆]⁺², [Cd(H₂O)₄]⁺², [Hg(H₂O)₂]⁺² aquacomplexes and monodentate O-, N- and S-donor ligands

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Abstract: In the last decades, the environmental pollution caused by heavy metals has increased principally due to anthropogenic activities. The release of zinc, cadmium and mercury in the biosphere is mostly due to the steel and metallurgical industries, mining, and agricultural activities [1]. These metal cations tend to accumulate in the liver, kidney, thyroid and bones leading to liver dysfunction, renal damages and cancer [2].

The pharmaceutical industry uses chelating agents to enhance the removal of harmful cations from the human body. In these medicines, the active site is usually constituted by polar groups [3] that bind the metal cation. However, the chelating agents have small metal cation specificity, which can also eliminate essential species [4].

The present study identifies the molecular block with the strongest affinity for the $[Zn(H_2O)_6]^{2+}$ aquacation. Additionally, evaluates the influence of the gas and aqueous (CPCM and Vukovic procedure [5]) media in the formation constant, Gibbs free energy, electrostatic and covalent terms (from EDA calculation) of the interaction.

The geometries of the octahedral Zn^{+2} aquacomplexes with the carboxylic acid, amide, esther, lactame, ammonia and thioesther ligands were fully optimized using the restricted B3LYP method with the 6-311+G(d,p) basis set for the O, N, S, C, H, Zn atoms and the LANL2DZ-ECP for Cd and Hg with CPCM and gas phase. The Gibbs free energy was calculated by the substitution of one water molecule by a ligand (Table 1). The formation constant of the complex in gas phase (log K_{Gas}) and with water solvent (log K_{Aq} and log K_{Vuk}) was obtained employing the following equation:

$$\log K = \frac{-\Delta G}{2.303RT}$$

The analysis of Table 1 shows that the O- donor ligands have a stronger interaction with the Zn^{+2} cation in gas phase (ΔG_{Gas}), however for the Vukovic (ΔG_{Vuk}) and the aqueous solvent (ΔG_{Aq}) calculations the N- donor ligand shows the strongest interaction. The S- donor ligands have a non-spontaneous interaction in the aqueous solvent and for Vukovic, due to its softness that favors the interaction with large cations.

The EDA results show that the covalent and electrostatic components are sensitive to the media (gas or aqueous). In the gas phase, the results indicate the electrostatic and covalent are stabilizing terms, with larger magnitude for the first one.



In the aqueous and Vukovic methods, the electrostatic component is positive and the covalent component is largely a negative term.

Table 1: Gibbs free energy calculated in gas phase (ΔG_{Gas}), in aqueous solvent (ΔG_{Aq}) and with Vukovic procedure (ΔG_{Vuk}) and electrostatic and covalent component of the metal-ligand interaction obtained from the EDA analysis, in kcal.mol⁻¹.

Zn												
Ligand	ΔG_{Gas}	Eelec.	E _{cov.}	ΔG_{Vuk}	Eelec.	E _{cov.}	ΔG_{Aq}	Eelec.	E _{cov.}			
-COOH	-16.73	-61.73	-44.58	-2.27	131.31	-199.31	0.25	132.95	-205.13			
-CONH ₂	-16.40	-68.85	-55.14	-2.12	123.00	-206.12	-0.64	125.46	-210.33			
-COO-	-14.69	-60.75	-44.9	0.26	130.42	-198.03	2.17	134.54	-202.94			
Lactame	-23.50	-74.15	-60.34	-3.52	116.44	-205.22	-1.80	122.20	-209.53			
NH ₃	-8.41	-81.61	-55.47	-8.03	106.65	-225.57	-7.04	109.94	-233.56			
Thioesther	-14.76	-67.02	-73.03	1.41	130.26	-223.40	3.05	139.10	-224.10			

Table 2 presents the formation constant values in gas phase and in both solvent methods and their absolute errors (in comparison with the experimental data). For the Zn^{+2} cation the gas phase result has the smallest absolute error. The Vukovic methodology presents the smallest absolute errors for the Cd^{+2} and Hg^{+2} complexes. The results from all methods show two correlations between the size of the metal cation and the absolute errors. In gas phase as the size of the metal cation increases, the error also increases, while for the aqueous and Vukovic calculations as the size of the atom increases the error decreases.

Table 2: Experimental formation constant (log K_{Exp}) for the Zn⁺², Cd⁺² and Hg⁺² complexes with the ammonia ligand and the formation constants calculated in gas phase (log K_{Gas}), in aqueous phase (log K_{Aq}) and with the Vukovic procedure (log K_{Vuk}) and the respective absolute errors (in comparison with the experimental values).

	log K _{Exp}	log K _{Gas}	Abs. Error	log K _{Vuk}	Abs. Error	log K _{Aq}	Abs. Error
Zn	2.18	3.36	1.18	5.88	3.70	5.16	2.98
Cd	2.65	5.92	3.74	5.25	2.59	6.65	2.72
Hg	8.8	35.28	33.10	8.28	0.52	6.69	2,11

As a continuing study we will also consider more functional groups for the evaluation of the coordination interactions of ligands with metal cations.

Key-words: metal cations, DFT, formation constant, EDA

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