Density Functional Theory (DFT) with Combined Investigation of the Selectivity of a Symmetrical Tetradentate N_2O_2-Coordination Schiff Base Ligand for Mn(II) Ion in the Presence of Mixing Mg(II), Mn(II), Ba(II), Ca(II) and Ni(II) Ions

Mahdeyeh SHEIKHSHOAIE[*], Vahid SAHEB and Tayebeh SHAMSPUR

Department of Chemistry, Shahid-Bahonar University of Kerman, Iran

([*]**Corresponding author's e-mail: mahdeyeh.sheikhshoaie@yahoo.com**)

Abstract

Theoretical study and computational models are capable of reliably predicting ligand selectivity towards variety of metal ions, and can be valuable tools for the advancement of practical works. In this paper, a theoretical study based on the optimum angles and distance between a tetradentate Schiff base ligand and some metal ions is characterized. These investigations are carried out based on *ab initio* calculations to estimate the pair wise interaction energy between the 2 molecules. The calculations show that the mentioned ligand is a suitable ligand for the extraction of Mn(II) ions from a mixture of Ba(II), Mg(II), Mn(II), Ca(II) and Ni(II) ions.

Keywords: DFT study, tetradentate, *ab initio*, metal ion, Schiff base ligand

Introduction

Schiff base ligands have gained favor due to both their relatively straight forward synthesis and their multidentate nature, which results in very high binding constants for many metals [1,2]. Schiff base ligands and their metal complexes have attracted a great deal of interest in recent years because they have applications in medicinal inorganic chemistry and in materials science. In medicine, lanthanide complexes are exploited as contrast agents for magnetic resonance imaging (MRI) [3-5] and are growing in importance in other diagnostic procedures [6] and as radio therapeutic drugs [7].

Chelate extraction [1-7] is a very effective analytical separation method for metal species in solution. Many chelate extraction systems have been developed for the separation, the concentration, and the selective determination of many kinds of metal cations. In chelate extraction, an extraction reagent should have at least 1 donor atom having a negative charge, to form a neutral (extractable) complex with a target metal cation. In general, however, only O, S and N have been used as the negatively charged donor [8-12].

On the other hand, computational chemistry methods have become increasingly important in complementing, if not supplanting, experimental procedures in nearly all areas of chemistry. So, in this work, the theoretical interaction of a tetradentate Schiff base ligand (**Figure 1**) is studied, with some metal ions as the host-guest model. The cavity of the host Schiff base molecule has, besides its shape and dimensions, sites where ion-pairing, ion-dipole and dipole-dipole interactions can occur with the guest metal ion [13]. Molecular modeling, applying computational chemistry tools, is now widely recognized as a powerful protocol for the design of new molecular ligands with specified properties, and for interpreting their stabilities. Using present day computational methods [14] along with a high speed parallel computer, we are on the threshold of a new era of molecular-based engineering and science, in which the properties

of complex molecular systems can be confidently predicted, and thus designed and optimized, for specific applications prior to their synthesis in the laboratory.

In the above context, the structure and energetic of Schiff base ligand in the gas phase has been reported earlier [15] using 6-31++G basis set. *Ab initio* calculations have been performed to study the proton affinity of tetradentate ligand (BHNDT) optimized geometry. The stability of the BHNDT -metal ion complexes has been studied using *ab initio* method with a minimal basis set. In the present work, a DFT based study is carried out to understand the microscopic interaction between Mn(II), Mg(II), Ba(II) and Ni(II) metal ions and tetradentate Schiff base ligand (**Figure 2**). A hybrid density functional, namely Becke's 3 parameter nonlocal hybrid exchange-correlation functional (B3LYP) [16] is applied using a split valence 6-311++G(d,p) basis function in a very systematic way. Structures of fully relaxed geometry and binding energy for this metal ion-ligand system are presented. **Figure 3** shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and its band gap. The present work will help in the molecular level understanding of the separation processes of mixture cations.
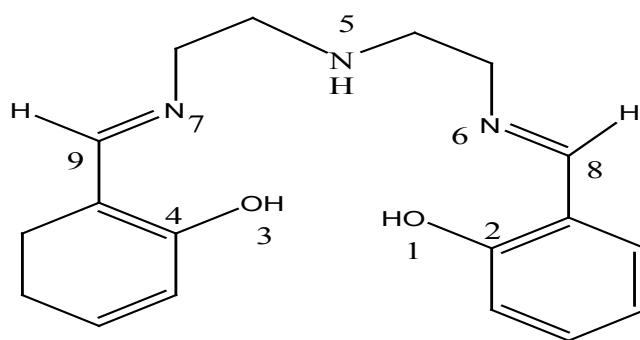

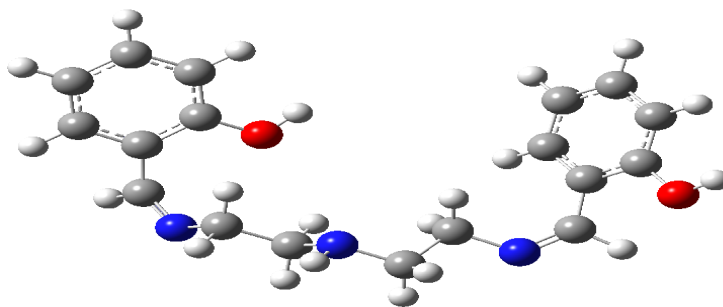**Figure 1** The structure of symmetrical tetradentate Schiff base ligand.

Figure 2 The optimized structure of tetradentate Schiff base ligand at the B3LYP/6-31++G(d,p) level.

Table 1 Calculated structural parameters for tetradentate Schiff base ligand at the B3LYP/6-31++G(d,p) level.

E$_{(HOMO)(a.u)}$	Heat of formation$_{(a.u)}$	E$_{(LUMO)(a.u.)}$	Dipole moment$_{(debye)}$	Band gape energy$_{(a.u)}$
−0.220	−1013.273	−0.049	5.955	0.171

The calculated Mulliken charge density on coordination atoms (**Figure 1**) are: O (1); −0.507, O (3); −0.502, N (6); −0.420, N (7); −0.480 and N (5); −0.032.
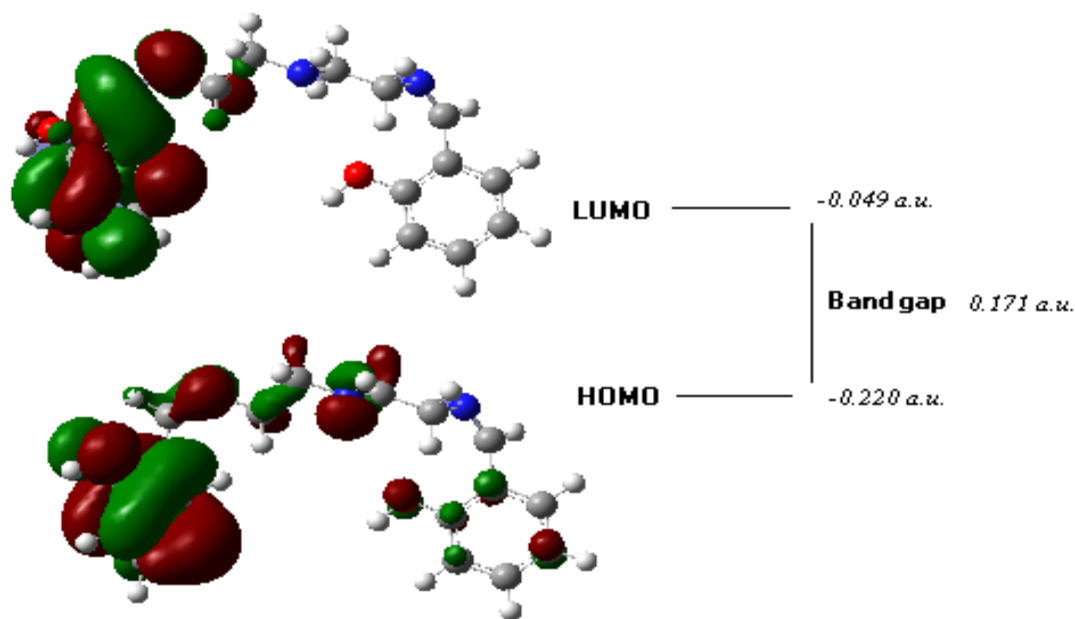

Figure 3 The plot of frontier molecular orbital HOMO and LUMO levels for tetradentate Schiff base ligand at the B3LYP/6-31G++ (d,p) level.

Computational method

Density functional theory-based electronic structure calculation has a very good predictability power for the various structural and thermodynamic properties of a molecular system [17]. Among the various density functional modules, B3LYP is the most popular. Thus, geometry optimizations for all metal complexes are performed with this correlated hybrid functional using 6-311++G (d,p) set of basis functions. Fully relaxed structures and binding energy for these metal cation-ligand systems with different ring metal sizes are calculated at B3LYP/6-311++G (d,p) level of the theory. Density Functional Theory (DFT) calculations are performed to predict the host-guest interaction between the Schiff base and various metal cations. The extraction power of an extractant for metal ions is closely related to the standard interaction energy charge of the complexation reaction that determines the relative stability of a "host-guest" system [18]. In research, to explicitly display the hydration of different metal cations, all metal cations are considered as 6-coordination $[M(H_2O)_6]^{+2}$ complexes and the following equations are

used to compute the relative binding energies. The binding energy (ΔE) of complexes 1 - 5 is calculated as the difference between the energy of complex with the optimized geometry ($E_{complex}$) and the sum of energies of the optimized ligands (E_{ligand}) and fragments $[M(H2O)_6]^{+2}$ (M = Mg, Ca, Ba, Mn and Ni). Eq. (1), is used to analyze their stability (**Table 2**).

$$\text{Binding energy} = \Delta E = [E_{(metal\ complex)}] - [E_{(ligand)} + E_{(M(H2O)6}{}^{+2}] \qquad (1)$$

All calculations are carried out with the Gaussian 03 package [19].

Table 2 The calculated binding energies (ΔE) for selected metal cations with tetradentate Schiff base ligand.

Free ligand & Metal cation	E[A]$_{(KJ/mol)}$	E[B]$_{(KJ/mol)}$	E[C]$_{(KJ/mol)}$	(ΔE)$_{(KJ/mol)}$
Free ligand	-	-	-1013.273	-
Mg^{+2}	-262.648	-1365.252	-	-89.331
Ca^{+2}	-350.017	-1454.332	-	-91.042
Ba^{+2}	-249.025	-1347.708	-	-85.410
Mn^{+2}	-421/067	-1537.351	-	-103.011
Ni^{+2}	-175.926	-1258.381	-	-69.182

A = (hexaaqua metal cation; B = metal complex; C = free tetradentate ligand; ΔE = E[B] - E[C] - E[A]
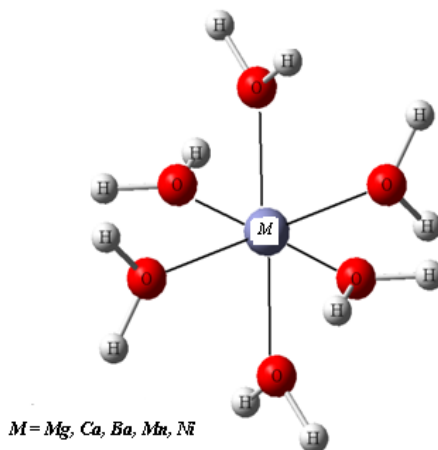
Table 1 shows some of the important calculated structural parameters and the fully relaxed equilibrated geometry of free Schiff base molecules is given in **Figure 2**. The optimized structure of bivalent anionic ligand, the optimized structure of metal complex and the optimized structure of hydrated cation are shown in **Figure 4**.

(a)

M = Mg, Ca, Ba, Mn, Ni

(b)
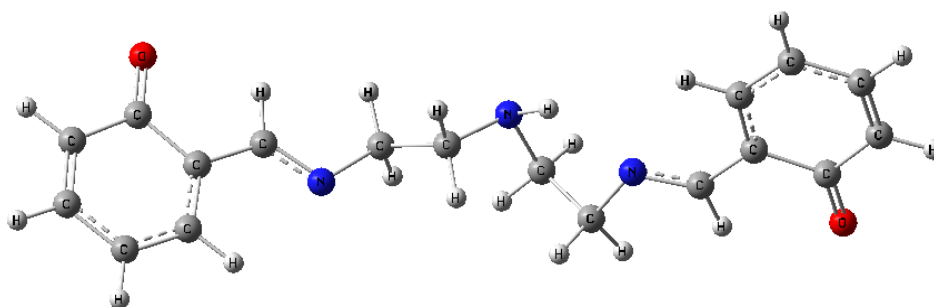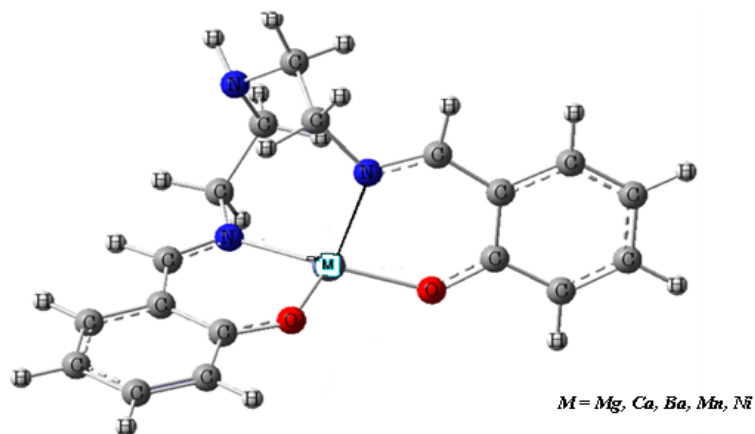
M = Mg, Ca, Ba, Mn, Ni

(c)

Figure 4 The optimized structure of bivalent anionic tetradentate ligand (a), The optimized structure of M(II) complex $[M(OH_2)_2(L)]^{+2}$ (b) and the optimized structure of $[M(OH_2)_6]^{+2}$ (c), M=Mg, Ca, Ba, Mn or Ni cations.

Results and discussion

B3LYP/6-311++G (d,p) optimized geometries of ligand show the coordination sites for the mentioned ligand are O(1), O(3), N(7) and N(6) atoms, so this ligand is a selective tetradentate ligand for separation of Mn(II) ions. The calculated binding energies of various bivalent cations, by DFT quantum chemical calculations, are shown in **Table 2**. These calculations reveal that the cations with more negative binding energies such as Mn^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+} and Ni^{2+} are more susceptible for reaction with the ligand. These theoretical results are in accordance with observations of the present solid-phase extraction method. However, the present chemical modeling cannot take into account all facts of the present complex chemical system. Although the present DFT calculations do not predict the exact trend observed in the extraction power of the Schiff-base ligand, they enable us to say which cations are more susceptible for extraction by the ligand or may act as interferences.

Conclusions

The symmetrical tetradentate ligand coordinates through 2 imine nitrogen and 2 phenolate oxygen atoms to the metal Mn^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+} and Ni^{2+} ions. The stabilization energy of free ligand, hexaaqua metal ions, and all these metal complexes are calculated by theoretical method. The calculated binding energies are in the following order: Mn(II) complex >> Ca(II) complex > Mg(II) complex > Ba(II) complex> Ni(II) complex. So, this tetradentate ligand is a good selective ligand for separation of Mn(II) in the presence of Mg^{2+}, Ba^{2+}, Ca^{2+} and Ni^{2+} ions.

Acknowledgements

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