



Evaluating the Performance of 2,3-dihydro-1H-phenothiazine-4(5aH)-one as an Ionophore in Construction of a Cation Selective Electrode by Density Functional Theory

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Abstract

In this study, the complexation of 2,3-dihydro-1H-phenothiazine-4(5aH)-one with 14 various cations were investigated by density functional theory. At the outset, the structures of the ligand, different cations and their derived complexes were optimized geometrically. Then, IR calculations were performed on them in order to acquire the formation enthalpy and Gibbs free energy values. The obtained results substantiate that 2,3-dihydro-1H-phenothiazine-4(5aH)-one forms the strongest and the most stable complex with Cr^{3+} cation. In addition, this ligand demonstrates an eminent selectivity toward chromium (III) ions. In this regard, it can be used as an electroactive sensing material in developing a Cr^{3+} selective potentiometric electrode. All calculations were applied by Density functional theory in the level of B3LYP / 6-31G(d).

Keywords: 2,3-dihydro-1H-phenothiazine-4(5aH)-one, Density Functional Theory, Complexation, Chromium, Ionophore.

1. Introduction

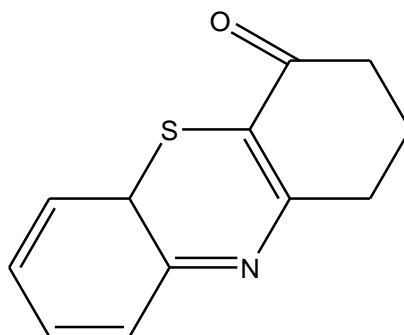
Determination of inorganic cations is very important for the international community. Because many of these cations are heeded as valuable micronutrients in the body of living organisms including humans and they play a decisive role in many biological processes. As a good instance, it can be referred to Calcium, Magnesium, Iron, Potassium and Sodium so that their deficiency can cause malnutrition-related problems such as osteoporosis, anemia, muscle cramps and so on. On the other hand, if the amount of these elements gets higher than the admissible limits in the body they can create some illnesses like high blood pressure, heath arrhythmia, kidney stones, etc. All of the mentioned matters imply that precise determination of these ions is of a great importance in medical fields [1-4].

It should be noted that in addition to these elements, there are also cations that not only have no nutritional value for humans but also are highly toxic and dangerous. And because of their un-degradability and accumulation in the human body, they can eventuate to many diseases, such as cancer, death, kidney and liver damage, hair loss, hearing loss and very severe toxic effects. Heavy metals like cadmium, mercury, lead and chromium are ideal examples for this type of cations. Hence, recognizing the presence of these cations and determining their amount in the environment, industrial wastewaters, foods and drinks, and any ambience that can in some way be able to bring these heavy and toxic metals into the human body and other living organisms could be extremely significant [5-8].

In addition, ion selective electrodes gather a huge attention in the recent decades. Because, this type of electrochemical sensors has worthwhile advantages including high selectivity, wide linearity domain, being portable, simplicity and being economical that makes them a preferable device for determination of ionic species. Ion selective electrodes have an electroactive sensing material in their membrane which is called ionophore or ion carrier. Neutral ion carriers must form a strong and stable complex with a cation that we want to measure its amount [9-12]. So, ligands can act as potential ionophores in developing cation selective electrodes. The next important feature for ionophores is selectivity; it means the utilized ionophore should only response to one analyte in order to produce an accurate and reliable potential response. Therefore, the complexation and selectivity of ionophores had better be inspected before being used in the construction of ion selective electrode [13-14].

Numerous experimental methods have been reported for investigating complexation of ligands with cations such as Uv-Visible spectrophotometry, NMR, polarography and conductometry. However, they have remarkable downsides such as being time consuming, needing intricate and expensive instruments, being costly, and using large amounts of non-degradable organic solvents which are hazardous for humans and also harmful for the environment. Thus, the above mentioned techniques are not preferable due to their substantial drawbacks [15-18]. Fortunately, Ab initio computational methods are in the opposite point

of the aforementioned techniques. Since, they are time saving, economical, accurate and environmental friendly. In this regard, 2,3-dihydro-1H-phenothiazine-4(5aH)-one (Fig 1) was selected as ligand because it has 1 nitrogen, 1 oxygen and 1 sulfur atoms. Moreover, its solubility in water is extremely poor. Therefore, in this study the interaction of 2,3-dihydro-1H-phenothiazine-4(5aH)-one with 14 cations was investigated for the first time by density functional theory [19-20].



2,3-dihydro-1H-phenothiazin-4(5aH)-one

Fig 1. The structure and IUPAC name of the investigated ligand.

2. Computational details

In this study, the pertinent calculations to 2,3-dihydro-1H-phenothiazine-4(5aH)-one, Cations and their complex derivatives were implemented by Spartan software. The computations took place in 25°C and atmospheric pressure in the Nitrobenzene solvent by density functional theory (DFT). For all materials, calculations were done via 6-31G(d) basis set except Ag^+ , Cd^{2+} , Pd^{2+} and their derived complexes where LANL2DZ (Los Alamos National Laboratory of Double Zeta) basis set were utilized. The studied reaction is as follows generally Equation 1:



At the outset, the compounds were optimized geometrically, and then IR calculations were performed in order to study thermodynamic parameters that are pertinent to the desired process.

3. Results And Discussions

3.1. Evaluating the Structure of the Complex

As it is obvious a cation can make a bond with a ligand from different sites. And this phenomenon can be seen more evidently when the use ligand has more than one electron donor heteroatom. In this regard, for finding out the structure of the derived complex products from the reaction of the ligand and evaluated cations, a zinc atom was put in two different situations. In condition A, the cation was placed between the

two oxygen and sulfur atoms (Fig 2). And in condition B, Zn^{2+} was inserted near the nitrogen atom of the studied ionophore (Fig 3). Then optimization step was performed on both of them and their SCF total energy was compared with each other. The acquired results indicate that condition A is more stable than condition B, because its SCF total energy was -7222996.0881 (Kj/mol) which is 126.8983 (Kj/mol) more negative than the SCF total energy value of condition B that is -7222869.1898 (Kj/mol). So, condition A was elected as the optimized structure of the complex for the rest of the calculations. Zinc (II) was selected for this step of evaluation due to its high affinity for forming the complex with nitrogen and sulfur containing ligands. It should be noted that for all computations 2,3-dihydro-1H-phenothiazine-4(5aH)-one and its complexes with various cations were considered in nitrobenzene solvent, since nitrobenzene is a relatively widely used plasticizer in the construction of PVC membrane ion selective electrodes. But the pertinent calculations for cations were implemented in the aqueous phase because the sensor should be able to measure the amount of the analyte in the aqueous test solution.

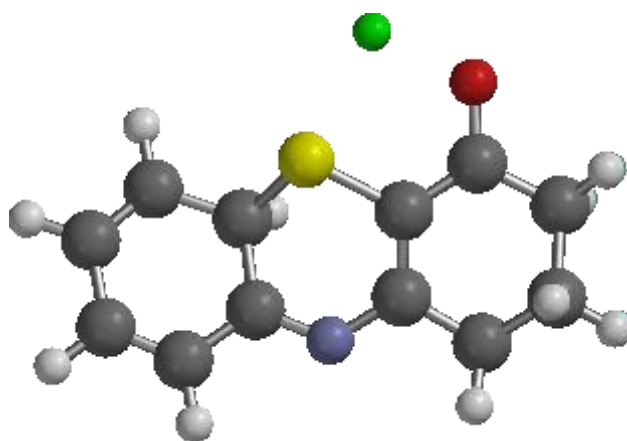


Fig 2. Condition A: Zn^{2+} attaches to the ligand via the oxygen and sulfur atoms.

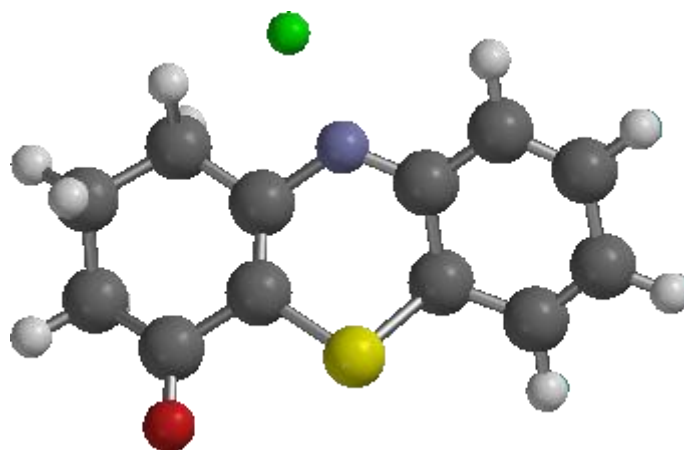


Fig 3. Condition B: Zn^{2+} attaches to the ligand via the nitrogen atom.

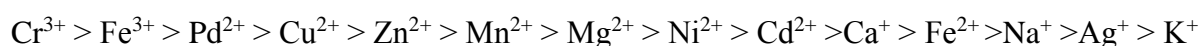
3.2. Calculation and Verifying the Values of Enthalpy Changes (ΔH_f)

The enthalpy values for raw materials and products were calculated by Spartan software. In order to obtain formation enthalpy variations the subsequent equations would be applied:

$$\Delta H_{\text{thermal}} = H_{\text{th complex}} - (H_{\text{th cation}} + H_{\text{th ligand}}) \quad \text{Equation 2}$$

$$\Delta H_f = \Delta H_{\text{thermal}} + \Delta \epsilon_o \quad \text{Equation 3}$$

The accomplished results of the equations are tabulated in table1 and Fig4. As it can be observed, all cations have the ability to form complex with 2,3-dihydro-1H-phenothiazine-4(5aH)-one exothermically. Indeed, all of the metals can react with the ligand without consuming any energy owing to their negative formation enthalpy value. It can be perceived from the provided data that Cr^{3+} complexation with the studied ion carrier is more exothermic in comparison to other ones. Because its formation enthalpy changes value is more negative than other cations with a significant discrepancy. If we want to compare the metals' affinity to form a complex with the mentioned ligand on the basis of formation enthalpy, they will be placed in the following order:



In addition, it can be realized from the achieved results that 2,3-dihydro-1H-phenothiazine-4(5aH)-one has better interaction with trivalent cations than bi and mono-valent ones. In other words by increasing the charge of cations a substantial decrease has occurred in the formation enthalpy values.

Table 1. Formation enthalpy changes values for the complexation reaction between 14 cations and 2,3-dihydro-1H-phenothiazine-4(5aH)-one.

Complexes	$H_{\text{th Complex}}$	$H_{\text{th Cation}}$	$H_{\text{th Ligand}}$	ΔH_{th} (kJ/mol)	$\Delta \epsilon_o$ (kJ/mol)	ΔH_f (kJ/mol)
Cr³⁺-Complex	605.397	6.197	609.214	-10.015	-2681.633	-2691.648
Fe³⁺-Complex	605.106	6.197	609.214	-10.306	-2404.635	-2414.941
Pd²⁺-Complex	612.6522	6.197	609.214	-2.759	-1012.952	-1015.712
Cu²⁺-complex	605.894	6.197	609.214	-9.518	-927.4816	-937.000
Zn²⁺-Complex	613.699	6.197	609.214	-1.713	-924.935	-926.648
Mn²⁺-Complex	605.578	6.197	609.214	-9.834	-875.066	-884.900
Mg²⁺-Complex	614.652	6.197	609.214	-0.760	-827.749	-828.509
Ni²⁺-Complex	614.897	6.197	609.214	-0.515	-827.749	-828.265
Cd²⁺-Complex	612.898	6.197	609.214	-2.514	-675.883	-678.397
Ca²⁺-Complex	614.094	6.197	609.214	-1.318	-543.670	-544.988
Fe²⁺-Complex	603.018	6.197	609.214	-12.394	-527.072	-539.465
Na⁺-Complex	615.206	6.197	609.214	-0.205	-245.119	-245.325
Ag⁺-Complex	614.426	6.197	609.214	-0.986	-230.180	-231.166
K⁺-Complex	614.470	6.197	609.214	-0.942	-181.524	-182.466

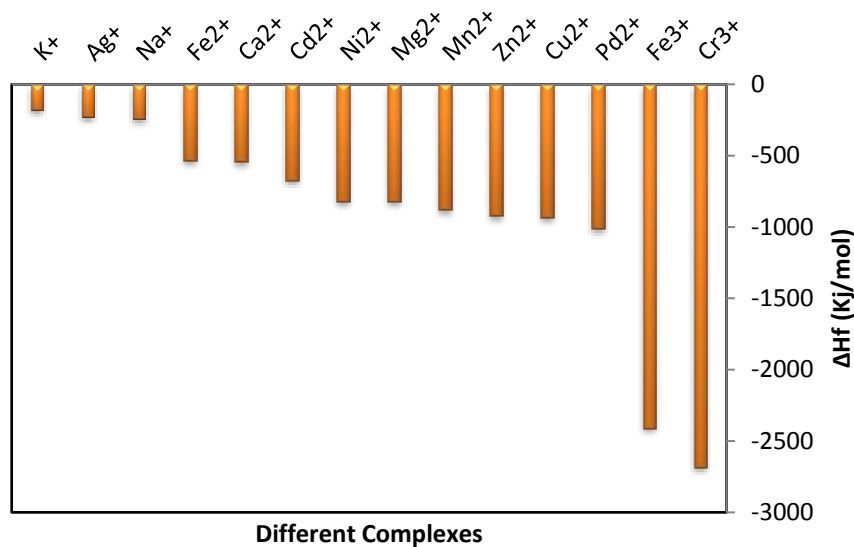


Fig 4. Formation enthalpy changes values for the complexation reaction between 14 cations and 2,3-dihydro-1H-phenothiazine-4(5aH)-one.

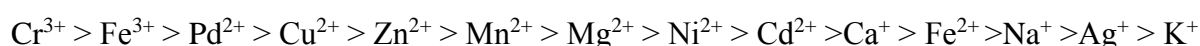
3.3. Calculation and Verifying the Values of Gibbs free energy Changes (ΔG_0)

The Gibbs free energies of the reactants and products were acquired by the calculation that carried out by Spartan software. Then, the Gibbs free energy alterations were obtained by the succeeding formulas:

$$\Delta G_{th} = G_{th \text{ complex}} - (G_{th \text{ cation}} + G_{th \text{ ligand}}) \quad \text{Equation 4}$$

$$\Delta G_0 = \Delta G_{th} + \Delta \epsilon_0 \quad \text{Equation 5}$$

As the provided data in (table 2) and (Fig 5) demonstrate obviously, the lowest ΔG_0 is acquired by the Cr^{3+} complex. Therefore, it can be inferred that Chromium (III) forms the strongest complex with 2,3-dihydro-1H-phenothiazine-4(5aH)-one among all of the studied cations. On the basis of both enthalpy and Gibbs free energy variations, it can be deduced that the thermodynamic reactivity of complexation of ion metals with the studied ligand (with the lowest total energy) are:



It should be noted that the acquired results from Gibbs free energy alterations are in a great accordance with the achieved results from formation enthalpy changes values. Both of them show that 2,3-dihydro-1H-phenothiazine-4(5aH)-one the complexation process become more spontaneous and exothermic by rising the charge of the cation and due to the fact that chromium (III) has the lowest Gibbs free energy and formation enthalpy. Therefore it can be utilized as a neutral ion carrier in the construction of PVC membrane Cr^{3+} selective electrode.

Table 2. Gibbs free energy changes values of the complexation process in the ambient temperature.

Complexes	Gth (complexes)	Gth (Cations)	Gth (Ligand)	ΔG_{th} (kJ/mol)	$\Delta \square 0$ (kJ/mol)	ΔG (kJ/mol)
Cr ³⁺ -Complex	472.818	-43.392	486.348	29.862	-2681.633	-2651.771
Fe ³⁺ -Complex	472.398	-43.668	486.348	29.717	-2404.635	-2374.918
Pd ²⁺ -Complex	480.165	-46.041	486.348	39.858	-1012.952	-973.094
Cu ²⁺ -complex	474.003	-44.106	486.348	31.761	-927.482	-895.721
Zn ²⁺ -Complex	482.517	-44.164	486.348	40.334	-924.935	-884.601
Mn ²⁺ -Complex	473.493	-43.601	486.348	30.745	-875.066	-844.321
Mg ²⁺ -Complex	485.185	-40.519	486.348	39.356	-827.749	-788.394
Ni ²⁺ -Complex	484.235	-43.798	486.348	41.686	-827.749	-786.064
Cd ²⁺ -Complex	479.723	-46.312	486.348	39.687	-675.883	-636.196
Ca ²⁺ -Complex	482.765	-42.417	486.348	38.834	-543.670	-504.836
Fe ²⁺ -Complex	469.059	-43.668	486.348	26.379	-527.072	-500.693
Na ⁺ -Complex	484.521	-40.362	486.348	38.535	-245.119	-206.585
Ag ⁺ -Complex	480.717	-46.076	486.348	40.446	-230.180	-189.735
K ⁺ -Complex	482.012	-42.323	486.348	37.987	-181.524	-143.538

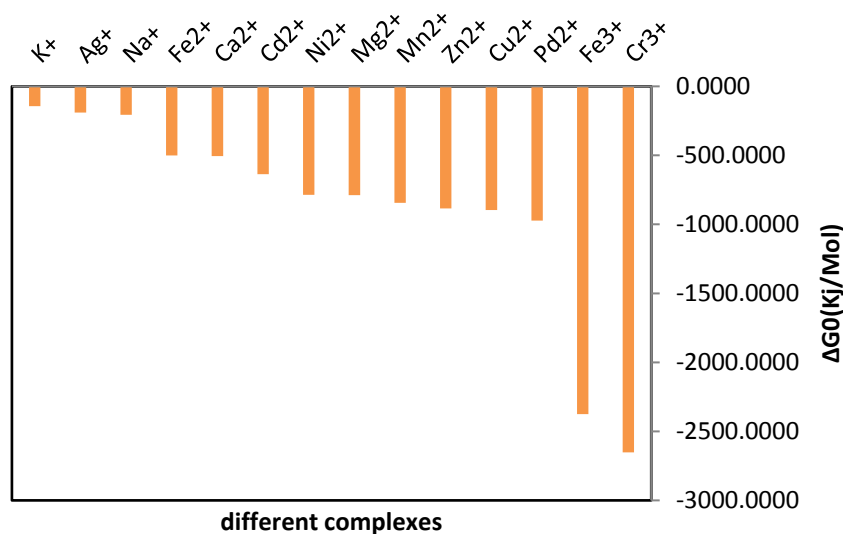


Fig 10. Gibbs free energy changes of the complexation process in the ambient temperature.

3.4. The lowest frequency and zero point energy values

The lowest frequency, zero point energy and the distance of cations from the oxygen and sulfur electron donating atoms are reported in table 3. As it can be observed from table 3, there is not any reported negative frequency. Thus, it can be concluded that all of the investigated complexes are not a transition state.

Table 3. The lowest frequency, zero point energy and the distance of cations from the oxygen and sulfur atoms.

Complexes	Distance from oxygen (Å)	Distance from sulfur (Å)	Low Frequency (Hz)	ZPE (Kj/mole)
Cr³⁺-Complex	1.883	2.883	52.232	572.8632
Fe³⁺-Complex	1.864	2.696	59.152	572.5255
Pd²⁺-Complex	1.883	2.507	61.363	580.7826
Cu²⁺-complex	1.797	2.358	67.271	573.6238
Zn²⁺-Complex	1.805	2.356	65.33	581.9391
Mn²⁺-Complex	1.893	2.592	69.18	573.2041
Mg²⁺-Complex	1.824	2.517	65.077	583.015
Ni²⁺-Complex	1.742	2.323	67.032	583.2459
Cd²⁺-Complex	2.079	2.698	59.658	580.8618
Ca²⁺-Complex	2.135	3.150	55.734	582.1184
Fe²⁺-Complex	1.963	4.260	65.746	570.2578
Na⁺-Complex	2.048	3.122	45.942	583.2110
Ag⁺-Complex	2.264	2.930	36.678	582.2687
K⁺-Complex	2.448	3.683	582.2569	30.466

5. Conclusions:

In this evaluation, the complexation of 2,3-dihydro-1H-phenothiazine-4(5aH)-one with 14 different mono, di and trivalent cations were investigated. The results show that cations can form complex with the ligand through the oxygen and sulfur atoms. Moreover, the ligand forms the most stable and the strongest complex with Cr³⁺ because the complex of this cation has the lowest ΔG_0 among all of the inspected cations. The obtained formation enthalpy changes were also the undermost value for chromium (III) which proves that the complexation procedure is exothermic. Therefore, it is recommended that the usage of 2,3-dihydro-1H-phenothiazine-4(5aH)-one as an ionophore in the construction of ion selective electrode for determination of Cr³⁺ will be evaluated by the experts of these fields.

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