



## THEORETICAL STUDY OF INTEGRATED CROWN ETHERS AND THEIR COMPLEXES WITH SOME TRANSITION AND LANTHANIDE IONS

Basim I. Mahdi

Department of Chemistry, College of Science, University of Baghdad. Baghdad- Iraq

### Abstract

Geometrical parameters, ultraviolet and vibrational frequencies, relative stabilities, and heat of association of the six crown ethers (12O4, 12N4, 12S4, 12O2N2, 12O2S2, 12N2S2) were calculated by HF/STO-6G and HF/6-31G level of theory. The energies were calculated by single-point MP2 method using polarized 6-31G basis functions. The potential energy surface and HOMO-LUMO of these ligands indicate a remarkable change in electron density of 12O4 when nitrogen and sulfur atoms replaced the oxygen atoms which result in a major change in their ion selectivity toward transition ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{2+}$ , and  $\text{Pd}^{2+}$ ) and lanthanide ( $\text{Nd}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Tm}^{2+}$ ,  $\text{Yb}^{2+}$ ) ions. The free ligands 12N4 and 12N2S2 were unstable in gas phase through geometry optimization but they are stable through complexation calculations. The heats of association with A-type and B-type ions were calculated by MMplus. In aqueous solution the 12N4 and 12S4 showed a high selectivity for  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$  ions while the ligand 12O4 preferred to select  $\text{Pd}^{2+}$  and  $\text{Rh}^{2+}$  ions. The six ligands showed the same tendency for the lanthanide metal ions in the gas phase but they behave in a different manner in the aqueous phase. The theoretical IR vibrational spectra showed that Pd-N stretching, Pd-O stretching, and Pd-S stretching have a similar values within the range 603-616  $\text{cm}^{-1}$ .

### دراسة نظرية لأثيرات تاجية ومعقداتها مع بعض ايونات الفلزات الانتقالية

باسم ابراهيم مهدي

قسم الكيمياء، كلية العلوم، جامعة بغداد. بغداد - العراق.

### الخلاصة

إن المعاملات الهندسية، الترددات فوق البنفسجية والاهتزازية، الاستقرار النسبي وحرارة التجمع للمركبات التاجية (12O4, 12N4, 12S4, 12O2N2, 12O2S2, 12N2S2)، قد تم حسابها بواسطة HF/STO-6G and HF/6-31G وتم حساب الطاقات باستخدام طريقة النقطة المنفردة MP2 والدالات الأساسية 6-31 G المستقطبة، ويشير سطح الطاقة الكامنة و HOMO- LUMO لهذه الليكاندات إلى حصول تغير واضح في الكثافة الإلكترونية في الليكاند 12O4 عند إحلل ذرات النيتروجين والكبريت محل ذرات الأوكسجين، حيث تؤدي إلى تغيرات أساسية بانتقائيتها الأيونية تجاه ايونات ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{2+}$ , and  $\text{Pd}^{2+}$ ) واللانثانات ( $\text{Nd}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Tm}^{2+}$ ,  $\text{Yb}^{2+}$ ). أما الليكاندات الحرة 12N4 و 12N2S2 فلم تكن مستقرة في الطور الغازي أثناء التمثيل الهندسي المثالي ولكنها استقرت عند حساب التعقيد. إن حرارة التجمع مع ايونات A-type و B-type قد تم حسابها باستخدام MM plus. وعند إذابتها في المحلول السائل فأُن كل من 12S4 و 12N4 قد أظهرت انتقائية عالية تجاه

ايونات  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$  بينما يميل الليكند 12O4 إلى انتقاء ايونات  $\text{Rh}^{2+}$  و  $\text{Pd}^{2+}$ . ان الليكندات الستة اعلاه اظهرت نفس الميل تجاه ايونات اللانثانات الفلزية في الطور الغازي ولكنها تصرفت بشكل مختلف في الطور المائي. وأظهرت اطياف ( I.R ) قيم متشابهة لترددات مط الأواصر Pd- N, Pd- O, Pd-S ضمن المدى (603- 616) سم<sup>-1</sup>.

## Introduction

The crown ether coordination chemistry is the most decisive factor for ions selectivity and complexation reactions. In reality, several parameters influence the ligand behavior. These are donor binding sites, shape topology, conformational flexibility and substituent effects [1,2].

In the classical crown ether, oxygen have been used as donor atoms which so called "hard" type (A-type donor) atoms. As A-type donors, they should most favorably combine with A-type metal ions (alkali/alkaline earth, lanthanide ions) according to hard and soft acid-base principle [3-6]. Thus, they show less compatibility to combine with B-type cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{2+}$  and  $\text{Pd}^{2+}$   $\text{Ag}^+$  etc.). On other hand, these B-type cations prefer to interact with "soft" B-type donors like N and S atoms. In general, the substitution of oxygen by sulfur or nitrogen, to form integrated crown ether (12N2O2, 12N2S2, 12O2S2 etc.) increases the binding ability towards B-type cation. One of the studies has been reported on stepwise substitution of nitrogen and sulfur atoms in crown ether frame and about their stabilizing effects on their complexation and selectivity towards A- and B-type ions[7]. The importance of conformational flexibility effects is particularly obvious with thia crown ether. Structural work has revealed that the 9S3, 12S4, 14S4, 15S5 and 18S6 adopt inside-out conformations in which the heteroatoms point out of the macrocyclic ring[8-11] Exodentate coordination of thioether groups has also been reported for Nb(V) and Hg(II) complexes of 1,4-dithia-18-crown-6 [12-14]. Unusual behavior contrasts with that of crowns containing oxygen or nitrogen atoms, and it has important ramification for coordination chemistry [15,16].

The theoretical calculations concerning the conformational flexibility and selectivity have been started since 1975. Pullman et al calculate the relative energies for two suggested theoretical models, maxidentate ( $\text{C}_{4v}$ ) and alternate ( $\text{C}_{2v}$ ) for 12O4, they found that the free conformer  $\text{C}_{2v}$  was more stable than  $\text{C}_{4v}$  by a 2.9 kcal/mol. They also estimated the binding energies for these two conformations with lithium ion using *ab initio* method (with bases set STO-3G). Their results showed that the complex  $12\text{O}4_{\text{C}_{2v}}+\text{Li}$  was more stable than  $12\text{O}4_{\text{C}_{4v}}+\text{Li}$  by a 0.5 kcal/mol [17]. Morokuma and Kitaura related the crown ether complexation energy to electrostatic, charge-transfer, polarization and exchange energies [18-20]. Yamabe *et al* have conducted several theoretical studies using CNDO/2 and *ab initio* on the stability of crown ether complexes of 12O4 and 18O6 with  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NHU}^+$ . They showed that the selectivity of crown ether affected mainly by hydration energy in addition to cavity size and electrostatic energy<sup>[21,22]</sup> These results were confirmed by Izatt *et al*[16,23] Other several theoretical calculations on crown ether complexes and selectivity have been reported using molecular mechanics[24-26], semi empirical[25-27] and *ab initio* [28-32] methods.

Our interest in the coordination chemistry of 12O4 crown ether led us to examine the change of its selectivity towards some transition metal ions, as ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{2+}$  and  $\text{Pd}^{2+}$ ), and lanthanide ions as ( $\text{Nd}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Tm}^{2+}$ , and  $\text{Yb}^{2+}$ ) when the oxygen atoms are replaced by N and S atoms through building a theoretical structures with different conformations to form its analogues of azoether and thioether and their integrated structures.

## -Abbreviations used;

|  |                        |
|--|------------------------|
| 9S3, 1,4,7-trithiacyclononane                | (trithia-9-crown-3)    |
| 12S4, 1,4,7,10-tetrathiacyclododecane        | (tetrathia-12-crown-4) |
| 14S4, 1,4,8,11-tetrathiacyclotetradecane     | (tetrathia-12-crown-4) |
| 15S5, 1,4,7,10,13-pentathiacyclopentadecane  | (pentathia-15-crown-5) |
| 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane | (hexathia-18-crown-6)  |
| 12O4, 1,4,7,10-tetraoxacyclododecane         | ( 12-crown-4)          |
| 18O6, 1,4,7,10,13,16-hexaoxacyclooctadecane  | ( 18-crown-6)          |

The initial structures of 12N4, 12O4, 12S4, 12N2O2, 12N2S2 and 12O2S2 for *ab initio* calculation were obtained by molecular mechanics (MMplus) [33]. Each structure was subjected to conformational search and the lowest energy structure was selected. The geometrical structures of 12N4, 12O4, 12S4, 12N2O2, 12N2S2 and 12O2S2 were optimized at HF/STO-6G [34, 36] and HF/6-31G [37, 39]. The energies were calculated by single-point MP [40,41] method using polarized 6-31G\* basis functions. The structures of the complexes of 12N4, 12O4, 12S4, 12N2O2, 12N2S2 and 12O2S2 with transition B-type metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{2+}$  and  $\text{Pd}^{2+}$ ) were optimized using semiempirical PM3 method.

The molecular mechanic program MMplus was used for complexes with lanthanide A-type metal ions ( $\text{Nd}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Tm}^{2+}$ , and  $\text{Yb}^{2+}$ ). The Polak-Ribiere was used as optimization algorithm for stable conformers while the steepest descend algorithm was used for unstable ligands. The initial guess of the MO coefficients was from a projected INDO calculation. The program HyperChem 7.5 [42] was used for the *ab initio*, semiempirical AM1[43], PM3[44] and MM plus[45] calculations.

## Results and Discussion

### Free Ligands

The minimized *ab initio* MP2/6-31G\*\*/6-31G\* energies were reported for the integrated ethers 12N4, 12O4, 12S4, 12N2O2, 12N2S2 and 12O2S2 in addition to their heat of formations and classical energies in gas phase and water calculated by molecular mechanic. Table-1 shows the geometrical parameters of these ligands which viewed in Figure-1. The relative

energies calculated in different methods are summarized in Table-2. The ligand 12N4 was unstable in gas phase through geometry optimization (Grad=0.01) and gave a distorted bond distance for C-C 3.2 Å. The integrated 12N2S2 was also unstable in gas phase through geometry optimization (Grad=0.01) for its two conformations (neighbor and alternate). In the neighbor conformation (S-C-C-S-C-C-N-C-C-N-C-C) the C-C bond become very long ca. 3.48 Å through geometry optimization, while the alternate conformation (S-C-C-N-C-C-S-C-C-N-C-C) forms a hydrogen bonding between C-H and N atoms. The steepest descend algorithm was used for these two ligands. The alternate conformation ( $\Delta H_f=19.064$  kcal/mol) was shown to be more stable than the neighbor ( $\Delta H_f=34.349$  kcal/mol) by 15.3 kcal/mol.

The potential energy surface of these ligand indicate to a dramatic change in electron density of 12O4 when nitrogen and sulfur atoms replaced the oxygen atoms which play a major factor in ion selectivity. The electron density localized on three oxygen atoms in 12O4, while it localized only at two nitrogen atoms in 12N4 and this property might give the two compounds (12O4 and 12N4) the same behavior toward ions. The atomic charges of donors and carbon atoms for these ligands are shown in Figure-2; the electron density in 12S4 is generalized over all atoms as shown in Figure-3. The charges on oxygen atoms (-0.727) is usually twice that of nitrogen (-0.40). In the 12S4 ligand the case is different, the atomic charges on carbon atoms (-0.63) is more negative than that of sulfur atoms (0.50). This mode of distribution of electron density made the oxygen atoms of hard type while nitrogen and sulfur are of soft type. The integrated ligands showed diverse atomic charges over the entire molecule.

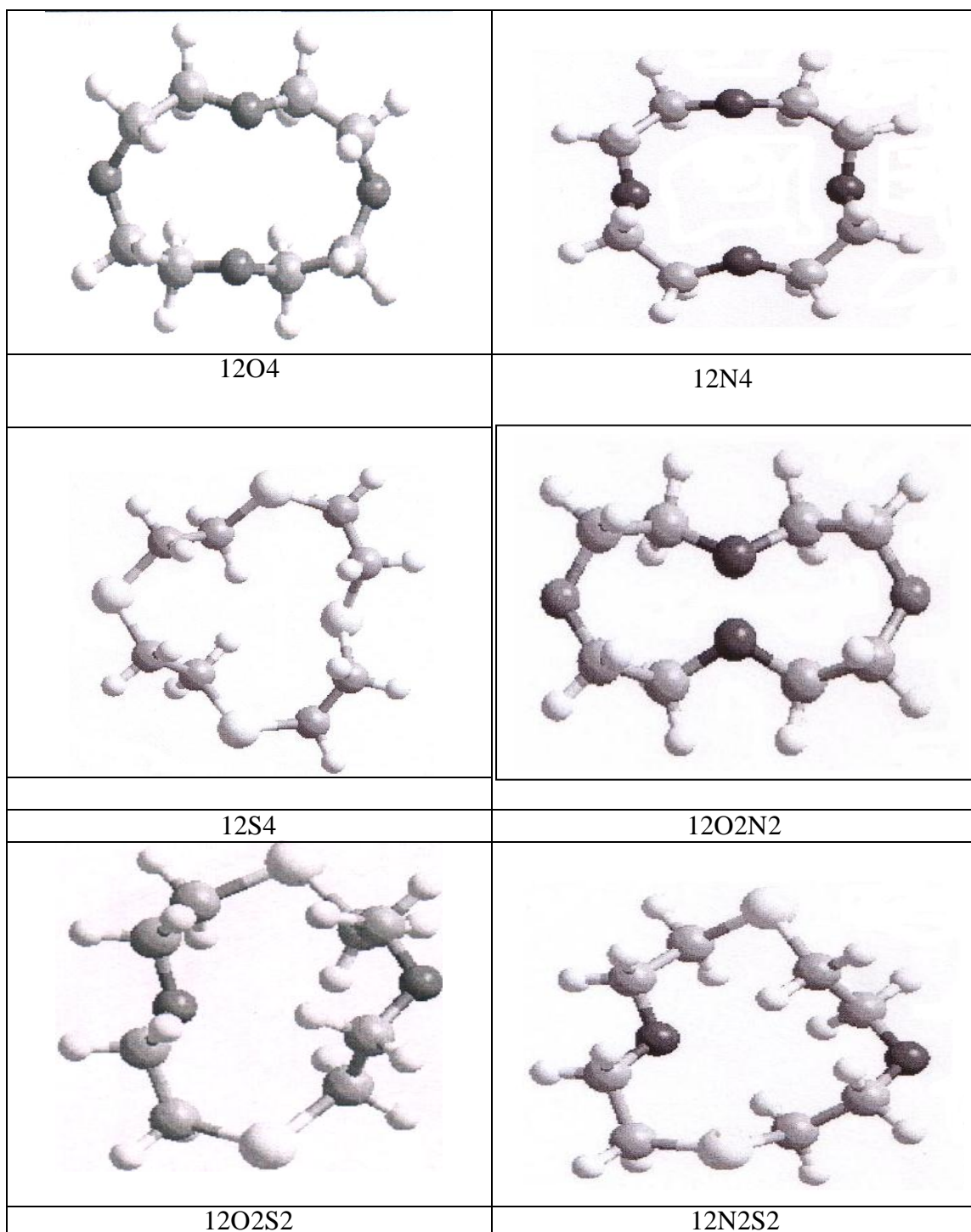
**Table 1: Internal coordinates for free ligands (r in Å &  $\theta$  in degree).**

| Ligand | C-C    | C-E        | C-E-C     | C-C-E-C              | E-C-C-E          |
|--------|--------|------------|-----------|----------------------|------------------|
| 12N4   | 1.5466 | 1.497      | 116.0     | 168, -104, 117, 110  | 80, -13, -67, 41 |
| 12O4   | 1.508  | 1.426      | 120.0     | 148, -148, 147, -148 | -76, 76, -76, 76 |
| 12S4   | 1.540  | 1.47       | 118.0     | 162, -146, 162, -147 | .48, 48, -48, 48 |
| 12N2O2 | 1.546  | 1.50, 1.43 | 112, 111  | 124, -171, 124, -171 | -71, 70, -71, 71 |
| 12N2S2 | 1.554  | 1.773      | 97.5, 109 | 161, 152, 161, 152   | -96, 96, -96, 96 |
| 12O2S2 | 1.550  | 1.43, 1.79 | 109, 102  | -178, 114, -178, 114 | 67, -67, 67, -67 |

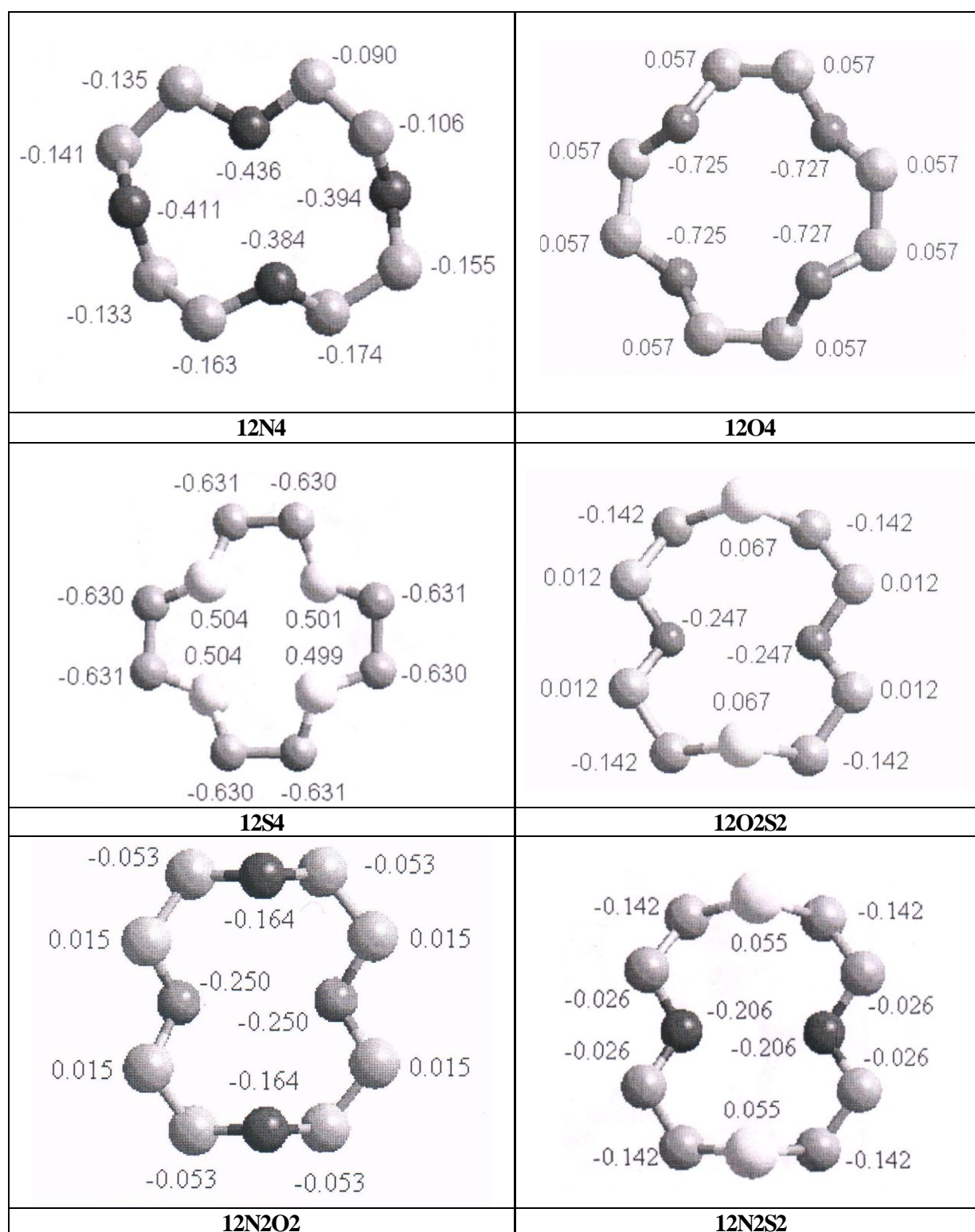
E=N,O,S donors atoms

**Table 2: Total and relative energies of integrated crown ether calculated from *ab initio*, PM3 and MMplus (kcal/mol) .**

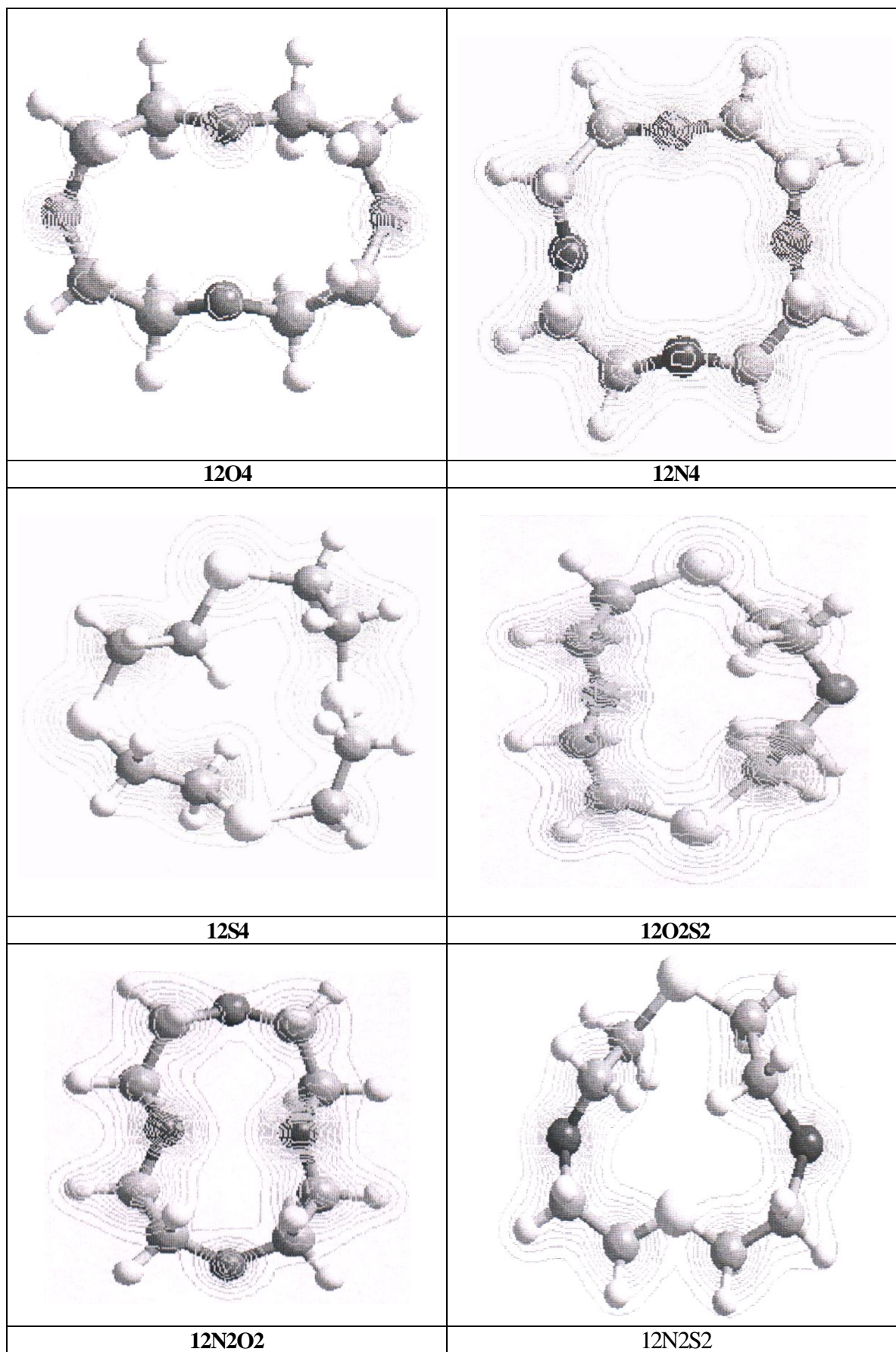
| <b>Ligands</b> | <b>Total Energy<br/>MP2/6-31G**//6-<br/>31G* (kcal/mol)</b> | <b>Total Energy<br/>(a.m.u)<br/><math>\Delta H_f</math> (kcal/mol)<br/><br/>PM3</b> | <b>Total Energy<br/>(a.m.u)<br/><math>\Delta H_f</math>(kcal/mol)<br/><br/>AMI</b> | <b>Total Energy<br/>MMplus<br/>(kcal/mol)</b> |
|----------------|---|---|--|---|
| <b>12N4</b>    | -531.6297   | -67.6285<br>(97.5395)   | -76.0619<br>(87.0946)  | (Gas) 2 1.250084<br>(Aqu) -529.9982           |
| <b>12O4</b>    | -612.5679   | -87.0547<br>(-155.4461)   | -92.8656<br>(-183.9242)  | (Gas) 25.408588<br>(Aqu) -526.6 126           |
| <b>12S4</b>    | -1903.1028  | -71.2830<br>(1.4570)  | -74.3578<br>(-14.7326)   | (Gas) 22.38 1382<br>(Aqu) -532.7357           |
| <b>12N2O2</b>  | -569.7393   | -77.3731<br>(-48.6901)  | -84.4639<br>(-48.4731)   | (Gas) 24.388723<br>(Aqu) -523.5 104           |
| <b>12N2S2</b>  | -1213.2386  | -69.5043<br>(19.0649)   | -75.2450<br>(14.1118)  | (Gas) 15.979326<br>(Aqu) -525.8492            |
| <b>12O2S2</b>  | -1258.6671  | -79.1698<br>(-77.5968)  | -83.6120<br>(-99.5259)   | (Gas) 23.465046<br>(Aqu) -529.6138            |



**Figure 1: Ball and stickview of integrated crown ether ligands .**



**Figure 2: Atomic charges of crown ether derivative ligands .**



**Figure 3: Electron density of crown ether ligands .**

### Integrated Crown Ether Complexes

The geometrical structures of the integrated crown ether complexes have been optimized by PM3 and viewed in Figure-4 (M= Pd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Rh<sup>2+</sup>, Co<sup>2+</sup>, Nd<sup>2+</sup>, Sm<sup>2+</sup>, Tm<sup>2+</sup>, Yb<sup>2+</sup>). The heat of formation  $\Delta H_f$  and heat of reaction  $\Delta H_{rea}$  of crown ether derivatives for transition metal ions are listed in Table-3 which reflects their

stability towards the metal ions. The heat of formation for lanthanide metal ions could not be calculated by PM3 due its lack of their parameters. The heat of reaction has been calculated from the heat of formations of products and reactants as follow:

$$\Delta H_{\text{reaction}} = \sum \Delta H_{f, \text{product}} - \sum \Delta H_{f, \text{reactant}}$$

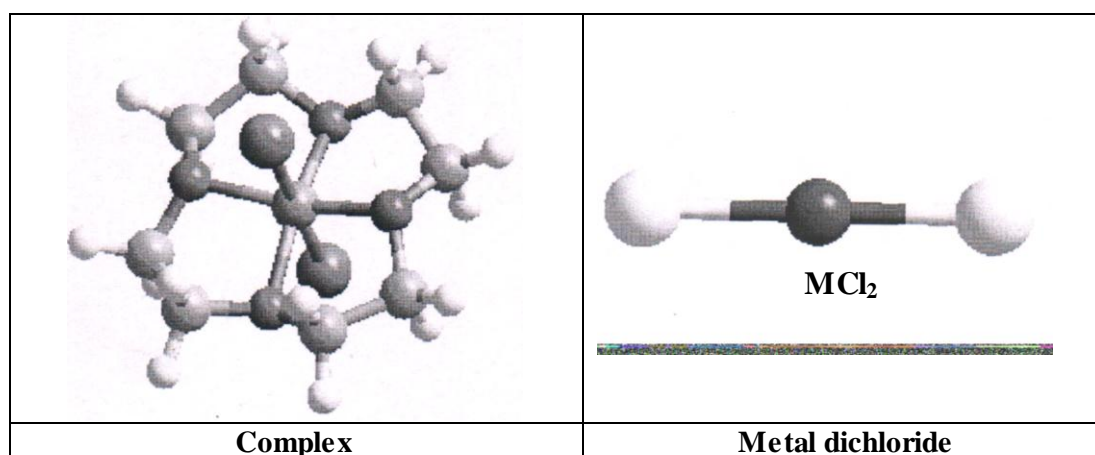


Figure 4: Ball and stick view of crown ether complex and MCl<sub>2</sub> salt [33].

The heat of complexation can also be calculated theoretically but it usually depends on the solvation energy which is somehow difficult to be treated theoretically and the final calculated values of complexation energies will be a rather high than the experimental values. An alternate approach for these calculations is come from molecular mechanics. The heat of association  $\Delta H_{\text{assoc}}$  of complexes is calculated from -

subtracting the heat of ether from the heat of the complex. The smaller the result, the more stable the complex. These calculations are carried out by molecular mechanics with MM+ program. Table-4 lists the heat of association  $\Delta H_{\text{assoc}}$  of these complexes with transition metal ions in gas phase and in aqueous solution. The selectivity for transition metal ions is listed as follow:

#### Selectivity in gas phase

**12N4:** Pd<sup>2+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>>Rh<sup>2+</sup>> Co<sup>2+</sup>  
**12O4:** Rh<sup>2+</sup>>Pd<sup>2+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>>Co<sup>2+</sup>  
**12S4:** Pd<sup>2+</sup>>Rh<sup>2+</sup>> Co<sup>2+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>  
**12N2O2:** Rh<sup>2+</sup>>=Pd<sup>2+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>>Co<sup>2+</sup>  
**12N2S2:** Rh<sup>2+</sup>>=Pd<sup>2+</sup>>Cu<sup>2+</sup>> Co<sup>2+</sup>> Ni<sup>2+</sup>  
**12O2S2:** Pd<sup>2+</sup>>Rh<sup>2+</sup>> Co<sup>2+</sup>>Ni<sup>2+</sup>>Cu<sup>2+</sup>

#### Selectivity in aqueous solution

**12N4:** Pd<sup>2+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>>Rh<sup>2+</sup>> Co<sup>2+</sup>  
**12O4:** Pd<sup>2+</sup>>Rh<sup>2+</sup>>Ni<sup>2+</sup>>Co<sup>2+</sup>>Cu<sup>2+</sup>  
**12S4:** Pd<sup>2+</sup>>Cu<sup>2+</sup>> Co<sup>2+</sup>>Ni<sup>2+</sup>>Rh<sup>2+</sup>  
**12N2O2:** Cu<sup>2+</sup>>Rh<sup>2+</sup>>Co<sup>2+</sup>>Pd<sup>2+</sup>>=Ni<sup>2+</sup>  
**12N2S2:** Rh<sup>2+</sup>>=Pd<sup>2+</sup>>Cu<sup>2+</sup>>Co<sup>2+</sup>>Ni<sup>2+</sup>  
**12O2S2:** Pd<sup>2+</sup>>Rh<sup>2+</sup>> Co<sup>2+</sup>>Ni<sup>2+</sup>>Cu<sup>2+</sup>

As predicted from distribution of the atomic charges on the donor atoms in the ligands 12N4 and 12S4 that the behavior of 12N4 toward ions will be similar to that of 12S4 (both are soft type ligands). So the selectivity of 12N4 and 12S4 in aqueous solution was mainly heading for Pd<sup>2+</sup> and Cu<sup>2+</sup> ions while the selectivity of ligand 12O4 was for Pd<sup>2+</sup> and Rh<sup>2+</sup>. The ligand 12N2O2 showed a different choice. It preferred to select Cu<sup>2+</sup> ion in solution.

Of course, two competition factors control the selectivity for metal ions at fixed cavity size of the ligand; these are the electron density and the d-orbital on the donor atoms in the ligand respectively. The d-orbital on sulfur atom compensate the factor of electron density decrease.



**Table 3: Total (relative) energies and heat of reaction of 12N4, 12O4 and 12S4 and their integrated complexes from PM3 calculations in gas phase (kcal/mol).**

| Complex                  | $\Delta H_f$ | Relative $\Delta H_f$ | Total Relative $\Delta H_f$ | Heat of Reaction $\Delta H_f$ |
|--------------------------|--------------|-----------------------|-----------------------------|-------------------------------|
| 12N4-CoCl <sub>2</sub>   | -324.486     | 0.000                 | 94.545                      | -283.091                      |
| 12N4-PdCl <sub>2</sub>   | -183.7674    | 140.719               | 235.264                     | -67.352                       |
| 12N4-NiCl <sub>2</sub>   | -138.774     | 185.712               | 280.257                     | -16.276                       |
| 12N4-RhCl <sub>2</sub>   | -110.315     | 214.171               | 308.716                     | -25.177                       |
| 12N4-CuCl <sub>2</sub>   | -35.153      | 289.333               | 383.878                     | -65.029                       |
| 12O4-CoCl <sub>2</sub>   | -419.031     | 0.000                 | 0.00                        | -124.650                      |
| 12O4-PdCl <sub>2</sub>   | -309.448     | 109.583               | 109.583                     | -172.878                      |
| 12O4-NiCl <sub>2</sub>   | -295.266     | 123.764               | 123.764                     | -182.778                      |
| 12O4-RhCl <sub>2</sub>   | -189.647     | 229.384               | 229.384                     | -39.800                       |
| 12O4-CuCl <sub>2</sub>   | -158.917     | 260.114               | 260.114                     | -24.113                       |
| 12S4-CoCl <sub>2</sub>   | -376.398     | 0.000                 | 42.633                      | -238.920                      |
| 12S4-PdCl <sub>2</sub>   | -219.777     | 156.621               | 199.254                     | -199.444                      |
| 12S4-RhCl <sub>2</sub>   | -180.331     | 196.067               | 238.700                     | -135.916                      |
| 12S4-CuCl <sub>2</sub>   | -141.298     | 235.101               | 277.733                     | -134.242                      |
| 12S4-NiCl <sub>2</sub>   | -91.323      | 285.075               | 327.708                     | -69.224                       |
| 12N2O2-CoCl <sub>2</sub> | -376.858     | 0.000                 | 42.173                      | -189.233                      |
| 12N2O2-PdCl <sub>2</sub> | -254.517     | 122.341               | 164.514                     | -224.703                      |
| 12N2O2-NiCl <sub>2</sub> | -242.640     | 134.218               | 176.391                     | -236.908                      |
| 12N2O2-RhCl <sub>2</sub> | -152.792     | 224.066               | 266.239                     | -109.700                      |
| 12N2O2-CuCl <sub>2</sub> | -87.946      | 288.912               | 331.085                     | -59.898                       |
| 12N2S2-CoCl <sub>2</sub> | -343.171     | 0.000                 | 75.86                       | -223.301                      |
| 12N2S2-PdCl <sub>2</sub> | -211.698     | 131.473               | 207.333                     | -249.639                      |
| 12N2S2-NiCl <sub>2</sub> | -143.808     | 199.363               | 275.223                     | -205.831                      |
| 12N2S2-RhCl <sub>2</sub> | -141.941     | 201.23                | 277.090                     | -166.605                      |
| 12N2S2-CuCl <sub>2</sub> | -47.063      | 296.108               | 371.968                     | -86.770                       |
| 12O2S2-CoCl <sub>2</sub> | -357.409     | 0.000                 | 61.622                      | -140.877                      |
| 12O2S2-PdCl <sub>2</sub> | -243.305     | 114.104               | 175.726                     | -184.585                      |
| 12O2S2-NiCl <sub>2</sub> | -199.223     | 158.186               | 219.808                     | -164.586                      |
| 12O2S2-RhCl <sub>2</sub> | -171.409     | 186                   | 247.622                     | -99.411                       |
| 12O2S2-CuCl <sub>2</sub> | -114.824     | 242.585               | 304.207                     | -57.869                       |

**Table 4: Heat of association of 12N4,12O4 and 12S4 and their integrated complexes with some transitional metal ions calculated by MMplus in gas phase and in an aqueous solution (kcal/mol).**

| <b>Complex</b>           | <b><math>\Delta H_{\text{assoc}}</math> in Gas phase</b> | <b><math>\Delta H_{\text{assoc}}</math> in Aqueous phase</b> |
|--------------------------|--|--|
| 12N4-CoCl <sub>2</sub>   | 36.784   | 44.3287  |
| 12N4-PdCl <sub>2</sub>   | 23.745   | 33.0105  |
| 12N4-NiCl <sub>2</sub>   | 28.256   | 39.7552  |
| 12N4-RhCl <sub>2</sub>   | 33.688   | 42.7268  |
| 12N4-CuCl <sub>2</sub>   | 25.720   | 34.4632  |
| -----                    |  |  |
| 12O4-CoCl <sub>2</sub>   | 28.437   | 43.1632  |
| 12O4-PdCl <sub>2</sub>   | 13.865   | 21.7507  |
| 12O4-NiCl <sub>2</sub>   | 27.562   | 41.6521  |
| 12O4-RhCl <sub>2</sub>   | 12.799   | 26.3447  |
| 12O4-CuCl <sub>2</sub>   | 25.409   | 47.1966  |
| -----                    |  |  |
| 12S4-CoCl <sub>2</sub>   | 58.039   | 76.7877  |
| 12S4-PdCl <sub>2</sub>   | 38.775   | 63.7303  |
| 12S4-RhCl <sub>2</sub>   | 43.159   | 88.1491  |
| 12S4-CuCl <sub>2</sub>   | 60.455   | 64.2288  |
| 12S4-NiCl <sub>2</sub>   | 72.434   | 82.5817  |
| -----                    |  |  |
| 12N2O2-CoCl <sub>2</sub> | 27.213   | 36.3104  |
| 12N2O2-PdCl <sub>2</sub> | 23.702   | 38.1644  |
| 12N2O2-NiCl <sub>2</sub> | 26.305   | 38.8338  |
| 12N2O2-RhCl <sub>2</sub> | 23.186   | 34.0763  |
| 12N2O2-CuCl <sub>2</sub> | 25.050   | 32.0252  |
| -----                    |  |  |
| 12N2S2-CoCl <sub>2</sub> | 45.426   | 50.7758  |
| 12N2S2-PdCl <sub>2</sub> | 36.595   | 41.5263  |
| 12N2S2-NiCl <sub>2</sub> | 50.565   | 54.6792  |
| 12N2S2-RhCl <sub>2</sub> | 36.574   | 41.2579  |
| 12N2S2-CuCl <sub>2</sub> | 43.904   | 45.1241  |
| -----                    |  |  |
| 12O2S2-CoCl <sub>2</sub> | 40.264   | 56.8648  |
| 12O2S2-PdCl <sub>2</sub> | 25.338   | 38.8197  |
| 12O2S2-NiCl <sub>2</sub> | 42.005   | 60.3706  |
| 12O2S2-RhCl <sub>2</sub> | 28.077   | 45.3029  |
| 12O2S2-CuCl <sub>2</sub> | 51.125   | 64.6494  |

Table 5: lists the heat of association  $\Delta H_{\text{assoc}}$  of these complexes with lanthanide metal ions in gas phase and in aqueous solutions. The selectivity for lanthanide metal ions is listed as follow:

### Selectivity in gas phase

**12N4:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Eu}^{2+} > \text{Nd}^{2+}$   
**12O4:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12S4:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12N2O2:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12N2S2:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12O2S2:**  $\text{Tm}^{2+} = \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$

### Selectivity in aqueous solution

**12N4:**  $\text{Tm}^{2+} > \text{Yb}^{2+} > \text{Nd}^{2+} > \text{Sm}^{2+} > \text{Eu}^{2+}$   
**12O4:**  $\text{Sm}^{2+} > \text{Nd}^{2+} > \text{Tm}^{2+} > \text{Yb}^{2+} > \text{Eu}^{2+}$   
**12S4:**  $\text{Sm}^{2+} > \text{Tm}^{2+} > \text{Yb}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12N2O2:**  $\text{Sm}^{2+} > \text{Nd}^{2+} > \text{Tm}^{2+} > \text{Yb}^{2+} > \text{Eu}^{2+}$   
**12N2S2:**  $\text{Tm}^{2+} > \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$   
**12O2S2:**  $\text{Tm}^{2+} > \text{Yb}^{2+} > \text{Sm}^{2+} > \text{Nd}^{2+} > \text{Eu}^{2+}$

The six ligands showed the same tendency for the lanthanide metal ions in the gas phase but they behave in a different manner in the aqueous phase. The ligands with large cavity like 12O4, 12S4, and 12N2O2 prefer the large samarium ion (dia= 2.59 Å) while the ligands with small cavity like 12N4, 12N2S2, and 12O2S2 prefer the small thulium ion (dia= 2.42 Å). In general, these ligands do not prefer  $\text{Eu}^{2+}$  in both phases in spite of the fact that it has the same diameter of samarium ion.

## Theoretical Electronic (UV) and Vibrational (IR) Spectra of Crown Complexes

### a. Theoretical electronic spectra (UV) of DDVP

The theoretical electronic spectra (UV) of 12N4, 12O4, and 12S4 molecules were calculated at PM3 levels. Three electronic main absorption peaks for 12N4 were found at 340, 358, and 467 nm as shown in Figure 5a, while two main peaks were found for 12O4 at 168 and 273 nm which are illustrated in Figure 5a. The 12S4 ligand gave five main peaks at 247, 338, 390, 433, and 448 nm which are illustrated in figure 5b.

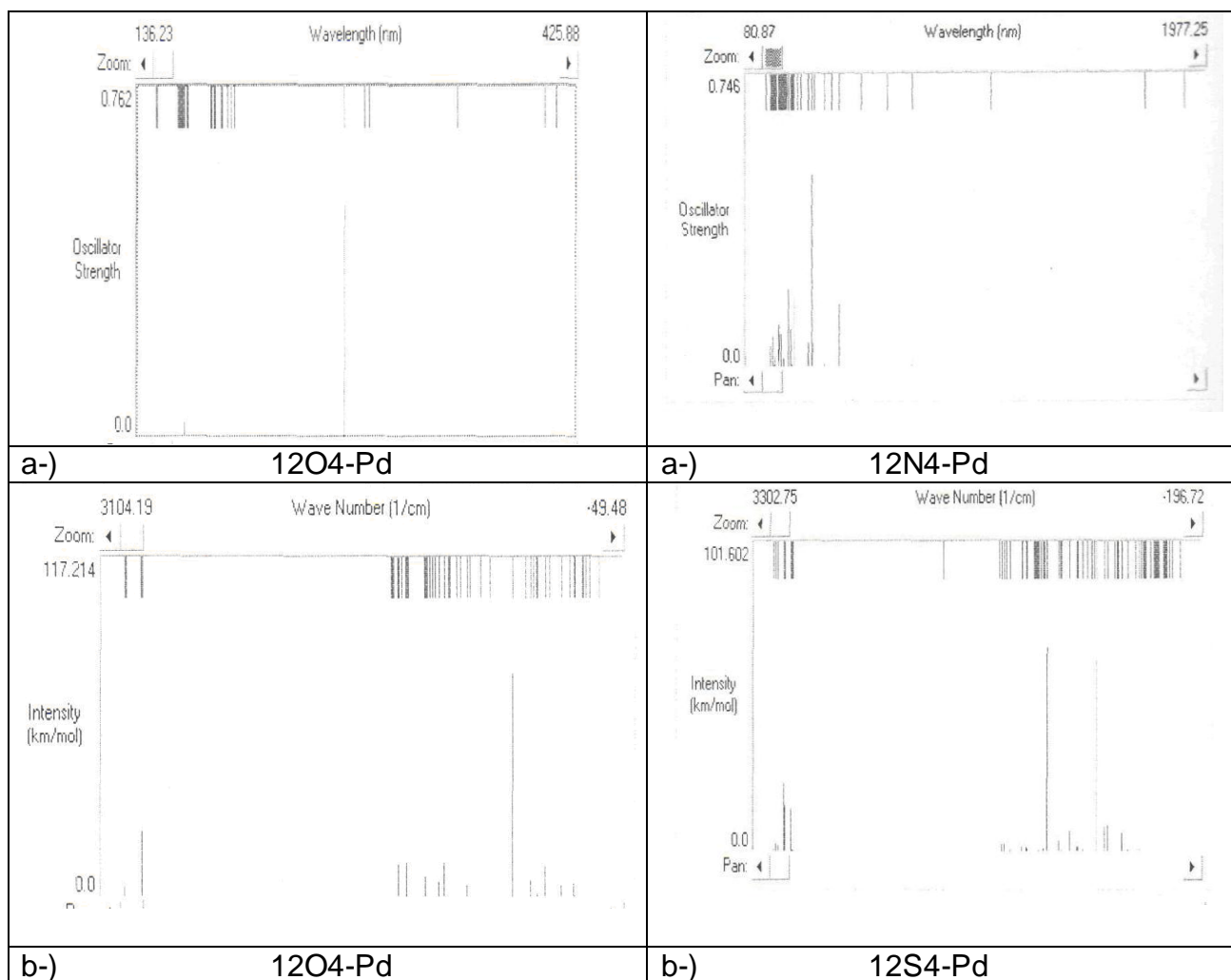
### b. Theoretical vibration frequencies of DDVP

Vibration frequencies are calculated at PM3 level of theory and assignments, "based on inspection of normal modes animation", and their spectra are illustrated in Figure 5b and listed in Table-6. The computed harmonic vibration frequencies are generally

overestimated due to neglect of anharmonicity. The absorption peaks of 12N4 at 413, 603, 977, and 1327  $\text{cm}^{-1}$  are assigned to Pd-N stretching, Pd-Cl stretching C-N bending and stretching respectively. The absorption peaks of 12O4 at 249, 420, 616, 1032 and 1143  $\text{cm}^{-1}$  are assigned to Pd-O bending, Pd-O stretching, Pd-Cl stretching C-O bending and stretching respectively. The absorption peaks of 12S4 at 614, 555, 417, and 823  $\text{cm}^{-1}$  are assigned to Pd-S bending, Pd-S stretching, Pd-Cl stretching C-S stretching respectively.

**Table5: Heat of association of 12N4,12O4 and 12S4 and their integrated complexes with some lanthanide metal ions calculated by MMplus in gas phase and in aqueous solution (kcal/mol) .**

| <b>Complex</b>            | <b><math>\Delta H_{\text{assoc}}</math><br/>in gas phase</b> | <b><math>\Delta H_{\text{assoc}}</math><br/>in aqueous</b> |
|---------------------------|--|--|
| 12N4-NdCl <sub>2</sub>    | 75.248718  | 88.701203  |
| 12N4-SmCl <sub>2</sub>    | 61.236061  | 89.951172  |
| 12N4-EuCl <sub>2</sub>    | 67.103668  | 97.494446  |
| 12N4-TmCl <sub>2</sub>    | 56.775124  | 77.404633  |
| 12N4-YbCl <sub>2</sub>    | 56.775124  | 78.055695  |
|                           |  |  |
| 12O4-NdCl <sub>2</sub>    | 62.558712  | 73.78243   |
| 12O4-SmCl <sub>2</sub>    | 60.318623  | 69.270528  |
| 12O4-EuCl <sub>2</sub>    | 81.075268  | 86.224172  |
| 12O4-TmCl <sub>2</sub>    | 53.087956  | 75.743032  |
| 12O4-YbCl <sub>2</sub>    | 53.087956  | 76.662496  |
|                           |  |  |
| 12S4-NdCl <sub>2</sub>    | 41.031353  | 71.539045  |
| 12S4-SmCl <sub>2</sub>    | 39.462742  | 65.454236  |
| 12S4-EuCl <sub>2</sub>    | 59.948544  | 82.17793   |
| 12S4-TmCl <sub>2</sub>    | 35.559818  | 66.84654   |
| 12S4-YbCl <sub>2</sub>    | 35.559818  | 66.973951  |
|                           |  |  |
| 12N2O2-NdCl <sub>2</sub>  | 58.037096  | 70.68023   |
| 12N2O2-SmCl <sub>2</sub>  | 56.158053  | 66.168328  |
| 12N2O2-EuCl <sub>2</sub>  | 73.780924  | 83.121972  |
| 12N2O2-TmCl <sub>2</sub>  | 50.08346   | 72.640832  |
| 12N2O2- YbCl <sub>2</sub> | 50.08346   | 73.560296  |
|                           |  |  |
| 12N2S2-NdCl <sub>2</sub>  | 44.478434  | 44.581774  |
| 12N2S2- SmCl <sub>2</sub> | 42.123484  | 43.439959  |
| 12N2S2-EuCl <sub>2</sub>  | 78.453848  | 77.809649  |
| 12N2S2-TmCl <sub>2</sub>  | 36.094832  | 37.39461   |
| 12N2S2-YbCl <sub>2</sub>  | 36.094832  | 39.625964  |
|                           |  |  |
| 12O2S2-NdCl <sub>2</sub>  | 31.299194  | 48.53656   |
| 12O2S2-SmCl <sub>2</sub>  | 29.832401  | 43.186096  |
| 12O2S2-EuCl <sub>2</sub>  | 45.803745  | 61.424622  |
| 12O2S2-TmCl <sub>2</sub>  | 25.676884  | 39.274963  |
| 12O2S2-YbCl <sub>2</sub>  | 25.676884  | 40.676605  |



**Figure 5: Theoretical a) electronic (UV) and b) vibrational (IR) spectra of some obtained crown ether complexes**

Table 6: Theoretical electronic (U.V) and vibrational (LR) bands.

| Ligand      | electronic spectra (U.V)<br>main absorption bands (nm)  | vibrational frequencies (IR)<br>( $\text{cm}^{-1}$ )  |
|-------------|---|---|
| <b>12N4</b> | 467 ( $n \rightarrow \pi^*$ )<br>358 ( $n \rightarrow \pi^*$ )<br>340 ( $n \rightarrow \pi^*$ )   | 56, 90, 95, 105, 142, 157, 164, 188, 215, 238,<br>280, 296, 331, 369, 399, 413, 434, 471, 496,<br>535, 565, 603, 625, 9, 742, 793, 796, 824, 829,<br>844, 883, 930, 952, 957, 977, 991, 997, 1004,<br>1016, 1018, 1037, 1051, 1074, 1079, 1084, 1089,<br>1099, 1107, 1124, 1132, 1134, 1148, 1163, 1183,<br>1232, 1259, 1268, 1271, 1288, 1306, 1325, 1327,<br>1343, 1353, 1372, 1377, 1380, 1382, 1390, 1391, 1394,<br>2766, 2880, 2880, 2885, 2888, 2895, 2900, 2918,<br>2949, 2974, 2984, 2986, 2988, 2989, 2995, 2998         |
| <b>12O4</b> | 273 ( $n \rightarrow \pi^*$ )<br>168 ( $\sigma \rightarrow \pi^*$ )   | 94, 145, 146, 171, 187, 188, 196, 238, 249, 250,<br>269, 319, 320, 388, 393, 420, 421, 465, 473,<br>489, 505, 509, 510, 539, 540, 541, 616, 760,<br>811, 812, 876, 882, 895, 896, 934, 958, 1000,<br>1002, 1003, 1008, 1032, 1033, 1037, 1063, 1065,<br>1066, 1068, 1086, 1103, 1104, 1125, 1135, 1143,<br>1144, 1152, 1252, 1260, 1261, 1267, 1295, 1306,<br>1307, 1313, 1340, 1342, 1343, 1344, 1347, 1351, 1352,<br>1358, 2858, 2856, 2858, 2859, 2860, 2862, 2863,<br>2864, 2953, 2954, 2955, 2956, 2959, 2960, 2961,<br>2962 |
| <b>12S4</b> | 448 ( $n \rightarrow \pi^*$ )<br>433 ( $n \rightarrow \pi^*$ )<br>390 ( $n \rightarrow \pi^*$ )<br>338 ( $n \rightarrow \pi^*$ )<br>247 ( $\pi \rightarrow \pi^*$ ) | 34, 47, 55, 75, 76, 94, 99, 113, 137, 144, 152,<br>156, 164, 177, 192, 230, 245, 253, 268, 288,<br>320, 376, 417, 423, 447, 453, 476, 529, 555,<br>614, 640, 650, 666, 690, 710, 728, 770, 787,<br>823, 827, 886, 897, 901, 919, 1005, 1020, 1024,<br>1030, 1047, 1059, 1068, 1072, 1090, 1091, 1100,<br>1101, 1158, 1178, 1192, 1193, 1195, 1201, 1297,<br>1315, 1339, 1343, 1355, 1369, 1370, 1375, 1813,<br>2995, 2997, 2999, 3008, 3009, 3014, 3056, 3059,<br>3059, 3062, 3065, 3067, 3068, 3107, 3124, 3143                  |

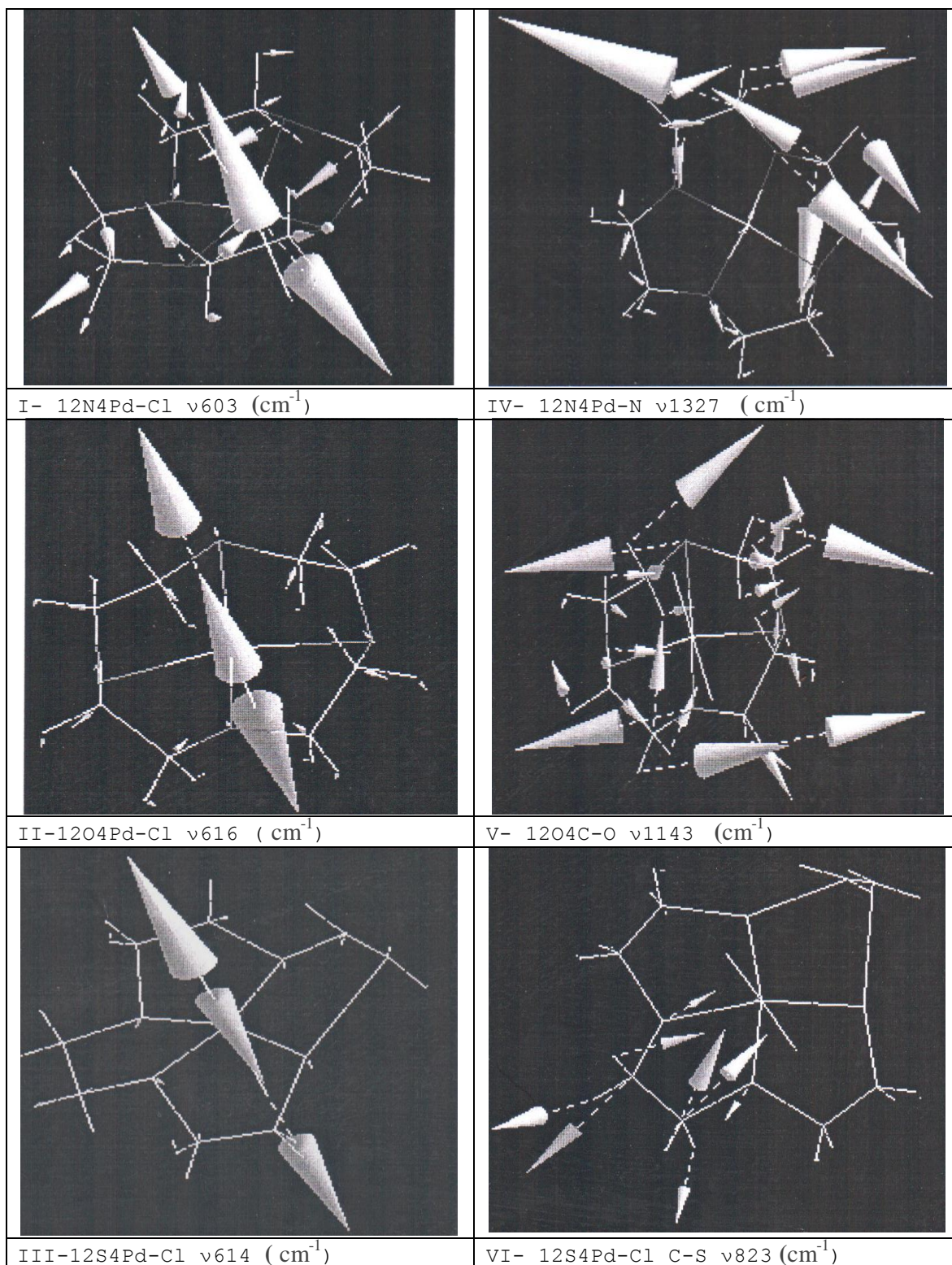


Figure 5(c): IR modes of stretching vibrations ( $\text{cm}^{-1}$ ) of 12N4, 12O4 and 12S4 crown ether complexes

### Conclusion

The *ab initio* study of crown ethers and their integrated compounds showed that the ligands! 12N4 and 12N2S2 was unstable molecules among the six ligands in gas phase. The

potential energy surface of these six ligands pointed to a spectacular change in electron density of 12O4 when nitrogen or sulfur atoms replaced the oxygen atoms. This change gave the 12N4 and 12S4 ligands a similar ion selectivity.

The six ligands behave in a different manner in the aqueous phase. In general the Co and Eu complexes are less stable than the others metal ions. The IR spectra showed that Pd-N stretching, Pd-O stretching, and Pd-S stretching have a similar values in the 12N4, 12O4 and 12S4 respectively. The results of this study agree with many studies in this field [46 -48].

## References

1. Toner, J.L., **1989**. *Crown Ethers and Analogs* (Eds S. Patai and Z. Rappoport), John Wiley and Sons, London P.79.
2. Hiroka, M., **1982**. *Crown Compounds, Their Characteristics and Application*, Vol.12; Elsevier scientific publishing Co. Amsterdam.
3. Searles, S., Jr. and Tamres M., **1976**. *The Chemistry of the Ether Linkage*, (Ed. S. Patai), John Wiley and Sons, London, P. 243.
4. Schwarzenbach, G., **1970**. Electrostatic and Non-Electrostatic Contributions to ion Association in Solution. *Pure Appl. Chem*, **24**:307-334.
5. Schwarzenbach, G. **1973**. *Chimia*, 27, 1.
6. Ho T.L., **1975**. *Chem. Rev.*, 75, 1, Ho T. L. **1977**, *Hard and Soft Acids and Bases Principle in Organic Chemistry*. Academic Press, New York, San Francisco-London.
7. Frensdorff, H. K., **1971**. *Stability Constants of Cyclic Polyether Complexes with Univalent Cations*, *J. Amer. Chem. Soc.*, **93**:600-606.
8. Glass, R. S.; Wilson G. S. and Setzer, W. N. **1980**. *Crystal and Molecular Structure of 1,4,7,-Triithiacyclononane*. *J. Am., Chern. Soc.* **102**:5068-5069.
9. DeSimone, R. E. and Click, M. D. **1976**. Structure of the Macrocyclic Polythiaether 1,4,8,11-Tetrathiacyclotradecar and Implications for Transition-Metal Chemistry (762-767), *J. Am. Chem. Soc.* **98**:762-767.
10. Dally, N. K.; Smith, S. J.; Larson, S. B.; Matheson, K. L.; Christensen, J. J. and Izatt, R. M. **1975**. x-Ray Crystal Structures of Three Cyclic Thioethers, *J. Chem. Soc., Chem. Commun.*:84-85.
11. Dally, N. K.; Smith, S. J.; Larson, S. B.; Matheson, K.; Izatt, R. M. and Christensen J. J., **1981**. The Crystal Structures of 10-Oxa-1,4,7-triliniacyclodecane, 7,10,13-Trioxa-1,4 dithiacyclooctadecane(1)" *J. Heterocyclic Chem.* **18**:463-466.
12. DeSimone R. E. and Click, M. D. **1975**. Structures of Macrocyclic Poly Thiaether 1,4,8,11- Tetrathiacyclotetradecane and Implications for Transition-Metal Chemistry, *J. Am. Chem. Soc.* **97**:942-943.
13. DeSimone R. E. and Tighe, T.M. **1976**. Complexes of Niobium Pentachloride with Cyclic Polythiaethers. *J. Inorg. Nucl. Chem.* **38**:1623-1625.
14. Dally, N. K.; Larson, S. B. **1975**. The Structure of N, N<sup>1</sup>-Ethylenebis [(2-hydroxy-1-naphthyl) methaniminato] nickel (II), *Acta Crystallogr* **B37**:84-88.
15. Goldberg, **1980**. *Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulfur Analogue*, S. Patai, Ed. Wiley: New York, Part 1, Suppl. E. p 175-214.
16. Izatt, R. M. and Christensen J. J., **1978**. *Synthetic Multidentate Macrocyclic Compounds*, Ed.; Academic Press: New York, N. K. Dalley, " Structural Studies of Synthetic Macrocyclic Molecules and their Action Complexes " , p 207-243.
17. Pullman, A.; Giessner-Prettre C. and Kruglyak, Yu. V. **1975**. Cation Binding to Crown Ethers-AB-Initio-Model Study, *Chem. Phys. Lett.*, **35**:156-160.
18. Kitaura, K. and Morokuma, K. **1976**. A new Energy Decomposition Scheme for Molecular Interactions within the Hartree-Fock-Approximation. *Int. J. Quant. Chem.*, **10**:325-340.
19. Kollman P.A., **1978**. Theoretical studies of the K<sup>+</sup> Affinities of Bases A comparison of K<sup>+</sup> and Li<sup>+</sup> Affinities, *Chem. Phys. Lett.*, **55** P.555-559.
20. Berthod H. and Pullman, A. **1980**. On The Affinities of Ammonia and Water for Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>. *Chem. Phys. Lett.*, **70**:434-437.
21. Yamabe T.; Hori, K. Akagi K; and Fukkui, K. **1979**. Stability of Crown Ether complexes I A MO Theoretical Study. *Tetrahedron*, **35**:1065-1072.
22. Hori, K.; Yamada H. and Yamabe, T. **1983**. Theoretical Study on the Nature of the Interaction between Crown Ethers and Alkali Cations. *Tetrahedron*, **39**:67-73.
23. Wiberg, K. B. **1965**. A Scheme for Strain Energy Minimization Application to Cycloalanes. *J. Am. Chem. Soc.*, **87**:1070-1078.
24. Bovill, M.J.; Chadwick D.J. and Sutherland, I.O. **1980**. Molecular Mechanics Calculations for Ethers the conformation of



- some Crown ether and the Structure of the complex of 18-crown-6 with Benzylammonium Thiocyanate. *J. Chem. Soc. Perkin-Trans II* :1529-1543.
25. Thompson ,M.A. **1995**. *J. Phys. Chem.*, **99**:4794-4804.
  26. Anet,F.A.L.; Krane,J.; Dale, J.; Daasvatn, K. and Kristiansen, P.O. **1973**. The conformation of 1,4,7,10,-Tetraoxacgclodeane and it's 1:1 Lithum Salt Complexes. *Acta. Chem. Scand.*,**27**:3395-3402.
  27. Bartsch R. A. and Carsky, P. **1980**. Complexation of Arenediazoniumlons by Crown Ethers: A CNDO/2 Study. *J. Org. Chem.*, **45**:4782-4784.
  28. a: Z. Li, J. Ni, Xu G. and Ren, J. **1985**, "New Frontiers in Rare Earth Science Applications", Proceedings of International Conference on Rare Earth Developments and pplications (Eds G. Xu and J. Xiao). Vol. I. Scientific Press, p. 293- 295.
  29. b: Z. Li, J. Ni, Xu G. and Ren,J.**1986**. *Kexue Tongbao(ForeignLang.Ed.)*,31, 956.
  30. Lao,K.; Tian, A Van. G.; and Liu H. **1986**. Simulated ab initio Molecular Orbital Calculation of Crown Ethers, *J. Mol. Sci. (Int. Ed.)*, **4**:333-341.
  31. Seidl,E.T.; Schaefer.H.F., **1991**. III, Anew configuration of 12- crown 4, *J. Phys. Chem.*, **95**:3589-3590.
  32. Anderson W.P.; Behm P. ;Glennon,T.M.; Graves S.H. and Zerner Prepr M.C., **1997**. Quantum Mechanic and Molecular Mechanics Studies of the Law Energy Conformations of 9-crown -3 , *Am. Chem. Soc., Div. Pet. Chem.*, **37**(2):1920-1926.
  33. Anderson,W.P.; Behm P. and Glennon T.M. **1997**. Quantum Mechanics and Molecula Mechanics Studies of the Low-Energy Conformations of 9-Crown -3. , *Phys.Chem. A*, **101**:1920-1926.
  34. Millar J.S. and Caulton, K.G. **1975**. Intramolecular Rearrangements of M (bidentate Phosphine)<sub>2</sub> X Y Species, *J. Am. Chem. Soc.*,**97**(5):1067-1073.
  35. Hehre W. J.; Stewart R. F.; and Pople J. A. **1969**. Self- Consistent Molecular-Orbital Methods. 1. Use of Gaussian Expansions of Slater. Type Atomic Orbitals, *J. Chem. Phys.*, **51**:2657-2664
  36. Collins, J. B.; Schleyer,P.V.; Binkley J. S. and Pople,J. A. **1976**. Self-Consistent Molecular Orbital Methods, XVII. Geometries and Binding Energies of Second-row Molecules. A comparison of Three Basis Sets. *Chem. Phys.*, **64**:5142-5149.
  37. Stewart R. F., **1970**. Small Gaussian Expansions of Slater-Type Orbitals, *J. Chem. Phys.*,**52**:431-438.
  38. Hehre, W.; Ditchfield,J R.; and Pople J. A. **1976**. Self-Consistent Molecular Orbital Methods, XII. Further Extensions of Gaussian-Type Bassis Sets for Use in Molecular Orbital Studies of Organic Molecules, *J. Chem. Phys.*,**56**,P.2257-2261.
  39. Hariharan P. C. and Pople,J. A. **1973**. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies, *Theoret. Chem. Acta*, **28**:213-222.
  40. Moeller C. and Plesset ,M. S. **1934**. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.*, **46**:618-622.
  41. Head-Gordon M.; Pople J. A. and Frisch M. J. **1988**. MP<sub>2</sub> Energy Evaluation by Dircet Methods, *Chem. Phys. Lett.*, **153**:503-506.
  42. Gordon,M. S. **1980**. The Isomers of Silacyclopropane. *Chem. Phys. Lett.*, **76**:163-168.
  43. HyperChem ,**2005**. 7.52, ,Hypercube, Inc., 1 1 15 NW 4<sup>1</sup>" Street,Gainesville, FL 3260! USA,e-mail:info@hvper.com(Licensed copy).
  44. Dewar M. J. S. *et al* ,**1985**. The Development and use of Quantum-Mechanical Molecular-Models. 76. AMI. A new General Purpose Quantum-Mechanical Molecular-Model, *J. Am. Chem. Soc.*,**107**:3902-3909.
  45. Skwartz ,J. J. P. **1989**.7. *Comp. Chem.*. 110, 209.
  46. Allinger, N. L. **1991**. special contribution to HyperCube. MM2.
  47. Janickis V, **2007**. Synthesis and Crystal Structure of Novel Selected Bromochal cogenates (IV/I). *CHEMIJA*. **18**(1):28-35.
  48. Gaballa A. S. 1 ; Teleb S.M. 2 ; Elmosallamy A.Eldin and El-Metwally N. 2, **2005**. Spectroscopic Studies on Charge-transfer Complexes of Hexamethyl- enetetramine with Some II-Electron Acceptors. *J. Appl. Sci*:**7**(2):27-37.
  49. Abed G.M.**2008**. Preparation , Study and Theoretical Treatment of some Transition Complexes with Shiff Bases Derivative from Amino Acid, M.Sc. Thesis Baghdad University.