

ORIGINAL ARTICLE

Theoretical Study of Metal Ion Complexation with Pyridine azathia ester crown bearing ethylene glycol and thioglycolic acid

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ABSTRACT

The capability of pyridineazaoxathia crown to form complexes with some metal cations (K^+ , Na^+ , Li^+ , Ca^{2+} , Mg^{2+} , Sr^{2+}) was investigated by computational methods in the gas phase. The calculations were performed at the DFT b3lyp/dgdzvp level of theory. The formation constants were used to evaluate the metal binding capability of the crown. The results of the calculations showed that the formation constants of the complexes decreased in the range of $K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+} < Sr^{2+}$. On the other hand, for more understanding about the aza crown and complexes the physical properties such as dipole moments, polarizability, hardness, energy, frontier orbitals (HOMO and LUMO) energies, band gap have been calculated. Also, For more information on the electron density on the crown and Sr^{2+} complex HOMO and LUMO orbitals were calculated and showed the interaction between electron donors and Sr^{2+} metal ion.

Keywords: Pyridine, thioglycolic acid, ethylene glycol, alkali metal ions, Sr^{2+} .

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INTRODUCTION

Since the first preparation and study by Pedersen in 1967[1], crown ethers have played a significant role in many areas of chemistry and related sciences. A distinctive feature of these materials is the non-covalent nature of interactions with a series of guests such as their metal-ion and molecular complexations. Non-covalent chemical interactions are covered by the special broad field of chemistry called supramolecular chemistry and host-guest chemistry [2]. Supramolecular chemistry has received widespread acceptance in a series of areas such as nanotechnology, biotechnology and nanomedicine[3]. Nowadays, supramolecular structures include not only cyclic polyethers, aza crown ethers, ester crowns, cyclic peptides and similar compounds, but also various more complex three-dimensional molecular architectures. These materials find wide applications in such new fields as nanotechnology [4], nuclear waste separations [5], enzymes [6] and new optical devices [7].

There are several factors that influence the complexation abilities of crown ethers, aza crowns. The most important factor is the relationship between the crown cavity size and the cation diameter [8]. If the metal ion is too large for the crown ether cavity, sandwich complexes may be formed [9]. It has also been revealed that a closed macrocycle cavity has much higher complexing ability than its corresponding open-chained structure named podand. An important property of macrocycles in host-guest chemistry is interaction between hosts and guests named preorganization. In this process before complete complex formation the structure of macrocycle rearrange to fit with guest and led to a more stable complex compared to open chain receptors; this phenomena is called "the macrocyclic effect". The strength of potassium ion complexation with 18-crown-6 was found to be 6000-fold higher than that of its open-chained analog [10].

A series of factors that influence the complexation strength of guests with receptors include the identities and placement of the heteroatoms in the ring, the number of heteroatoms in the cavity, the flexibility of the macrocycle ring and the addition of the side arms that provide additional ligating functionalities to the complexing species. The identities and placement of the heteroatoms in the ring and in the whole macrocycle structure influence complexation according to the Hard-Soft Acid Base theory of Pearson [11]. According to that theory, oxygen atoms that are hard Lewis base as donor atoms in the macrocycle cavity favor significant interaction with hard cations, such as alkali and alkaline earth metal cations. Soft Lewis base donors, such as sulfur or nitrogen, into the crown ring binds stronger towards softer cations, such as transition metals.

In this research work theoretical study of complexation of a new azaester thiacyclic bearing pyridine, with metal ions was investigated.

COMPUTATIONAL METHODS

All calculations were carried out using the Gaussian 09 software package [12]. For Optimization of complexes guest cations were placed at the crown center using Gauss View 5 [13]. Aza crown structure and complexes were optimized at the DFT b3lyp/dgdzvp level of theory, and the corresponding frequency calculations at the same level identify the optimized structures as energy minima without imaginary frequencies. Physical properties such as dipole moments, polarizability, hardness, total energy, frontier orbitals (HOMO and LUMO) energies, band gap have been calculated using optimization methods and frequency calculations. Formation constants were calculated using frequency output calculations. For more investigation on the electron density distribution on the crown and Zn²⁺ complex of crown HOMO and LUMO orbitals were calculated using the DFT b3lyp/dgdzvp level of theory.

RESULTS AND DISCUSSION

Fig. 1 shows the structure for the azaester thia crown (1). At first, azaesterthia crown (1) was optimized using semi empirical methods (PM6) and the frequency calculation shows that the first frequency mode is positive and there are no imaginary structures. Then, for comparison, the azaoxathia crown (1) was optimized using DFT B3LYP/Lanl2DZ. On the other hand, 1 and its metal ion complexes were optimized using DFT B3LYP/Lanl2DZ. The calculated physical properties are summarized in table 1. Total energy, dipole moments, frontier orbitals energies (HOMO and LUMO) were extracted from output data. The hardness and polarizability and band gap calculated according to the following equations.

For investigation on the theoretical calculation of polarizability, the mean diagonal polarizability on the main axes was calculated as the polarizability.

$$\alpha = (1/3) (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

More polarizability shows the less stability of molecule or complex. Band gap is the difference between HOMO and LUMO orbitals. The higher band gaps between frontier orbitals show the more stability of the molecule or complex.

$$\text{Band gap} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

According to the following equation hardness (η) is related to the ionization potential and electron affinity. The ionization potential and electron affinity could be obtained from the HOMO and LUMO energies.

$$\eta = (IP - EA)/2 = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$$

$$EA = -E_{\text{LUMO}} \quad IP = -E_{\text{HOMO}}$$

Band gap and Hardness of 1 and its complexes showed in Fig. 2. According to the chart, band gap of 1 and its complexes are the same. The hardness of complexes is remarkably larger than that of aza ester crown (1). According to the Fig. 3 the polarizability of potassium complex is larger than that of 1 and other complexes.

Fig. 4 shows the optimized structure of 1 and Fig. 5 shows the structure of Sr²⁺ complex.

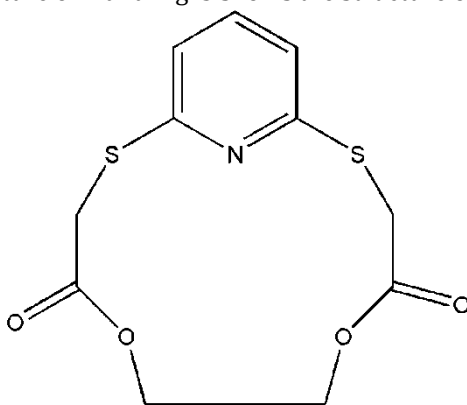
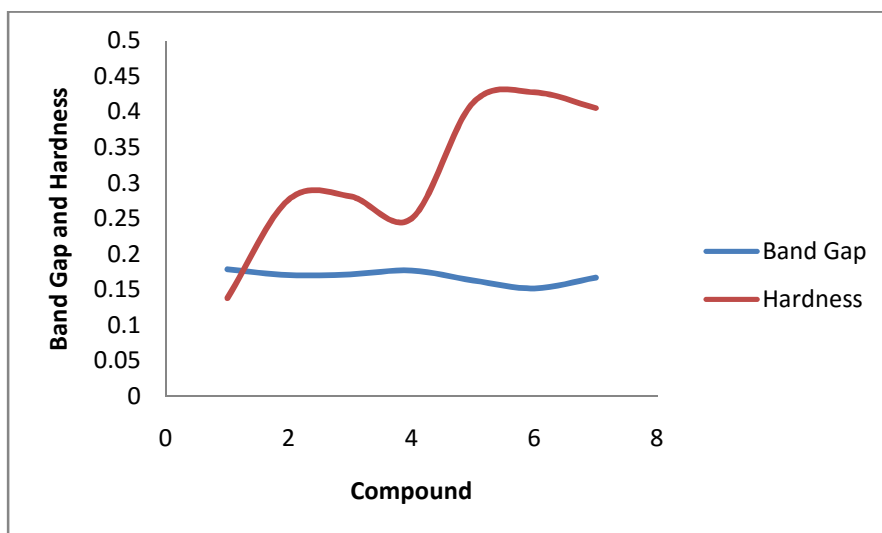
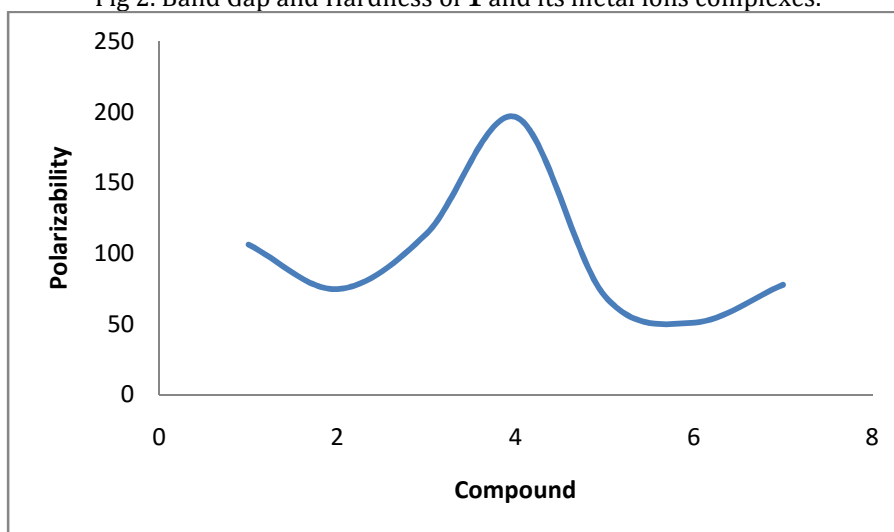


Fig. 1. Aza ester thiaCrown (1).

Table 1. Calculated physical properties of aza ester thia crown (**1**) and its metal ion complexes.

	Entry	Energy/A.U.	$E_{\text{HOMO}}/\text{ev}$	$E_{\text{LUMO}}/\text{ev}$	Band Gap/ev	Hard. ^b	Dip./D. ^c	Polar. ^d
1	2 ^a	-1577.86518	-0.22763	-0.04888	0.17875	0.138255	3.7830	106.327
2	2.Li ^{+a}	-1585.26460	-0.36210	-0.19162	0.17048	0.27686	2.9734	74.798
3	2.Na ^{+a}	-1740.01305	-0.36726	-0.19561	0.17165	0.281435	2.1207	114.205
4	2.K ^{+a}	-2177.61806	-0.33875	-0.16171	0.17704	0.25023	3.8220	196.594
5	2.Ca ^{2+a}	-2254.96938	-0.49458	-0.33143	0.16315	0.413005	2.2363	69.787
6	2.Mg ^{2+a}	-1777.45248	-0.50351	-0.35159	0.15192	0.42755	3.0019	51.027
7	2.Sr ^{2+a}	-4710.46621	-0.48902	-0.32202	0.167	0.40552	2.0460	77.886

a: DFT b3lyp/dgdzvp; b: Hardness; c: Dipole moments (Debye); d: Polarizability

Fig 2. Band Gap and Hardness of **1** and its metal ions complexes.Fig 3. Polarizability of **1** and its metal ion complexes.Table 2. Calculated thermochemical properties (ΔH and ΔG) of **1** and its complexes.

Entry	$\Delta H, \text{Hartree/Part.}^b$	Hartree/Part. $\Delta G,$	Entry	$\Delta H, \text{Hartree/Part.}$	Hartree/Part. $\Delta G,$
2 ^a	-1577.63440	-1577.69761	Li ^{+b}	-7.29622	-7.28111
2.Li ^{+a}	-1585.03018	-1585.09251	Na ^{+a}	-162.08273	-162.06594
2.Na ^{+a}	-1739.77867	-1739.84519	K ^{+a}	-599.70103	-599.68350
2.K ^{+a}	-2177.38411	-2177.45101	Ca ^{2+b}	-676.83746	-676.81989
2.Ca ^{2+b}	-2254.73528	-2254.79856	Mg ^{2+b}	-199.22446	-199.20761
2.Mg ^{2+b}	-1777.21802	-1777.27946	Sr ^{2+c}	-3118.34865	-3118.32996
2.Sr ^{2+c}	-4710.23225	-4710.29746			

a: DFT b3lyp/dgdzvp, b: Hartree/Particle = 627.509 Kcal/mol

Table 3. Calculated thermochemical properties (ΔH and ΔG) of complex formation reactions.

Entry	$\Delta\Delta H$, Hartree/Part. ^b	Hartree/Part. $\Delta\Delta G$,	$\Delta\Delta H$, Kcal/mol	Kcal/mol $\Delta\Delta G$,	K_f	$\text{Log}K_f$
2.Li⁺ ^a	-0.09956	-0.11379	-62.47479	-71.40424	2.186×10^{52}	52.339
2.Na⁺ ^a	-0.06154	-0.08164	-38.61690	-51.22983	3.562×10^{37}	37.551
2.K⁺ ^a	-0.04868	-0.0699	-30.54713	-43.86287	1.418×10^{32}	32.151
2.Ca²⁺ ^a	-0.26342	-0.28106	-165.29842	-176.36767	1.899×10^{129}	129.278
2.Mg²⁺ ^a	-0.35916	-0.37424	-225.37613	-234.83896	1.375×10^{172}	172.138
2.Sr²⁺ ^a	-14.2492	-14.26989	-8941.50124	-8954.48440	4.973×10^{6563}	6563.696

a: DFT b3lyp/dgdzvp, b: Hartree/Particle = 627.509 Kcal/mol

Based on the data reported in table 2 and table 3, formation constants of complexes is in the order of $K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+} < Sr^{2+}$. The complexes of metal ions with two charges are more stable than metal ions with one equivalent charge. Complex formation between crown and metal ions depend on the several factors such as the size of crown ring and the radius of metal ion, charge, solvent, three dimensional structure of crown, temperature and so on.

In Fig. 4 optimized structure of **1** with numbering was showed and in Fig. 5 the optimized structure of Zn²⁺ complex with **1** from two sides was reported.

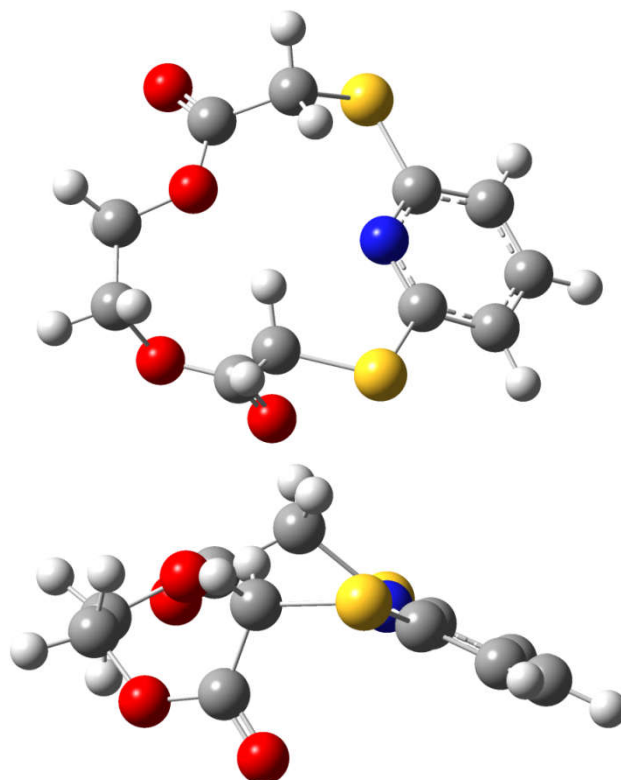


Fig. 4. The calculated 3D structure of crown ether (**1**) from two sides.

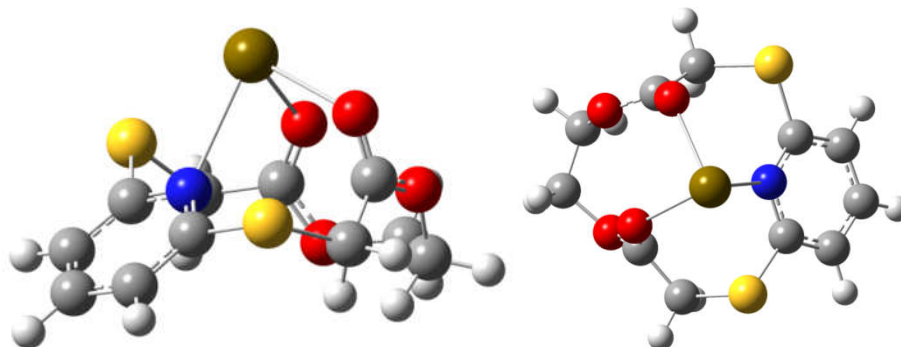


Fig. 5. The calculated 3D structure of Sr²⁺ complex with crown ether (**1**) from two sides.

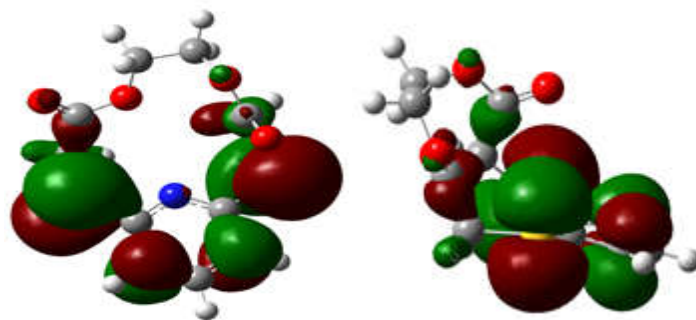
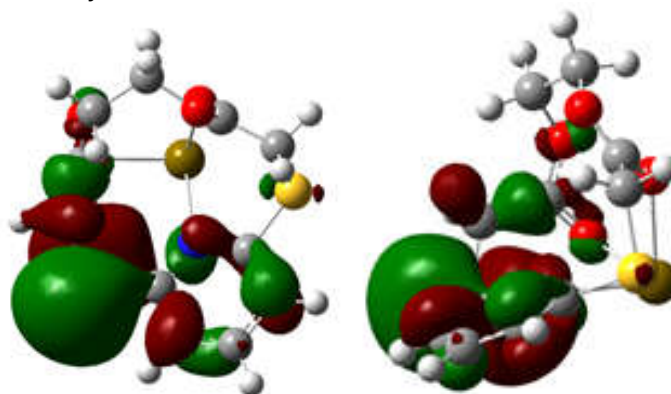
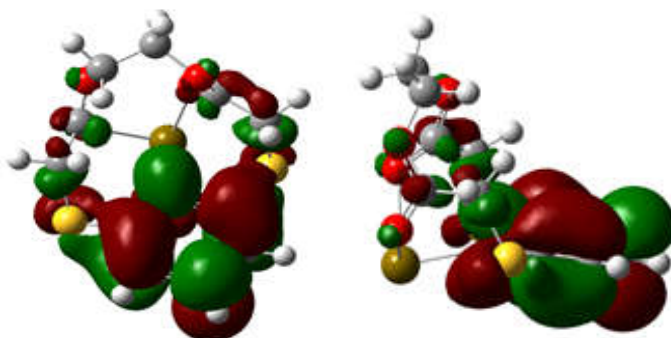


Fig. 6.HOMO orbital of crown ether (1) from two sides.



Fig. 7.LUMO orbital of crown ether (1) from two sides.

HOMO and LUMO orbitals of **1** were reported in Fig. 6 and Fig. 7. The HOMO orbital is distributed weakly on the pyridine ring and extensively on the sulfur atoms. The LUMO orbital was distributed extensively on the pyridine ring and weakly on the sulfur atoms.

Fig. 8.HOMO orbital of crown ether (1) Sr²⁺ complex from two sides.Fig. 9.LUMO orbital of crown ether (1) Sr²⁺ complex from two sides.

HOMO and LUMO orbitals of Sr^{2+} complex of **1** were reported in Fig. 8 and Fig. 9. The HOMO orbital is distributed weakly on the pyridine ring and extensively on one sulfur atom. Sr^{2+} metal ion is bare. The LUMO orbital was distributed extensively on the pyridine ring and weakly on the sulfur atoms. Again, the Sr^{2+} metal ion is bare.

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