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Theoretical study of metal ion complexation with phloroglucinol 13-Crown-4 bearing methoxy diethylene glycol as side chain

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Abstract
The capability of Phloroglucinol 13–crown-4 to form complexes with some metal cations (K^+,Na^+,Li^+,Ca^{2+},Mg^{2+},Ag^+, Hg^{2+}, Pb^{2+}) was investigated by computational methods in the gas phase. The calculations were performed at the DFT b3lyp/6-31g and HF/6-31g and HF/Lanl2DZ levels 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 $Na^+<K^+<Ag^+<Li^+<Ca^{2+}<Pb^{2+}<Hg^{2+}<Mg^{2+}$. On the other hand, for more understanding about the crown ether and complexes the physical properties such as dipole moments, polarizability, hardness, energy, frontier orbitals (HOMO and LUMO) energies and band gap have been calculated. Also, for more information on the electron density on the crown and Mg^{2+} complex, HOMO and LUMO orbitals were calculated and showed the interaction between electron donors and Mg^{2+} metal ion.

Keywords: Phloroglucinol, triethylene glycol, alkali metal ions, Mg^{2+}, theoretical study

1. Introduction

Since the first preparation and investigation by Pedersen in 1967[1], crown ethers have played an outstanding role in many branches of chemistry and material sciences. A characteristic aspect of crowns is the non-covalent nature of interactions with a series of guests such as metal-ions and molecules. Non-covalent interactions are covered by the particular 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, nanomedicine and biochemistry [3]. Nowadays, supramolecular structures include not only cyclic polyethers, aza crown ethers, estercrowns, cyclic peptides and similar compounds, but also various more complex three-dimensional molecular architectures such as metal-organic frameworks. These materials find wide applications in such new fields as nanotechnology [4], nuclear waste separations and purifications [5], enzymes and actuators [6] and new optical devices such as organic electronics materials [7].

There are several features that influence the complexation capabilities of crown ethers and aza crowns. The most important characteristic is the correlation 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 construction named podand. An important feature of macrocycles in host-guest chemistry is interaction between hosts and guests before complex formation specified as preorganization. In this operation before complete complex formation the structure of macrocycle rearrange to fit with guest and led to a more stable complex compared to open chained receptors; this phenomenon is called “the macrocyclic effect”. The strength of potassium ion complex formation with 18-crown-6 was found to be 6000-fold higher than that of its open-chained analog [10].

A series of aspects that influence the complexation strength of various guests with receptors include the identities and placement of the heteroatoms in the ring and structure, the number of heteroatoms in the cavity or in the effective positions, the flexibility of the macrocycle ring and backbone and the addition of the side arms and chains that provide additional ligating functionalities to the complexing species. The identities and placement of donor heteroatoms in the ring and in the whole macrocycle structure influence complexation ability according to the Hard-Soft Acid Base theory of Pearson [11]. According to that theory, oxygen atoms are

hard Lewis base as donor atoms in the macrocycle cavity favor remarkable interaction with hard cations, such as alkali and alkaline earth metal cations. Soft Lewis base donors, such as sulfur or nitrogen, into the crown ether and macrocycle ring and structure binds stronger towards softer cations, such as transition metals.

In this research work theoretical study of complex formation between a 13–crown–4 new crown ether bearing Phloroglucinol, with metal ions was investigated.

2. 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 GaussView 5 [13]. Aza crown structure and complexes were optimized using DFT b3lyp/6-31g, HF/6-31g and HF/Lanl2DZ levels 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 ether, HOMO and LUMO orbitals were calculated and studied.

3. Results and Discussion

Fig. 1 shows the structure of crown (**1**). At first, 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, methods and basis sets are compared, crown (**1**) and its metal ion complexes were optimized using DFT b3lyp/6-31g, HF/6-31g and HF/Lanl2DZ levels of theory. 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, 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.

$\alpha = (1/3)\ (\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ})$

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

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

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.

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

$EA = -E_{LUMO}$ $IP = -E_{HOMO}$

Band gap and Hardness of **1** and its complexes showed in Fig. 2. According to the chart, band gap of **1** is greater than that of its complexes. The hardness of complexes is remarkably larger than that of crown (**1**). According to the Fig. 3 the polarizability of Ag+ complex is larger than that of **1** and other complexes.

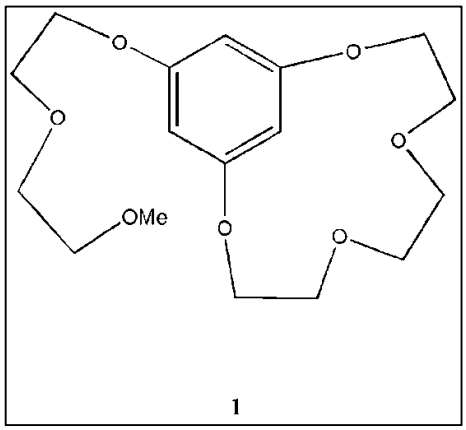

Fig 1: Crown ether (1).

Table 1: Calculated physical properties of crown (1) and its metal ion complexes.

	Entry	Energy/A.U.	E_{HOMO}/ev	E_{LUMO}/ev	Band Gap/ev	Hardness	Dip. Mom./D[d]	Polar.[e]
1	3[a]	-1189.57341	-0.20524	0.01924	0.22448	0.093	3.0201	130.672
2	3[b]	-1182.32388	-0.30254	0.16288	0.46542	0.06983	3.2558	157.429
3	3[c]	-1182.51855	-0.30704	0.14849	0.45553	0.07927	3.3968	173.239
4	$3.Li^{+}$ [a]	-1197.03294	-0.31858	-0.09813	0.22045	0.20835	8.6303	84.561
5	$3.Na^{+}$ [a]	-1351.70758	-0.30939	-0.18754	0.12185	0.24846	10.3209	194.591
6	$3.K^{+}$ [a]	-1789.37904	-0.30193	-0.13287	0.16906	0.2174	13.1362	178.582
7	$3.Ca^{2+}$ [b]	-1858.6758	-0.54186	-0.23998	0.30188	0.39092	14.6497	199.665
8	$3.Mg^{2+}$[b]	-1381.5963	-0.54757	-0.12828	0.41929	0.33792	11.9400	90.518
9	$3.Ag^{+}$ [c]	-1327.27981	-0.42323	-0.06169	0.36154	0.24246	9.1246	419.606
10	$3.Hg^{2+}$ [c]	-1223.40448	-0.57545	-0.22034	0.35511	0.39789	8.4915	107.559
11	$3.Pb^{2+}$ [c]	-1185.41856	-0.57083	-0.19612	0.37471	0.38347	4.6744	133.311

a: DFT b3lyp/6-31g, b: HF/6-31g, c: HF/Lanl2DZ, d: Dipole moment/Debye, e: Polarizability

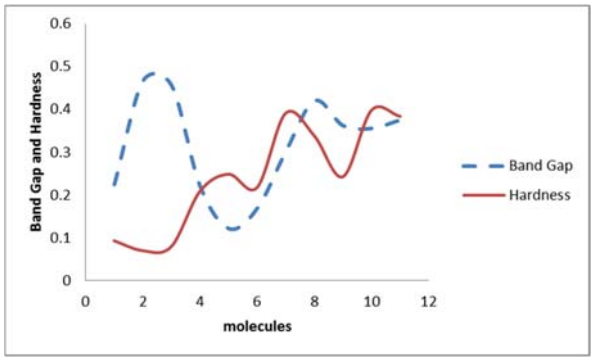

Fig 2: Band Gap and Hardness of 1 and its metal ions complexes.

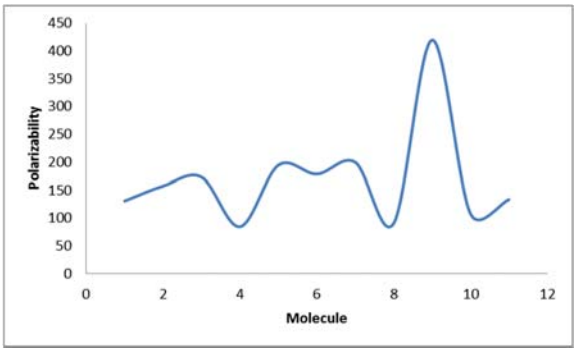

Fig 3: Polarizability of 1 and its metal ions complexes.

Table 2: Calculated thermochemical properties (ΔH and ΔG) of **1** and its complexes.

Entry	ΔH, Hartree/Part.[d]	ΔG, Hartree/Part.	Entry	ΔH, Hartree/Part.	ΔG, Hartree/Part.
3[a]	-1189.1209	-1189.2046	3.Pb^{2+} [c]	-1184.9327	-1185.0137
3[b]	-1181.8402	-1181.9211	Li^{+} [a]	-7.2821	-7.2972
3[c]	-1182.0349	-1182.1164	Na^{+} [a]	-162.0788	-162.0956
3.Li^{+} [a]	-1196.5764	-1196.6558	K^{+} [a]	-599.7216	-599.7391
3.Na^{+} [a]	-1351.2523	-1351.3419	Ca^{2+} [b]	-676.1015	-676.1191
3.K^{+} [a]	-1788.9234	-1789.0099	Mg^{2+} [b]	-198.8093	-198.8261
3.Ca^{2+} [b]	-1858.1899	-1858.2684	Ag^{+} [c]	-144.6567	-144.6757
3.Mg^{2+}[b]	-1381.1090	-1381.1846	Hg^{2+} [c]	-40.4916	-40.5114
3.Ag^{+} [c]	-1326.7931	-1326.8781	Pb^{2+} [c]	-2.5993	-2.6192
3.Hg^{2+} [c]	-1222.9174	-1222.9990			

a: DFT b3lyp/6-31g, b: HF/6-31g, c: HF/Lanl2DZ, d: Hartree/Particle = 627.509 Kcal/mol

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

Row	Entry	ΔΔH, Hartree/Part.[d]	ΔG,Δ Hartree/Part.	ΔΔH, Kcal/mol	ΔG,Δ Kcal/mol	K_f	$LogK_f$
1	3.Li^{+} [a]	-0.1734	-0.154	-108.810	-96.636	6.836×10^{70}	70.834
2	3.Na^{+} [a]	-0.0526	-0.0417	-33.006	-26.167	1.514×10^{19}	19.180
3	3.K^{+} [a]	-0.0809	-0.0662	-50.765	-41.541	2.816×10^{30}	30.449
4	3.Ca^{2+} [b]	-0.2482	-0.2282	-155.747	-143.197	9.212×10^{104}	104.964
5	3.Mg^{2+} [b]	-0.4595	-0.4374	-288.340	-274.472	1.548×10^{201}	201.189
6	3.Ag^{+} [c]	-0.1015	-0.086	-63.692	-53.965	3.603×10^{39}	39.556
7	3.Hg^{2+} [c]	-0.3909	-0.3712	-245.293	-232.931	5.495×10^{170}	170.739
8	3.Pb^{2+} [c]	-0.2985	-0.2781	-187.311	-174.510	8.260×10^{127}	127.916

a: DFT b3lyp/6-31g, b: HF/6-31g, c: HF/Lanl2DZ, d: Hartree/Particle = 627.509 Kcal/mol

Based on the data reported in table 2 and table 3, formation constants of complexes are in the order of $Na^{+}<K^{+}<Ag^{+}<Li^{+}<Ca^{2+}<Pb^{2+}<Hg^{2+}<Mg^{2+}$. 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 depends 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.

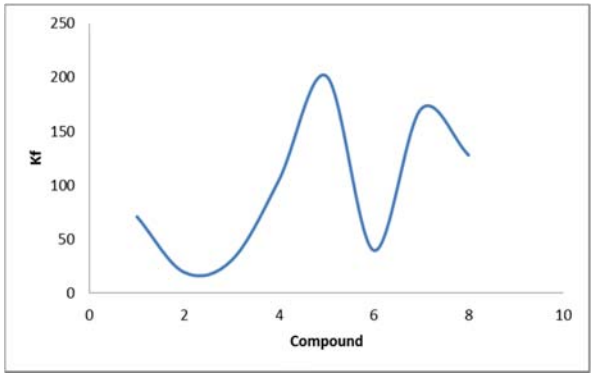

Fig 4: Formation constants of complexes.

In Fig. 5 and Fig. 6 the optimized structure of 1 showed and in Fig. 7 and Fig. 8 the optimized structure of Mg^{2+} complex with 1 from two sides was reported.

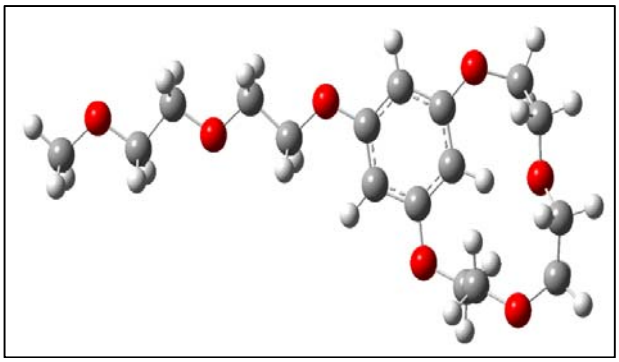

Fig 5: The calculated 3D structure of crown ether (**1**) from top view.

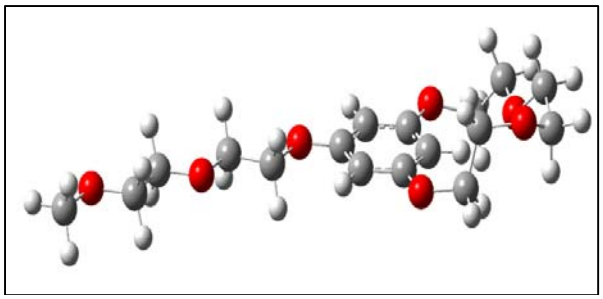

Fig 6: The calculated 3D structure of crown ether (**1**) from side view.

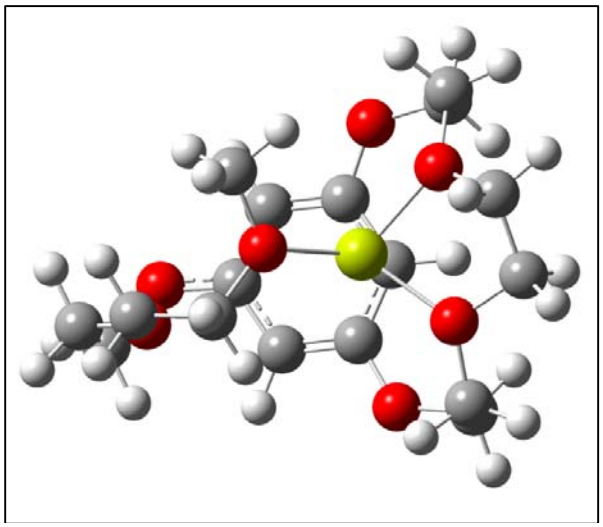

Fig 7: The calculated 3D structure of Mg^{2+} complex with crown ether (**1**) from top view.

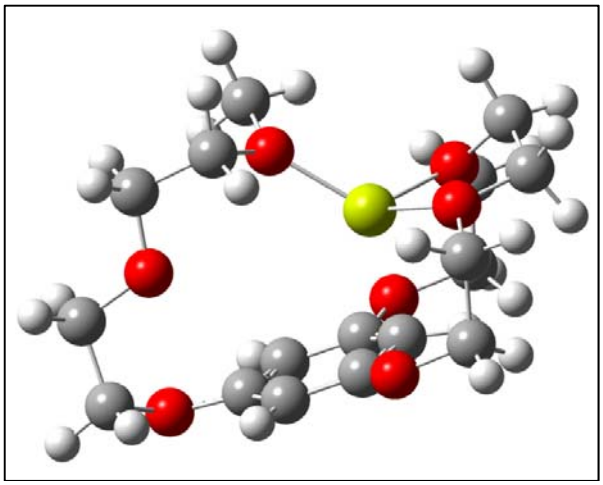

Fig 8: The calculated 3D structure of Mg^{2+} complex with crown ether (**1**) from side view.

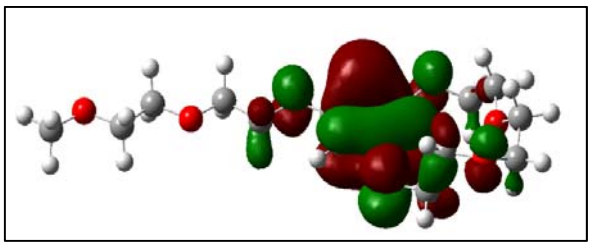

Fig 9: HOMO orbital of crown ether (**1**) from top view.

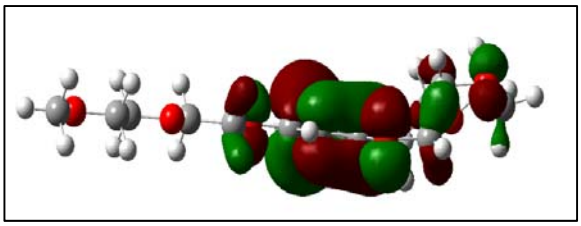

Fig 10: HOMO orbital of crown ether (**1**) from side view.

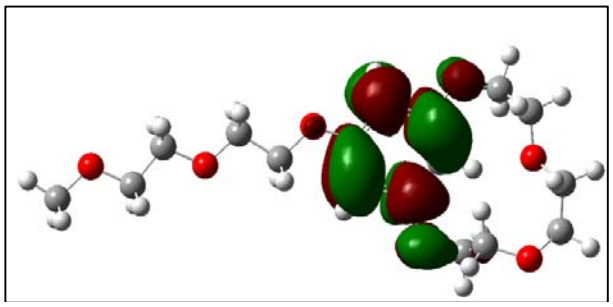

Fig 11: LUMO orbital of crown ether (**1**) from top view.

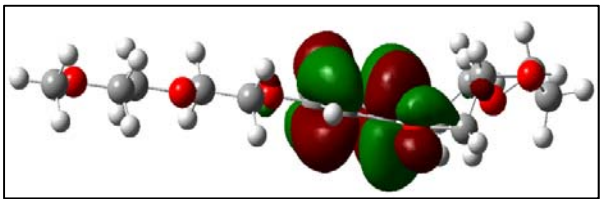

Fig 12: LUMO orbital of crown ether (**1**) from side view.

HOMO and LUMO orbitals of 1 were reported in Fig. 9, Fig. 10, Fig 11 and Fig. 12. The HOMO orbital is distributed strongly on the benzene ring and crown cavity oxygen atoms. The LUMO orbital was distributed extensively on the benzene ring and weakly on the oxygen atoms of crown ether cavity.

4. Acknowledgement

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5. References

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