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REGULAR ARTICLE

# Conformational study of the structure of free 12-thiacrown-4 and some of its cation metal complexes

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**Abstract** Conformational search of 12-thiacrown-4, 12t4, was performed using the CONFLEX method and the MMFF94S force field whereby 156 conformations were predicted. Optimized geometries of the 156 predicted conformations were calculated at the HF, B3LYP, CAM-B3LYP, M06, M06L, M062x and M06HF levels using the 6-311G** basis set. The correlation energy was recovered at the MP2 level using the same 6-311G** basis set. Optimized geometries at the MP2/6-311G** level and G3MP2 energies were calculated for some of the low energy conformations. The $D_4$ conformation was predicted to be the ground state conformation at all levels of theory considered in this work. Comparison between the dihedral angles of the predicted conformations indicated that for the stability of 12t4, a SCCS dihedral angle of 180° requirement is more important than a gauche CSCC dihedral angle requirement. Conformational search was performed also for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes using the CONFLEX method and the CAChe-augmented MM3 and MMFF94S force fields. Conformations with relative energies less than 10 kcal/mol at the MP2/6-31+G*//HF/6-31+G* level, with double zeta quality basis set on the metal cations, were considered for computations at the same levels as those used for free 12t4, using also the 6-311G** basis set. The cc-pVTZ-pp basis set was used for the metal cations. The predicted ground state conformations of the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes are the $C_4$, $C_4$, $C_4$, $C_{2v}$ and $C_4$ conformations, respectively. This is in agreement with the experimental X-ray data for the 12t4–$Ag^+$ and $Cd^{2+}$ cation metal complexes, but experimentally by X-ray, the 12t4–$Bi^{3+}$ and $Cu^+$ cation metal complexes have $C_s$ and $C_4$ structures, respectively.

**Keywords** 12-thiacrown-4 · Metal complexes · Conformational analysis · Crown ethers · DFT functionals

## 1 Introduction

Since their discovery by Pedersen in 1967 [1, 2], there was much interest in the chemistry of crown ethers. This interest is due to their outstanding ability to form complexes selectively with different metal ions. As a result, crown ethers have been used in a quite variety of applications. The most important crown ethers are 12-crown-4 (12c4) and 18-crown-6 (18c6). Similar and interesting molecules can be obtained by replacing the oxygen atoms of crown ether with sulphur, called thiacrown, or nitrogen, called azacrown, atoms.

Our objective is the study of the vibrational spectra of crown ethers and their metal complexes. Crown ethers are large ring flexible molecules and may exist in large number of conformations. Therefore, a conformational study to predict the possible conformations of the considered crown ether has to be performed first. In two previous publications, conformational analysis was reported for free 12c4 [3] and free 18c6 [4], and in a third publication for 12c4–alkali metal cation complexes [5]. In the conformational

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analysis in these three reports [3–5], the efficient CONFLEX method for the conformational search of cyclic molecules implemented in the CAChe program was used [6–10]. In the conformational analysis of free 12c4 [3], the study confirmed the previous reports [11–13] that the $S_4$ conformation of 12c4 is the ground state conformation and this $S_4$ conformation is more stable than the experimentally known $C_i$ conformation. Vibrational study of free 12c4 [14] concluded that free 12c4 exists in the solid, liquid and considered solution phases conclusively in the $C_i$ conformation. Previous studies showed that free 12c4 undergoes rapid interconversion between the $C_i$ and $C_4$ conformations [15]. For 12c4–alkali metal cation complexes, the combined conformational and vibrational study concluded that 12c4–alkali metal cation complexes exist in the $C_4$ conformation [5, 16]. This with the exception of the 12c4–$Li^+$ complex which may exist in the $C_4$ or $C_s$ conformation. These findings were later supported by IR predissociation spectroscopy study of argon-tagged gas-phase 12c4–alkali metal cation complexes [17].

The aim of the current report is to perform a detailed conformational study of the sulphur analogue of 12c4, 12t4 and some of its cation metal complexes. This study is necessary for the subsequent study of the vibrational spectra of free 12t4 and its cation metal complexes. To the best of our knowledge, there are no previous vibrational studies of free 12t4 or its cation metal complexes. However, it is known experimentally by X-ray that free 12t4 exists in the $D_4$ conformation [18, 19]. Different symmetries were reported, also experimentally by X-ray, for the 12t4–cation metal complexes depending on the metal cation as will be discussed in the results and discussion section. There are a few previous conformational analysis reports of free 12t4 [20–23]. Hill and Feller [20] used molecular dynamics simulation at high temperature to predict the low-lying conformations of 9-thiacrown-3, 9t3, 12t4, 15-thiacrown-5, 15t5, and 18-thiacrown-6, 18t6. Five conformations of the lowest relative MM/CVFF energy of about 2 kcal/mol of 12t4 were considered for further ab initio computations. The ab initio computations were done at the MP2/aug-cc-pVDZ level. The ground state predicted conformation was the experimentally known $D_4$ conformation. Bultinck et al. [21] used a combination of Monte Carlo analysis and systematic search to perform conformational analysis of 12t4. Conformations with relative energy less than 8 kcal/mol were considered for computations at the HF/6-31G** level. Similar to what was predicted in Ref. [20], the $D_4$ conformation was predicted to be the ground state conformation. 9t3 was also the subject of a few conformational analysis studies [20, 22, 23].

Our experience with free 12c4, free 18c6 and 12c4–alkali metal cation complexes [3–5] has shown that a more detailed conformational study at a higher level of theory than that reported in Refs. [20] and [21] is required for an accurate and thorough vibrational study of free 12t4 and its cation metal complexes. A conformational study of the smaller 12t4 and its cation metal complexes can also be used as a guide for the conformational study of the larger 18t6 and its cation metal complexes. Such a study is useful to understand the structure of both molecules and what the factors that affect their conformational stability are.

12t4 is known also as 1,4,7,10-tetrathiacyclododecane or 12-thiacrown-4 or tetrathia-12-crown-4 or [12]ane$S_4$ or $(CH_2CH_2S)_4$ and abbreviated as 12t4 or 12S4. The conformational and vibrational analysis of free 12c4 and free 12t4 is probably quite similar to the structural and vibrational study of furan and thiophene [24, 25]. This study has concluded that the B3LYP method performs poorly for the sulphur atom–containing molecules, and a correlated level as the MP2 level should be used [24–29].

It might be significant here to point out some of the differences between 12c4 and 12t4. In the former, the hydrogen bond is one of the main factors that affects the conformational stability which is absent in the later. Consequently, free 12c4 adopts an endodentate structure, with the oxygen atoms pointing towards the ring centre, while free 12t4 with the larger sulphur atoms adopts an exodentate structure [18, 19] with the sulphur atoms pointing away from the ring centre. In the conformational analysis report of free 12c4, comparison between the geometries of the different predicted conformations revealed that the $S_4$ conformation has more hydrogen bonds and at distances shorter than any of the other predicted conformations of free 12c4 [3]. In addition, 12c4 prefers to form complexes with alkali and alkaline earth metal cations, whereas 12t4 prefers to form complexes with transition metal cations such as the $Cu^{2+}$, $Cd^{2+}$, $Pd^{2+}$, $Ru^+$ and $Ru^{2+}$ metal cations. These differences should guide our study in the conformational and vibrational analysis of 12t4.

## 2 Computational details

There are few methods to predict the possible conformations of a given molecule [30]. The simplest method is the systematic, also called the grid, search. In this method, bonds are rotated by 360° in increments. The number of generated conformations depends on the number of rotatable bonds and the angle increment size. Although this method is simple and efficient to span all the possible conformational space, it has major disadvantages. Large number of rotatable bonds and smaller rotational increments can generate an unaffordable number of conformations making calculations impossible. Also, large rotational increments may overlook some conformations. The second method is the random, also called the Monte Carlo or stochastic, search method. This method is to avoid the large possible number of conformations in the systematic method. There are two ways to implement the random method. The first is through the random change in the molecular Cartesian coordinates and the second is through the random change in the dihedral angles. The generated structures, if they correspond to new conformations, are stored and subjected to the process of random change. The search ends when no new conformations are located or every located conformation is located a certain number of times. For ring molecules, a check has to be made for ring closure requirements. The third method is the molecular dynamics method. This method depends on using high temperature to overcome the energy barriers between different conformations and to ensure that the search is not stuck in a local minimum conformation on the potential energy surface. The fourth method is the distance geometry method where a distance matrix between the atoms is formed. Distances are changed randomly between certain high and low limits. The high and low limits are set to ensure that a reasonable structure is obtained. The fifth method is the CONFLEX method. This method is to avoid the ring closure requirement for cyclic molecules. In this method, starting from an initial geometry, perturbed conformations are generated by corner flap, edge flip and stepwise rotation. Corner flap generates new conformations by motion of corner ring-atoms to the other side of the plane. Corner flip generates new conformations by flipping ring bonds. Stepwise rotation generates new conformations by stepwise rotations of bonds. This stepwise rotation is for the acyclic part of the molecule. The rotation angles are typically 120° and −120°. Each of the generated conformations is also used an initial conformation and subjected to perturbation, until no new conformations are generated.

In order to know whether a generated structures corresponds to a new conformation, optimized geometry of the predicted conformations has to be located at a certain level of theory. A fast method to calculate the optimized geometries is used, as computations at the ab initio level can be unaffordable and result in a slow conformational search. The optimized geometry is usually calculated at the molecular mechanics (MM) level with the different MM force fields available. Before the end of the search, vibrational frequencies of the generated structures are calculated and conformations with imaginary vibrational frequencies are excluded. After the end of the conformational search, the stored geometries of the predicted conformations may be used to perform computations at the required level of theory.

Contrary to the conformational search of free 12c4 [3] and free 18c6 [4] where the conformational search was done using the CAChe program [6–10], prediction of the initial conformations of free 12t4 was performed using the CONFLEX program [6–9, 31]. In both programs, the CONFLEX conformational search method was used, but in the CAChe program, the CAChe-augmented MM3 force field was used, whereas the CONFLEX program uses the MMFF94S force field [32]. The number of predicted conformations of free 12t4 was 156 conformations. This is compared to 180 conformations predicted for free 12c4 [3].

To get a better estimate of the energy order of the predicted conformations of free 12t4, optimized geometries were calculated for all of the 156 predicted conformations at the HF, B3LYP, CAM-B3LYP, M06, M06L, M062x and M06HF levels using the 6-311G** basis set with the correlation energy recovered at the MP2 level using also the 6-311G** basis set. The latter calculations, for example at the HF level, are termed the MP2/6-31G**//HF/6-31G** level. In addition, to compare between the conformations predicted in this report and those predicted in Ref. [21], optimized geometries were calculated at the HF/6-31G** level with the correlation energy recovered at the MP2 level. Optimized geometries were also calculated at the MP2/6-311G** level for conformations with relative energy less than 7 kcal/mol, according to the MP2/6-311G**//B3LYP/6-311G** energy and for all other conformations with symmetry higher than the $C_1$ symmetry for a total of 41 conformations. To probe the accuracy of the energy order at the different levels of theory considered in this work, G3MP2 energies were calculated for the 20 lowest energy conformations, according to the MP2/6-311G** energy.

For the 12t4–cation metal complexes, conformational search was performed for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes. Since MM force field is not available for most of these metal cations in the CONFLEX program, conformational search of some of the 12t4–cation metal complexes was tried for metal cations for which force field is available as the $Zn^{2+}$, $Cu^+$ and $Co^{2+}$ cations. 9 conformations were predicted for these complexes which had similar structures. Consequently, conformations of the 12t4–cation metal complexes considered in the present work were constructed similar to these 9 conformations. Conformational search was performed with the CAChe program. This resulted in 69 predicted conformations. Conformations were also constructed with the $Cu^+$ cation and in separate calculations with the $Ag^+$ cation positioned about 4.0 Å above the ring plane for the 156 predicted conformations of free 12t4. Geometry optimization was performed for these conformations using the HF/6-31+G* basis set for the C, S and H atoms and the Hay and Wadt's effective core potential valence basis set for the $Ag^+$ and $Cu^+$ cations [33]. This basis set will be referred hereafter as the 6-31+G* basis set. The predicted conformations with this method were of high relative energy, more than 10 kcal/mol, for both the

Cu$^+$ and Ag$^+$ complexes, and these computations were also quite time demanding. These computations were then not tried for the other metal cations. In addition, using the optimized structures of 12t4–cation metal complexes which had relative energies of less than 10 kcal/mol for one metal cation complex, conformations were constructed for the other metal cation complexes by replacing the metal cation with each of the other four metal cations. Optimized energies and vibrational frequencies were calculated at the HF/6-31+G* level, and conformations with imaginary vibrational frequencies were excluded. For the Bi$^{3+}$, Cd$^{2+}$ and Sb$^{3+}$ cations, the cc-pVDZ-pp basis set obtained from EMSL was used [34–36].

Further computations of the predicted conformations were performed for conformations of relative energy higher than 10 kcal/mol from the corresponding lowest energy conformation. These further computations were done at the HF, B3LYP, CAM-B3LYP, M06, M06L, M062x, M06HF and MP2 levels using the 6-311G** basis set for the S, C and H atoms and the cc-pVTZ-pp basis set [34, 35] for the metal cations. This basis set will be referred hereafter as the 6-311G** basis set. The correlation energy was calculated also at the MP2 level at the HF, B3LYP, CAM-B3LYP, M06, M06L, M062x and M06HF optimized geometries. The number of basis functions with the 6-31+G*/6-311G** basis sets for the 12t4–Ag$^+$ and Cu$^+$ complexes are 286/407, for the 12t4–Bi$^{3+}$/Sb$^{3+}$ complexes are 287/383 and for the 12t4–Cd$^{2+}$ complex are 302/407 basis functions.

All the ab initio computations were performed using the Gaussian 03 and Gaussian 09 suite of programs [37, 38]. Geometry optimization at any level for a given conformation was started from that determined by the CONFLEX or CAChe programs. The MP2 calculations were done with the fixed core option for the inner electrons.

## 3 Results and discussion

Table S1, for space reasons provided as supplementary material, lists the relative energies, with respect to the ground state conformation, conformation **1** of $D_4$ symmetry, hereafter the $D_4$ conformation of free 12t4, of the 156 predicted conformations of free 12t4. Only conformations considered for calculation at the G3MP2 level are listed in Table 1. Conformation **124** had the same energy as conformation **25** at most of the levels considered in this work and therefore was excluded from computations at the G3MP2 level. Each conformation in Tables 1 and S1 is given a number according to the MMFF94S energy order and is typed in bold face. Conformation number of the predicted conformations in Ref. [21] is added in Table S1 at the corresponding conformation predicted in the current work. Only six conformations were predicted in the

**Table 1** Relative energies of free 12t4, in kcal/mol, using the 6-311G** basis set

| No. | Sym | MM | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $D_4$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2** | $C_1$ | 2.18 | 6.52 | 6.68 | 6.24 | 6.03 | 5.14 | 4.63 | 3.83 |
| **3** | $C_2$ | 2.39 | 5.50 | 5.54 | 5.36 | 5.31 | 5.27 | 4.68 | 4.40 |
| **5** | $C_1$ | 2.62 | 3.96 | 3.84 | 3.55 | 3.18 | 2.63 | 2.04 | 1.62 |
| **6** | $C_2$ | 2.82 | 2.30 | 1.88 | 2.09 | 1.40 | ftc | ftc | 1.87 |
| **7** | $C_2$ | 3.07 | 4.78 | 5.13 | 4.76 | 5.11 | 4.77 | 3.73 | 2.69 |
| **9** | $C_{2h}$ | 3.14 | 2.63 | 2.14 | 2.50 | 2.23 | 2.76 | 2.68 | 2.81 |
| **11** | $C_1$ | 3.27 | 6.34 | 6.12 | 5.89 | 5.38 | 4.38 | 4.23 | 4.14 |
| **12** | $C_1$ | 3.52 | 6.97 | 6.94 | 6.50 | 5.28 | 4.52 | 4.67 | 4.73 |
| **13** | $C_1$ | 3.55 | **10** | **10** | 5.40 | 5.20 | 4.36 | 3.98 | 3.14 |
| **25** | $C_1$ | 4.40 | 5.79 | 5.63 | 5.46 | 5.23 | 4.86 | 4.30 | 4.20 |
| **33** | $C_1$ | 4.56 | 7.05 | 6.67 | 6.48 | 5.83 | 5.24 | 5.03 | 4.90 |
| **35** | $C_1$ | 4.70 | 5.69 | 5.03 | 5.07 | 4.72 | 4.28 | 4.08 | 3.72 |
| **38** | $C_1$ | 4.82 | **8** | 9.31 | 7.11 | 6.85 | 5.59 | 5.04 | 3.88 |
| **43** | $C_s$ | 5.05 | 5.64 | 4.91 | 5.09 | 4.96 | 4.93 | 5.01 | 5.29 |
| **52** | $S_4$ | 5.22 | 5.56 | 4.87 | 5.08 | 4.20 | 3.36 | 3.66 | 4.19 |
| **54** | $C_1$ | 5.32 | 7.37 | 7.13 | 6.80 | 6.35 | 5.50 | 5.02 | 4.21 |
| **58** | $C_1$ | 5.51 | 6.87 | 6.35 | 6.22 | 5.48 | 4.92 | 5.15 | 5.87 |
| **67** | $C_2$ | 5.90 | 7.35 | 6.67 | 6.46 | 5.93 | 5.17 | 5.45 | 5.41 |
| **124** | $C_1$ | 10.01 | **25** | **25** | 5.46 | 5.23 | 4.86 | 5.71 | 4.82 |
| **MAD** | | 0.68 | 1.55 | 1.39 | 1.14 | 0.68 | 0.41 | 0.39 | 0.64 |

**Table 1** continued

| No. | MP2//HF | MP2//B3LYP | MP2//CAM | MP2//M06 | MP2//M06L | MP2//M062x | MP2//M06HF | MP2 | G3MP2 |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **2** | 6.37 | 6.28 | 6.23 | 6.34 | 6.26 | 6.18 | 6.29 | 6.12 | 4.54 |
| **3** | 6.59 | 6.60 | 6.65 | 6.82 | 6.80 | 6.71 | 6.79 | 6.69 | 3.82 |
| **5** | 3.61 | 3.57 | 3.39 | 3.42 | 3.18 | 3.20 | 3.28 | 3.08 | 2.70 |
| **6** | 2.22 | 2.20 | 2.15 | 2.07 | ftc | ftc | 2.15 | 1.97 | 1.74 |
| **7** | 5.01 | 5.07 | 4.90 | 4.93 | 4.90 | 4.80 | 4.80 | 4.74 | 4.08 |
| **9** | 2.92 | 2.92 | 2.96 | 2.98 | 2.90 | 2.92 | 3.10 | 2.94 | 2.29 |
| **11** | 6.15 | 5.95 | 5.83 | 5.95 | 5.68 | 5.66 | 5.75 | 5.55 | 4.47 |
| **12** | 6.45 | 6.33 | 6.16 | 6.14 | 5.97 | 5.94 | 6.02 | 5.89 | 4.32 |
| **13** | **10** | **10** | 5.67 | 5.65 | 5.53 | 5.49 | 5.65 | 5.42 | 3.93 |
| **25** | 5.57 | 5.57 | 5.44 | 5.41 | 5.24 | 5.28 | 5.36 | 5.19 | 4.50 |
| **33** | 6.50 | 6.75 | 6.45 | 6.85 | 6.31 | 6.32 | 6.35 | 6.16 | 5.32 |
| **35** | 6.00 | 5.93 | 6.01 | 5.89 | 5.77 | 5.44 | 5.53 | 5.37 | 4.35 |
| **38** | **8** | 9.85 | 6.82 | 6.92 | 6.78 | 6.69 | 6.80 | 6.65 | 5.11 |
| **43** | 6.24 | 6.12 | 6.21 | 6.35 | 6.28 | 6.35 | 6.50 | 6.24 | 4.74 |
| **52** | 5.09 | 5.18 | 4.90 | 5.06 | 4.66 | 4.58 | 4.67 | 4.54 | 4.41 |
| **54** | 6.32 | 6.16 | 6.06 | 6.06 | 6.02 | 5.92 | 5.98 | 5.85 | 5.26 |
| **58** | 6.57 | 6.45 | 6.49 | 6.61 | 6.56 | 6.59 | 6.73 | 6.44 | 4.52 |
| **67** | 6.84 | 6.58 | 6.57 | 6.61 | 6.51 | 6.56 | 6.68 | 6.43 | 5.31 |
| **124** | **25** | **25** | 5.43 | 5.41 | 5.24 | 6.56 | 7.01 | 6.43 | 4.50 |
| **MAD** | 1.42 | 1.52 | 1.28 | 1.34 | 1.25 | 1.28 | 1.34 | 1.15 | 0.00 |

No is the conformational number, sym stands for symmetry, MM stands for the MMFF94S force field, CAM for the CAM-B3LYP functional, and MP2//HF stands for the MP2/6-311G**//HF/6-311G** level. For conformation **1**, the energy at the HF level is −1,902.464754, at the MP2//HF level is −1,904.204534, at the B3LYP level is −1,907.43588, at the MP2//B3LYP level is −1,904.20476, at the CAM-B3LYP level is −1,907.21243, at the MP2//CAM-B3LYP level is −1,904.207049, at the M06 level is −1,907.04250, at the MP2//M06 level is −1,904.20760, at the M06HF level is −1,907.27372, at the MP2//M06HF level is −1,904.20743, at the M06L level is −1,907.29622, at the MP2//M06L level is −1,904.20782, at the M062x level is −1,907.15478, at the MP2//M062x level is −1,904.20787, at the MP2 level is −1,904.20827 and at the G3MP2 level is −1,904.89144 au. The number given instead of the energy difference is the conformational number to which conformation converges to. Relative energy of conformation **13** at the HF, MP2//HF, B3LYP and MP2//B3LYP levels is 5.78, 5.82, 5.61 and 5.70 kcal/mol, respectively. Relative energy of conformation **38** at the HF and MP2//HF levels is 7.40 and 7.07 kcal/mol, respectively. Relative energy of conformation **124** at the HF, MP2//HF, B3LYP and MP2//B3LYP levels is 5.79, 5.57, 5.63 and 5.57 kcal/mol, respectively. ftc stands for failed to converge after a specified number of iterations. MAD stands for the mean absolute deviation. MAD is calculated excluding conformation **1**

conformational search reported in Ref. [20], and these were also predicted in the conformational search reported in Ref. [21]. Therefore, no reference will be made to these conformations unless otherwise significant. The structure of the 10 lowest energy conformations, according to the MP2/6-311G**//B3LYP/6-311G** energy, of free 12t4 is depicted in Fig. 1. Conformation **124** was excluded from Fig. 1 as was explained before since it has the same energy as conformation **25** at most of the levels considered in this work. Table 2 lists the structure of the $D_4$ conformation of free 12t4, for various levels of theory and also the reported experimental structures [18, 19]. Table S2 lists the calculated geometry of the lowest energy $D_4$ conformation at all levels considered in this work. Figure 2 shows the atom numbering of the $D_4$ conformation of free 12t4.

Table S3 lists the relative energies of all predicted conformations of the 12t4–Ag$^+$, Bi$^{3+}$, Cd$^{2+}$, Cu$^+$ and Sb$^{3+}$ cation metal complexes at the HF/6-3+1G* and MP2/6-3+1G*//HF/6-3+1G* levels. The number of predicted conformations of the 12t4–Ag$^+$ and 12t4–Cu$^+$ complexes is significantly higher than those for the other 12t4–cation metal complexes. This is because, as was mentioned in the computational details section, conformations with the Ag$^+$ and Cu$^+$ metal cations positioned about 4 Å above the ring plane of free 12t4 were tried. This was not tried for the other cation metal complexes. Notice that most of these conformations of the 12t4–Ag$^+$ and 12t4–Cu$^+$ complexes are of high energy, higher than 10 kcal/mol and mainly of $C_1$ symmetry. Table S4 lists the energy of the ground state conformation of the 12t4–Ag$^+$, Bi$^{3+}$, Cd$^{2+}$, Cu$^+$ and Sb$^{3+}$ cation metal complexes. Tables 3, 4, 5, 6 and 7 list the relative energies, with respect to the ground state conformation as shown in Table S4, of all the predicted conformations of relative energy less than 10 kcal/mol of the 12t4–Ag$^+$, Bi$^{3+}$, Cd$^{2+}$, Cu$^+$ and Sb$^{3+}$ cation metal

**Fig. 1** Structure of the 10 lowest energy conformations of free 12t4

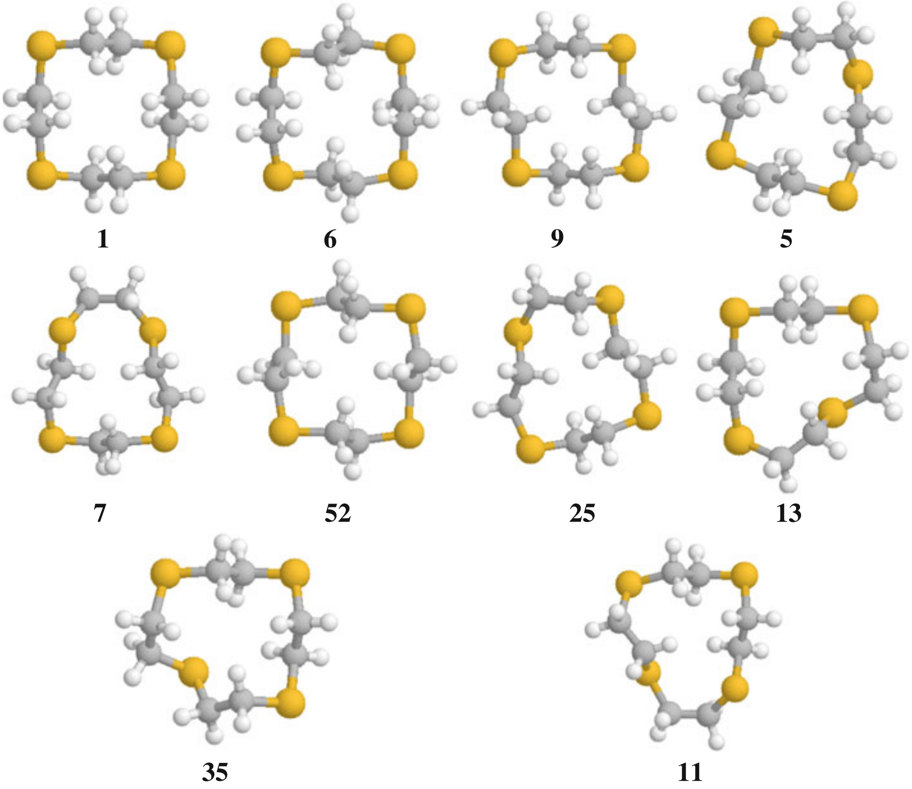

**Table 2** Geometry of the $D_4$ conformation of free 12t4, using the 6-311G** basis set

| Coordinate | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 | Exp. [18] | Exp. [19] |
|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$–$C_2$ | 1.822 | 1.843 | 1.824 | 1.828 | 1.822 | 1.823 | 1.825 | 1.816 | 1.816 | 1.816 |
| $C_2$–$C_3$ | 1.527 | 1.530 | 1.522 | 1.514 | 1.518 | 1.523 | 1.529 | 1.525 | 1.512 | 1.514 |
| $C_2$–$H_{13}$ | 1.082 | 1.093 | 1.090 | 1.094 | 1.092 | 1.091 | 1.087 | 1.094 | | |
| $C_2$–$H_{14}$ | 1.081 | 1.093 | 1.090 | 1.095 | 1.094 | 1.091 | 1.087 | 1.093 | | |
| $C_{12}S_1C_2$ | 102.3 | 101.4 | 101.2 | 99.6 | 100.1 | 100.3 | 100.2 | 99.8 | 101.3 | 101.2 |
| $S_1C_2C_3$ | 114.0 | 113.9 | 113.8 | 113.3 | 113.4 | 113.2 | 112.7 | 113.2 | 113.8 | 113.3 |
| $S_1C_2H_{13}$ | 105.2 | 105.1 | 105.3 | 105.6 | 105.6 | 105.6 | 105.8 | 106.0 | | |
| $C_3C_2H_{13}$ | 109.9 | 110.3 | 110.2 | 110.2 | 110.5 | 110.0 | 109.4 | 109.7 | | |
| $S_1C_2H_{14}$ | 109.0 | 108.9 | 109.0 | 109.0 | 109.1 | 109.1 | 109.3 | 109.5 | | |
| $C_3C_2H_{14}$ | 111.6 | 111.5 | 111.5 | 111.7 | 111.6 | 111.7 | 111.7 | 111.4 | | |
| $S_1C_2C_3S_4$ | 172.3 | 173.2 | 173.5 | 175.3 | 174.8 | 174.7 | 174.9 | 175.4 | 173.4 | 173.6 |
| $C_2C_3S_4C_5$ | 72.0 | 72.2 | 72.2 | 72.4 | 72.3 | 72.2 | 72.1 | 72.2 | 72.2 | 72.1 |
| $C_{12}S_1C_2H_{13}$ | 167.5 | 166.9 | 167.1 | 166.9 | 166.6 | 167.4 | 168.4 | 167.6 | | |
| $S_4C_3C_2H_{13}$ | −69.9 | −68.8 | −68.5 | −66.6 | −66.9 | −67.5 | −67.7 | −66.5 | | |
| $C_{12}S_1C_2H_{14}$ | 53.4 | 52.9 | 53.0 | 52.7 | 52.8 | 52.9 | 52.8 | 52.7 | | |
| $S_4C_3C_2H_{14}$ | 48.2 | 49.5 | 49.6 | 51.7 | 51.1 | 51.0 | 51.4 | 51.5 | | |

Bond lengths in Å and angles in degrees. Atom numbering is according to Fig. 2. Values of each coordinate reported in Refs. [18] and [19] are calculated as the average of these coordinates in the CSD, hits FOPCAO and FOPCA001, respectively. CAM stands for the CAM-B3LYP functional

complexes, respectively. Each conformation of a given complex is given a number typed in bold face according to its energy order at the MP2/6-311G** level. Figures 3, 4, 5, 6 and 7 depict the structures of the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes, respectively, of relative energy less than 10 kcal/mol.

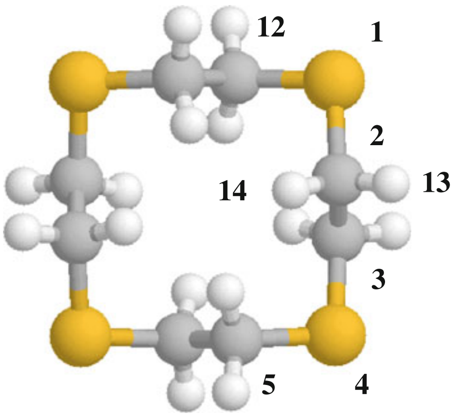

**Fig. 2** Atom numbering of the $D_4$ conformation of free 12t4

## 3.1 Structure and CDB

Search in the Cambridge Structure Database (version 5.29, Nov. 2007) of the 12t4 backbone yielded 39 hits. Two hits correspond to free 12t4 with CDB codes FOPCAO [18] and FOPCA001 [19]. Both structures are consistent with $D_4$ conformation of free 12t4. The $D_4$ conformation is found also in the $Sn^{4+}$ complex, hit AQARAL [39], in the $Al^{3+}$ complex, hit GAJLOS [40], $I_2$ complex, hits LINHEV [41] and RUKKAJ [42], and one of the $Cu^+$ complexes, hit QITZUO [43]. The $C_4$ conformation is found in the $Cu^+$ complex, hit CEFXAM [44]; this is a rather distorted $C_4$ structure, in the $Cd^{2+}$ complex, hit KEMYIL [45], in the $Pd^{2+}$ complex, hit KEXYES [46], in the $Pt^{2+}$ complex, hits PIBVUR [47] and YEFKID [48], in the $Hg^+$ complex, hit QAHNIX [49], in the $Ag^+$ complex, hit QAHNET [49], and in the $Cu^+$ complex, hits QITZAU [43] and QITZEY [43]. Hits QITZIC [43] and QITZOI [43] represent two distorted $C_4$ structures of the $Cu^+$ complex. There are two $C_s$ structures. One is found in the $Mn^{2+}$ complex, hit MEDHOS [50], and in the $Bi^{3+}$ complex, hit VOSTEC [51]. The other $C_s$ conformation is found in the $Rh^{3+}$ complex, hit LEFGEI [52], in the $Ru^+$ complex, hits LEWSIP [53], LEWWIT [53], LEWXEQ [53], LEXFOJ [53], PARWIP [53], REPJIG [54], REPJOM [55], and SEBDEJ [56], and in the $Mn^{2+}$ complex, hit MEDJAG [50]. The $C_{2v}$ structure is found in the $Ru^{2+}$ complexes, hits LEWTIQ [53], LEXGUQ [53], NIWGOP [57], NIWGUV [57], NIWHAC [57], and TALRUU [58]. The $Pd^{2+}$ complex has a $C_1$ structure, hit KUNMEL [53].

Vibrational frequencies were calculated for free 12t4 assuming the above-mentioned $C_4$, $C_{2v}$ and $C_1$ conformations and the two different $C_s$ conformations at the HF/6-31G* optimized geometry. The $C_4$, $C_{2v}$ and one of the $C_s$ conformations had one imaginary vibrational frequency, thus correspond to transition states. The other $C_s$ and $C_1$ conformations had no imaginary vibrational frequencies. The former three conformations were not predicted in the

**Table 3** Relative energies, kcal/mol, of the 12t4–$Ag^+$ cation complexes

| No.<br>Sym | 1<br>$C_4$ | 2<br>$C_s$ | 3<br>$C_{2v}$ | 4<br>$C_1$ | 5<br>$C_s$ | 6<br>$C_1$ | 7<br>$C_1$ | 8<br>$C_1$ |
|---|---|---|---|---|---|---|---|---|
| HF[a] | 0.00 | 5.69 | 3.93 | 5.68 | 2.83 | 2.27 | 11.01 | 6.69 |
| MP2//HF[a] | 0.00 | 3.89 | 3.58 | 4.66 | 2.89 | 2.13 | 9.75 | 6.18 |
| HF | 0.00 | 5.08 | 3.70 | ftc | 2.79 | ftc | 10.40 | 12.21 |
| MP2//HF | 0.00 | 2.36 | 3.02 |  | 2.97 |  | 9.73 | 13.10 |
| B3LYP | 0.00 | 1.79 | 1.63 | 3.20 | 2.39 | 3.19 | ftc | 9.96 |
| MP2//B3LYP | 0.00 | 0.63 | 1.94 | 2.51 | 2.90 | 2.53 |  | 11.33 |
| CAM | 0.00 | 1.68 | 1.88 | 3.17 | 2.62 | ftc | 7.39 | 10.23 |
| MP2//CAM | 0.00 | 0.47 | 1.99 | 2.45 | 2.91 | ftc | 7.44 | 11.39 |
| M06 | 0.00 | 2.25 | 2.55 | 3.96 | 3.09 | 9.30 | 9.07 | 12.02 |
| MP2//M06 | 0.00 | 0.71 | 2.16 | 2.61 | 2.99 | 8.02 | 7.73 | 11.81 |
| M06L | 0.00 | 1.34 | ftc | 2.36 | 2.58 | 7.53 | 7.23 | 10.88 |
| MP2//M06L | 0.00 | 0.85 |  | 2.56 | 2.88 | 7.42 | 7.43 | 11.26 |
| M062x | 0.00 | 2.47 | 3.16 | ftc | 2.69 | ftc | 8.98 | 12.23 |
| MP2//M062x | 0.00 | 1.52 | 2.40 |  | 2.89 |  | 8.14 | 11.86 |
| M06HF | 0.00 | 1.75 | 3.56 | 2.86 | 2.68 | ftc | 8.86 | 12.06 |
| MP2//M06HF | 0.00 | 0.97 | 2.31 | 2.77 | 2.95 |  | 7.89 | 11.62 |
| MP2 | 0.00 | 0.07 | 1.85 | 2.10 | 2.84 | ftc | 6.99 | 11.07 |

Sym stands for symmetry, MP2//HF stands for MP2 energy at the HF optimized geometry using the same basis set, and CAM stands for CAM-B3LYP. ftc stands for failed to converge

[a] Using the 6-31+G* basis set, see text

**Table 4** Relative energies, kcal/mol, of the 12t4–Bi$^{3+}$ cation complexes

| No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Sym | $C_4$ | $C_1$ | $C_s$ | $C_{2v}$ | $C_s$ | $C_1$ | $C_s$ |
| HF | 0.00 | 1.56 | 2.72 | 2.02 | 3.62 | 5.20 | 9.34 |
| MP2//HF | 0.00 | 2.02 | 2.85 | 3.19 | 3.95 | 5.48 | 9.28 |
| HF | 0.00 | 1.54 | 2.63 | 2.12 | 3.52 | 4.94 | 8.87 |
| MP2//HF | 0.00 | 1.95 | 2.82 | 3.13 | 3.34 | 4.86 | 8.49 |
| B3LYP | 0.00 | 1.74 | 2.40 | 2.74 | 4.92 | 6.31 | 9.60 |
| MP2//B3LYP | 0.00 | 1.94 | 2.90 | 3.03 | 3.35 | 4.90 | 8.45 |
| CAM | 0.00 | 1.71 | 2.52 | 2.63 | 4.28 | 5.68 | 9.12 |
| MP2//CAM | 0.00 | 1.91 | 2.85 | 3.07 | 3.27 | 4.81 | 8.33 |
| M06 | 0.00 | 1.76 | 2.81 | 3.16 | 4.74 | 6.13 | 9.67 |
| MP2//M06 | 0.00 | 2.01 | 2.85 | 3.30 | 3.33 | 4.78 | 8.19 |
| M06L | 0.00 | 2.08 | 2.51 | 3.58 | 4.74 | 6.09 | 9.35 |
| MP2//M06L | 0.00 | 2.04 | 2.90 | 3.42 | 3.53 | 5.02 | 8.41 |
| M062x | 0.00 | 2.04 | 2.83 | 3.41 | 3.53 | 4.99 | 8.46 |
| MP2//M062x | 0.00 | 1.87 | 2.82 | 3.15 | 3.27 | 4.81 | 8.28 |
| M06HF | 0.00 | 1.70 | 2.80 | 2.77 | 0.74 | 2.30 | 6.00 |
| MP2//M06HF | 0.00 | 1.97 | 2.99 | 3.42 | 3.25 | 4.82 | 8.25 |
| MP2 | 0.00 | 1.85 | 2.76 | 3.18 | 3.19 | 4.68 | 8.07 |

See the corresponding footnotes in Table 3

**Table 5** Relative energies, kcal/mol, of the 12t4–Cd$^{2+}$ cation complexes

| No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| Sym | $C_4$ | $C_s$ | $C_{2v}$ | $C_1$ | $C_s$ | $C_1$ | $C_s$ | $C_1$ |
| HF | 0.00 | 6.08 | 2.41 | 2.04 | 3.06 | 8.57 | 12.21 | 14.10 |
| MP2//HF | 0.00 | 2.25 | 1.78 | 1.87 | 3.13 | 5.41 | 9.25 | 9.42 |
| HF | 0.00 | 5.69 | 2.17 | ftc | 2.93 | 8.16 | 11.77 | ftc |
| MP2//HF | 0.00 | 1.58 | 2.89 |  | 2.89 | 4.50 | 8.24 |  |
| B3LYP | 0.00 | 3.08 | 1.28 | 1.47 | 2.37 | 5.60 | 8.75 | 9.62 |
| MP2//B3LYP | 0.00 | 1.34 | 1.25 | 1.66 | 2.85 | 4.26 | 7.97 | 8.70 |
| CAM | 0.00 | 2.70 | 1.24 | 1.55 | 2.58 | 5.50 | 8.95 | ftc |
| MP2//CAM | 0.00 | 1.22 | 1.31 | 1.64 | 2.84 | 4.19 | 7.94 |  |
| M06 | 0.00 | 3.05 | 1.97 | 2.02 | 3.16 | 5.77 | 9.15 | 10.54 |
| MP2//M06 | 0.00 | 1.43 | 1.46 | 1.75 | 2.88 | 4.35 | 8.03 | 8.78 |
| M06L | 0.00 | 3.36 | 2.10 | 1.82 | 2.47 | 5.55 | 8.47 | 9.81 |
| MP2//M06L | 0.00 | 1.71 | 1.69 | 1.74 | 2.81 | 4.69 | 8.28 | 8.93 |
| M062x | 0.00 | 3.00 | 2.15 | 1.84 | 2.71 | 5.43 | 8.70 | 9.96 |
| MP2//M062x | 0.00 | 1.78 | 1.70 | 1.76 | 2.91 | 4.75 | 8.36 | 9.24 |
| M06HF | 0.00 | 1.37 | 2.05 | 1.57 | 2.79 | 4.13 | 7.84 | 8.45 |
| MP2//M06HF | 0.00 | −0.02 | 1.42 | 1.57 | 2.83 | 4.30 | 8.05 | 8.82 |
| MP2 | 0.00 | 1.09 | 1.36 | 1.59 | 2.79 | 4.06 | 7.75 | 8.42 |

See corresponding footnotes in Table 3

current work, while the other two conformations were predicted in the current study, conformations **87** and **12**, Table S1, respectively. This is an indication of the good performance of the conformational search used in the current study.

Optimized geometries were calculated for the $D_4$, $C_4$, $C_{2v}$ and the two $C_s$ conformations of the five 12t4–Ag$^+$, Bi$^{3+}$, Cd$^{2+}$, Cu$^+$ and Sb$^{3+}$ cation metal complexes at the HF/6-31+G* level. The $D_4$ conformations resulted in Hessians with one or more imaginary vibrational frequencies for the

**Table 6** Relative energies, kcal/mol, of the 12t4–$Cu^+$ cation complexes

| No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym | $C_{2v}$ | $C_s$ | $C_1$ | $C_1$ | $C_1$ | $C_1$ | $C_{2v}$ | $C_1$ | $C_4$ | $C_s$ | $C_s$ |
| HF | 0.00 | −9.21 | −3.23 | −8.03 | −3.33 | −3.74 | −10.28 | −10.99 | −12.97 | −6.38 | −10.17 |
| MP2//HF | 0.00 | −3.87 | 1.03 | −1.12 | 2.39 | 2.08 | −2.12 | −1.97 | −3.51 | 1.54 | −0.81 |
| HF | 0.00 | −8.65 | −3.34 | −7.48 | −3.26 | −3.60 | −9.10 | −9.67 | −11.56 | −5.72 | −8.83 |
| MP2//HF | 0.00 | −1.02 | 2.48 | 1.46 | 3.99 | 3.82 | 1.36 | 2.09 | 1.66 | 4.08 | 2.93 |
| B3LYP | 0.00 | −1.02 | 2.48 | 1.46 | 3.99 | 3.82 | 1.36 | 2.09 | 1.66 | 4.08 | 2.93 |
| MP2//B3LYP | 0.00 | 2.49 | 5.93 | 6.36 | 7.90 | 7.93 | 7.56 | 8.59 | 8.99 | 9.88 | 9.42 |
| CAM | 0.00 | −0.98 | 2.59 | 1.75 | 4.10 | 3.95 | 1.81 | 2.62 | 2.09 | 4.52 | 3.48 |
| MP2//CAM | 0.00 | 2.71 | 6.22 | 6.81 | 8.28 | 8.32 | 8.03 | 9.09 | 9.54 | 10.41 | 9.82 |
| M06 | 0.00 | −1.59 | 2.63 | 1.63 | 4.76 | 4.83 | 1.90 | 2.57 | 1.77 | 4.81 | 3.61 |
| MP2//M06 | 0.00 | 1.27 | 5.05 | 5.65 | 7.24 | 7.25 | 6.71 | 7.95 | 8.28 | 9.44 | 8.87 |
| M06L | 0.00 | −2.84 | −0.25 | −0.22 | 1.48 | 1.52 | 0.75 | 1.09 | 1.15 | 2.62 | 2.71 |
| MP2//M06L | 0.00 | 2.31 | 5.54 | 6.41 | 7.61 | 7.69 | 7.40 | 8.52 | 9.13 | 10.09 | 9.86 |
| M062x | 0.00 | −7.73 | ftc | ftc | −1.54 | −1.79 | −5.62 | −6.10 | −7.65 | −3.03 | −5.17 |
| MP2//M062x | 0.00 | 0.13 | ftc | ftc | 5.87 | 5.73 | 3.75 | 5.32 | 4.38 | 7.53 | 6.77 |
| M06HF | 0.00 | −9.02 | −2.58 | −7.18 | −1.17 | −1.91 | −6.81 | −7.80 | −9.59 | −4.42 | −7.00 |
| MP2//M06HF | 0.00 | 0.65 | 4.85 | 4.73 | 7.07 | 7.28 | 3.96 | 5.52 | 4.19 | 8.66 | 6.80 |
| MP2 | 0.00 | 2.84 | 6.55 | 7.94 | 9.14 | 9.23 | 9.40 | 9.97 | 11.38 | 11.69 | 12.49 |

See corresponding footnotes in Table 3

**Table 7** Relative energies, kcal/mol, of the 12t4–$Sb^{3+}$ cation complexes

| No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Sym | $C_4$ | $C_s$ | $C_1$ | $C_s$ | $C_{2v}$ | $C_1$ | $C_s$ |
| HF | 0.00 | 0.70 | 1.08 | 2.51 | 1.07 | 2.31 | 6.41 |
| MP2//HF | 0.00 | 2.07 | 1.78 | 2.68 | 2.63 | 3.65 | 7.44 |
| HF | 0.00 | 0.76 | 1.11 | 0.76 | 1.34 | 2.12 | 5.89 |
| MP2//HF | 0.00 | 1.47 | 1.67 | 1.47 | 2.62 | 2.95 | 6.38 |
| B3LYP | 0.00 | 2.81 | 1.49 | 2.81 | 2.18 | 4.31 | 7.51 |
| MP2//B3LYP | 0.00 | 1.33 | 1.61 | 1.33 | 2.46 | 2.88 | 6.20 |
| CAM | 0.00 | 1.99 | 1.41 | 1.99 | 1.99 | 3.46 | 6.79 |
| MP2//CAM | 0.00 | 1.28 | 1.56 | 1.28 | 2.52 | 2.80 | 6.11 |
| M06 | 0.00 | 2.41 | 1.67 | 2.79 | 2.72 | 3.92 | 7.37 |
| MP2//M06 | 0.00 | 1.25 | 1.57 | 2.52 | 2.64 | 2.71 | 5.93 |
| M06L | 0.00 | 2.40 | 1.61 | 2.17 | 2.91 | 3.81 | 6.93 |
| MP2//M06L | 0.00 | 1.31 | 1.46 | 2.48 | 2.61 | 2.84 | 6.09 |
| M062x | 0.00 | 1.42 | 1.51 | 2.37 | 2.71 | 2.75 | 5.90 |
| MP2//M062x | 0.00 | 1.31 | 1.60 | 2.55 | 2.62 | 2.82 | 6.12 |
| M06HF | 0.00 | −0.48 | 1.46 | 2.56 | 2.51 | 0.65 | 3.78 |
| MP2//M06HF | 0.00 | 1.04 | 1.51 | 2.47 | 1.16 | 2.57 | 5.82 |
| MP2 | 0.00 | 1.27 | 1.54 | 2.51 | 2.65 | 2.74 | 5.97 |

See corresponding footnotes in Table 3

five complexes. The other four $C_4$, $C_{2v}$ and the two $C_s$ conformations were in fact predicted in the conformational search performed in the current study. These correspond to, respectively, conformations **1**, **3**, **4** and **5** for the 12t4–$Ag^+$ complex, conformations **1**, **3**, **4** and **5** for the 12t4–$Bi^{3+}$ complex, conformations **1**, **3**, **5** and **2** for the 12t4–$Cd^{2+}$ complex, conformations **2**, **3**, **6** and **1** for the 12t4–$Cu^+$ complex and conformations **1**, **5**, **4** and **2** for the 12t4–$Sb^{3+}$ complex, as shown in Tables 3, 4, 5, 6, and 7 and Figs. 3, 4, 5, 6, and 7, respectively.

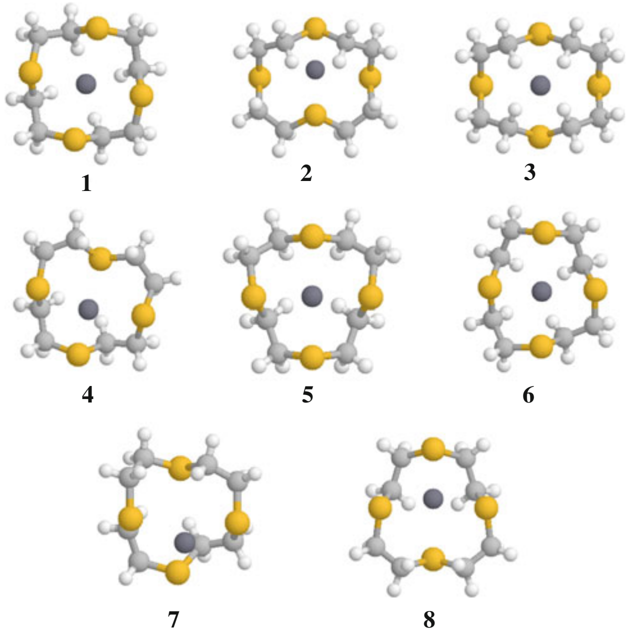

**Fig. 3** Structure of the predicted 12t4–$Ag^+$ conformations

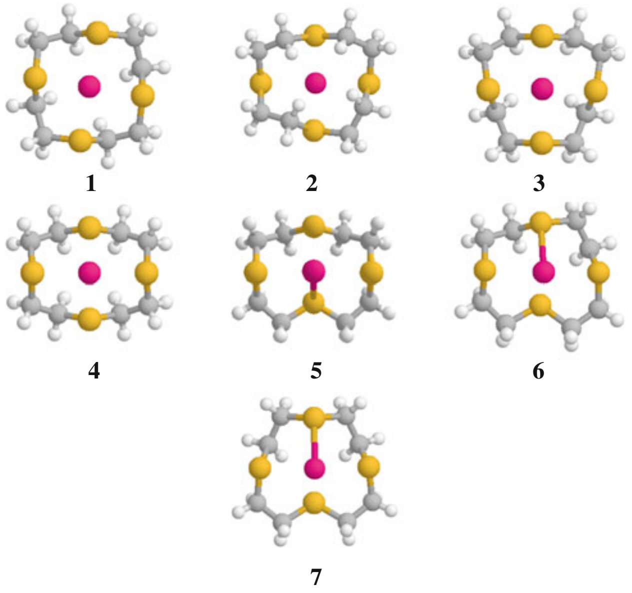

**Fig. 4** Structure of the predicted 12t4–$Bi^{3+}$ conformations

## 3.2 Predicted conformations of free 12t4

The predicted ground state conformation of free 12t4 in this work at all levels considered, Tables 1 and S1, including that predicted by the CONFLEX program using the MMFF94S and MM3 force fields, is the $D_4$ conformation. The same result was reached in the conformational search reported in Refs. [20] and [21]. Comparison between the HF/6-31G** relative energies of the

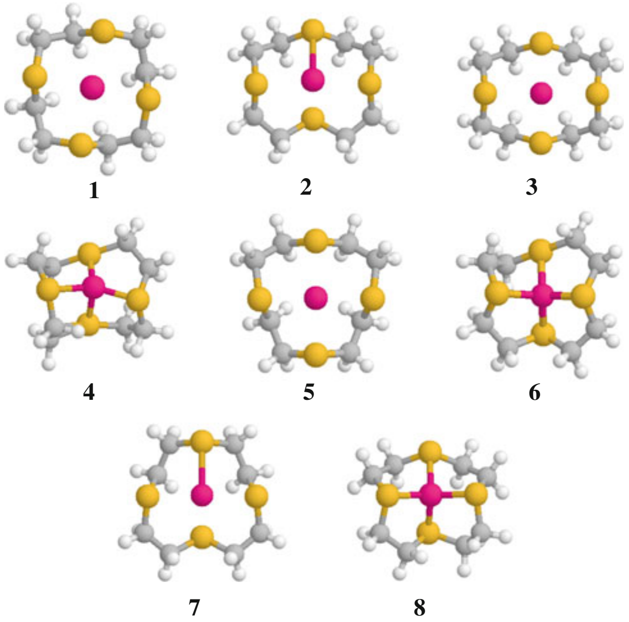

**Fig. 5** Structure of the predicted 12t4–$Cd^{2+}$ conformations

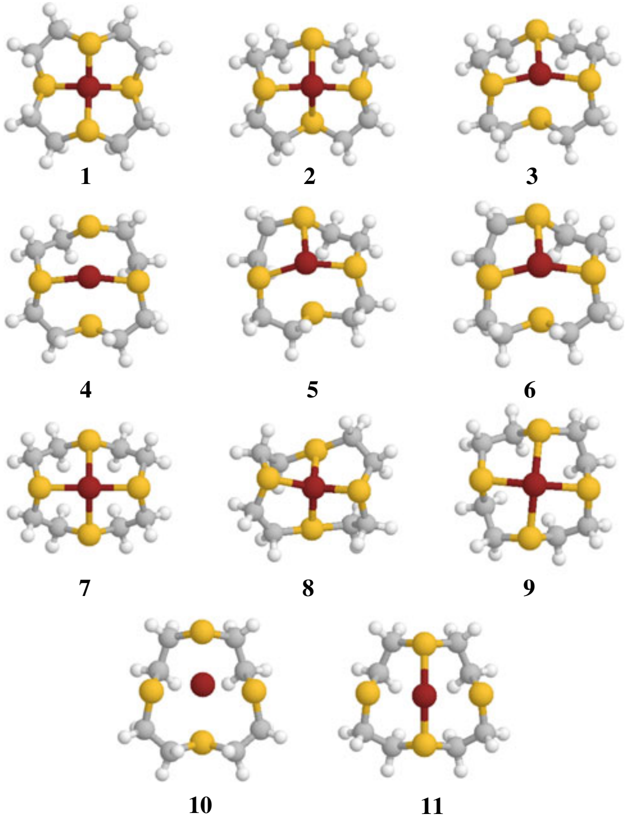

**Fig. 6** Structure of the predicted 12t4–$Cu^+$ conformations

conformations reported in this work along with the conformational description of the torsion angles, Table S1 and those reported in Ref. [21] at the same HF/6-31G** level, indicates that all but six conformations reported in

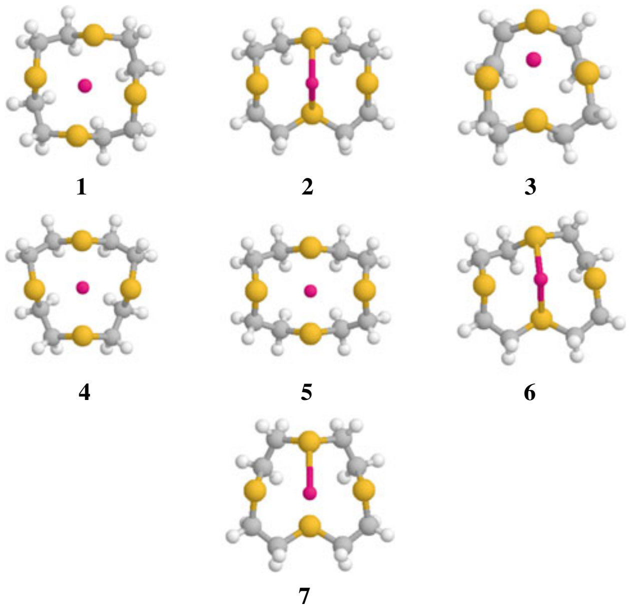

**Fig. 7** Structure of the predicted 12t4–$Sb^{3+}$ conformations

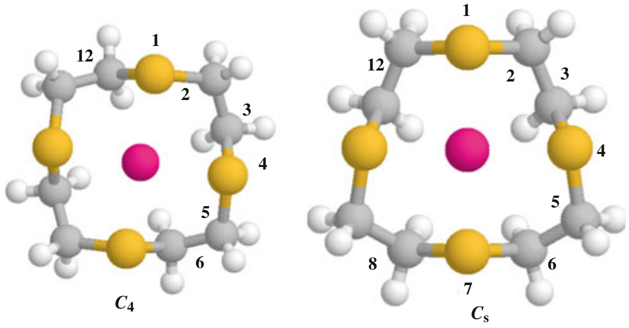

**Fig. 8** Atom numbering of the $C_4$ and $C_s$ structures of the 12t4–cation metal complexes

Ref. [21] were also predicted in this work. These six conformations are conformations **11**, **14**, **16**, **20**, **21** and **22** in Table 3 in Ref. [21]. We redid the conformational search using the same MM3 force field as that used in Ref. [21] using the CONFLEX program. In Ref. [21], only conformations with relative MM3 energies of less than 8 kcal/mol were considered where 25 conformations were predicted. Notice that in the conformational search reported in Ref. [21], a combination of the Monte Carlo analysis and systematic search was used. In the same 8 kcal/mol relative MM3 energy range in the present work using the CONFLEX conformational search method and the MM3 force field, 36 conformations were predicted. It was found that all of the 25 conformations of less than 8 kcal/mol relative MM3 energy range predicted in Ref. [21] were predicted in the conformational search done by us using the same MM3 force field. However, geometry optimization of these 36 conformations at the HF/6-31G** level showed that the HF/6-31G** relative energies in Table 3 in Ref. [21] have different HF/6-31G** relative energies. For example, conformation 11 in Ref. [21] of MM3 relative energy of 6.20 and of 11.13 kcal/mol relative HF/6-31G** energy claimed to be of $C_4$ symmetry. This conformation has the same MM3 relative energy as conformation 11 predicted in this work using the same MM3 force field which corresponds to conformation **9** in the present work using the MMFF94S force field but has a relative HF/6-31G** energy of 2.70 kcal/mol and of $C_1$ symmetry. As was mentioned before, this $C_4$ conformation has a negative vibrational frequency [59]. Therefore, the efficiency of the conformational search and accuracy of the results reported in Ref. [21] is questionable, and consequently, no further comparison will be made with the data reported in Ref. [21]. As a reference, the MM3 relative energy of the 36 predicted conformations in this work using the same MM3 force field as that used in Ref. [21] is added to Table S1. The corresponding 25 conformations reported in Ref. [21] are assigned according to the MM3 relative energy.

On the other hand, in the same 8 kcal/mol relative MM3 energy range considered in Ref. [21] where 25 conformations were predicted, 99 conformations were predicted in the current study using the MMFF94S force field. Notice that in the conformational search of free 12c4 [3] and free 18c6 [4] which was performed quite similar to that done for free 12t4 in the current study, all conformations predicted in the previous reports [11, 12, 60–76] were also predicted in those conformational searches.

Four conformations were considered in Ref. [20] of free 12t4 that were not predicted in their conformational search but were constructed merely similar to four of the important conformations of free 12c4. These four conformations are of $S_4$, $C_4$, $C_i$ and $C_s$ symmetries. The $C_4$ conformation is the same as the $C_4$ conformation predicted in the conformational search in Ref. [21]. As was mentioned before, this $C_4$ conformation has one imaginary vibrational frequency at the HF/6-31G* optimized geometry [59]. Geometry optimization was performed by us in the current work for the other three $S_4$, $C_i$ and $C_s$ conformations. These three conformations were found to correspond to, in the current work, conformations **16**, **14** and **87**, respectively. None of these three conformations were predicted in the conformational search reported in Ref. [21].

### 3.3 Predicted conformations of the 12t4–cation metal complexes

The predicted ground state conformations of the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes are the $C_4$, $C_4$, $C_4$, $C_{2v}$ and $C_4$ conformations, respectively, Tables 3, 4, 5, 6 and 7. This is in agreement with the experimental X-ray data for the 12t4–$Ag^+$ [45] and $Cd^{2+}$ [41] cation metal complexes, but experimentally, also by X-ray, the 12t4–$Bi^{3+}$ [48] and $Cu^+$ [40, 46] cation metal complexes have $C_s$ and $C_4$ structures, respectively. To the best of our knowledge, there is no experimental geometry available for the 12t4–$Sb^{3+}$ cation metal complex. The difference in energy between the theoretically predicted ground state $C_4$ conformation of the 12t4–$Bi^{3+}$ cation metal complex and the experimentally observed $C_s$ structure at the MP2/6-311G** level is only 2.76 kcal/mol. The energy difference between the theoretically predicted ground state $C_{2v}$ conformation of the 12t4–$Cu^+$ cation metal complex and the experimentally observed $C_4$ structure also at the MP2/6-311G** level is 11.38 kcal/mol. Notice that this ground state $C_{2v}$ predicted conformation of the 12t4–$Cu^+$ cation complex, Fig. 6, is different from the $C_{2v}$ conformation found in the X-ray data of some of the 12t4–cation metal complexes as described in the CDB. The $C_{2v}$ conformation found in some of the 12t4–cation metal complexes is similar to conformation **7** of the 12t4–$Cu^+$ cation metal complex, Fig. 6. The geometrical parameters of this ground state $C_{2v}$ conformation of the 12t4–$Cu^+$ cation metal complex are close to that of a $D_{2d}$ symmetry. However, the calculated vibrational frequencies at the optimized geometry at the HF/6-31+G* level of the $D_{2d}$ structure of the 12t4–$Cu^+$ cation metal complex have one imaginary vibrational frequency. It is interesting also to ask whether a similar $C_{2v}$ structure was predicted for the other 12t4–cation metal complexes considered in this work. This $C_{2v}$ conformation corresponds to conformations, Table S3, **16**, **8**, **10** and **8**, with relative energies of 17.60, 16.45, 10.97 and 12.26 kcal/mol, respectively, at the MP2/6-31+G*//HF6-31+G* level for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$ and $Sb^{3+}$ cation metal complexes, respectively. Since this conformation has relative energies, for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$ and $Sb^{3+}$ cation metal complexes, higher than 10 kcal/mol, this conformation was not considered for computations at higher levels of theory using the larger 6-311G** basis set.

The $C_s$ conformation found in the X-ray crystal structure of some of the 12t4–cation metal complexes, for example conformation **2** in Fig. 3 of the 12t4–$Ag^+$ cation metal complex, corresponds to conformations **2**, **5**, **2**, **2** and **2** for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes, respectively, with relative energies of, at the MP2/6-311G** level, 0.07, 3.19, 1.09, 2.84 and 1.27, respectively.

The energy order of the predicted conformations of the 12t4–cation metal complexes considered in this work showed little dependence on the level of theory used. This is with the exception of the 12t4–$Cu^+$ cation metal complex which showed large dependence on the level of theory considered. For this complex, the experimental $C_4$ conformation is the ground state conformation at the HF, M062x and M06HF levels.

The important question now is the reason that the predicted ground state conformation is different from the experimentally known conformation for the 12t4–$Bi^{3+}$ and $Cu^+$ cation metal complexes. This may be attributed to that computations correspond to gas-phase isolated molecule, and the experimental X-ray data are measured for the solid state where crystal packing plays an important role in the structure of these complexes. It is interesting to see what an experimental and theoretical vibrational study may reveal about the structure of these complexes. Such study is planned to be performed in our laboratory.

It is interesting to notice the similarity between the predicted conformations of the 12c4–alkali metal cation complexes [5] and the conformations predicted in the current work for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes. This similarity is between the $C_4$, $C_{2v}$ and the two $C_s$ conformations of the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes, Figs. 3, 4, 5, 6 and 7, from one side and the similar conformations predicted for the 12c4–alkali metal cation complexes on the other side. Most important is the similarity between the ground state $C_4$ conformations for both types of metal cations. This $C_4$ conformation is predicted to be the ground state conformation for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$ and $Sb^{3+}$ cation metal complexes and also for the 12t4–$Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ cation metal complexes. This suggests structural factors rather than electronic factors that affect the structure of these complexes.

### 3.4 Energy order of the predicted conformations of free 12t4

An important point to be addressed here is how reliable the energy order of the predicted conformations of free 12t4 is. For example, at a given level of theory, one conformation is the most stable conformation or more stable than another conformation, but at different level, the energy order of these two conformations might be reversed. For this purpose, we performed G3MP2 computations to test the accuracy of the energy order of the predicted conformations at the different levels of theory used in this work. This is to take advantage of the large number of the new DFT functionals as the CAM-B3LYP, M06, M06L, M062x and M06HF functionals used in the current study. Notice that all computations, except most of those at the HF level, were done using the triplet zeta 6-311G** basis set. In addition, computations were performed at the MP2/6-311G** level for conformations with relative energy less than 7 kcal/mol, according to the MP2/6-311G**//B3LYP/6-311G** energy and for other conformations with symmetry higher than the $C_1$ symmetry for a total of 41 conformations and at the G3MP2 level for the 20 lowest energy conformations, according to the MP2/6-311G** level energy. These 20 conformations are shown in Table 1 and are arranged according to the MMFF94S energy order.

Comparing the energy order of the predicted conformations of free 12t4 at the different levels in Table 1, or rather in Table S1, it is noticed that none of these levels has the same energy order or very close to that at the G3MP2 level, including that at the MP2/6-311G** level. The energy order by most of the different methods probably performs equally. This is with the exception of that at the HF level. Compared to the energy order at the G3MP2 level, conformation **5** is less stable at all the DFT and MP2 levels, and conformation **10** is more stable at the DFT, MP2 and most of the HF levels. Otherwise, it is not possible to find a preference for one level over the other among the DFT functionals and MP2 level used in the current study. Finally, the energy order at the HF level using the STO-3G, 3-21G and 4-31G basis sets has the worst agreement with the energy order at the G3MP2 level. But, the performance becomes better using the higher 6-31G** and 6-311G** basis sets.

To get a quantitative estimate of the performance of the relative energies of the different computational methods used in the current study, the mean absolute deviation (MAD) of the difference between the relative energies computed at any level and that at the G3MP2 level was calculated. This is appended at the bottom of Table 1. It is interesting to notice that the four M06 functionals, M06, M06L, M062x and M06HF, have the lowest MAD of only about 0.4 at the M062x and M06HF levels and about 0.7 at the M06 and M06L levels. Although these small values seem important, it is reasonable to assume that this might be fortuitous as it is applied for only a single molecule. Adding the electron correlation at the MP2 level for any of these functions, the MAD increases to about 1.2, a comparable value to that obtained at the MP2/6-311G** level.

It is worth mentioning here that initial computations were performed for the ten lowest energy conformations of free 12t4 at the MP2 level using the 6-31G*, 6-31+G*, 6-31G**, 6-311G** and 6-311++G** basis sets. Compared to the G3MP2 energy order, it was found that the energy order at the MP2/6-311G** level had a comparable energy order to that at the MP2/6-311++G** level and better than that using the other, smaller, basis sets. This rationalized the use of the 6-311G** basis set in the current study.

### 3.5 Structure of the ground state $D_4$ conformation of free 12t4

The last point to be addressed in the study of free 12t4 and probably one of the most important points is the structure of the ground state $D_4$ conformation of free 12t4 and the difference between the structure of the $S_4$ ground state conformation of free 12c4 and the $D_4$ ground state conformation of free 12t4. Another point that is related to the above two points is what are the factors that affect the conformational stability of the $D_4$ conformation. The advantage of the conformational search of free 12t4 performed in the current study is that it predicts low and high energy conformations. Comparison between the structure of the low and high energy conformations may reveal what the factors governing the conformational stability of free 12t4 are.

The first point about the structure of the ground state $D_4$ conformation of free 12t4 and the ground state $S_4$ conformation of free 12c4 has in fact been considered in detail before and is assumed to be well understood [18]. It is well established that all the sulphur atoms in free 12t4, 14t4 and 18t2 adopt the exodentate structure, while in free 18t6 two of the sulphur atoms violate the exodentate rule and adopt endodentate structure. In Ref. [18], an explanation was given for this, which as will be shown shortly is not accurate enough. This is that all of the CSCC dihedral angles without exception adopt the gauche structure. Contrary to thiacrown ethers, the oxygen analogues of thiacrown ethers, crown ethers adopt the endodentate structure, a statement as will be shown below is not fully correct.

Assuming that free 12c4 and free 18c6 adopt full endodentate structure, free 12c4 and free 18c6 would have similar structure to that found in their metal complexes of $C_4$ [5, 16, 17] and $D_{3d}$ [77–81] symmetries, respectively. In fact, our previous study of free 12c4 [3] and free 18c6 [4] has shown that the structure of both molecules is governed by the hydrogen bond, and free 12c4 and free 18c6 have $S_4$ and $S_6$ structures, respectively. This is because in the $S_4$ and $S_6$ conformations of free 12c4 and free 18c6, respectively, there is one hydrogen bond per oxygen atom and at distances shorter than any of the other conformations of both molecules. Consequently, both molecules adopt a structure close to, but not fully, endodentate.

For free 12t4, Table 8 lists the SCCS and CSCC dihedral angles according to the B3LYP/6-311G** geometry of some selected conformations of free 12t4 including some of the lowest and highest MP2/6-311G**//B3LYP/6-311G** energy conformations. According to the MP2/6-311G**//B3LYP/6-311G** energy order, conformations **1**, **6** and **9** are the three lowest energy conformations, and conformations **105**, **132** and **144** are among the highest energy conformations. Conformations **46** and **83** are two conformations of average relative energy compared to the ground state conformation, conformation **1**, Table S1.

Examination of the dihedral angles of conformations **6**, **9** and **52** indicates that in these three conformations, all of

**Table 8** Dihedral angles of some of free 12t4 conformations at the B3LYP/6-311G** level

| No. | Order | Sym | SCCS | CSCC |
|---|---|---|---|---|
| **1** | 1 | $D_4$ | 173.2 | 72.2 |
| **6** | 2 | $C_2$ | 171.2, 166.0 | 77.3, 79.6<br>80.9, −96.4 |
| **9** | 4 | $C_{2h}$ | 169.3 | 83.3, 90.4 |
| **52** | 7 | $S_4$ | 168.5 | 76.7, 102.3 |
| **46** | 69 | $C_1$ | 88.3, 64.2<br>150.9, 76.6 | 71.6, 175.8<br>45.3, −97.0<br>−175.6, 62.7<br>−83.8, −80.4 |
| **83** | 89 | $C_1$ | 61.3, 55.8<br>−73.9, −121.7 | 127.9, −65.4<br>68.0, 37.4<br>−174.2, 58.0<br>−163.1, 102.4 |
| **105** | 131 | $C_s$ | 55.5, 64.5 | 76.0, 178.7<br>66.4, −133.6 |
| **132** | 140 | $C_2$ | 64.3, −69.3 | 77.9, −93.4<br>−126.2, 145.0 |
| **144** | 147 | $C_1$ | 99.2, 149.8<br>−54.7, 70.1 | 56.0, −73.9<br>134.8, −134.5<br>83.8, −152.0<br>−58.6, −93.5 |

No is the conformational number, order is the energy order according to the MP2/6-311G**//B3LYP/6-311G** energy and sym is the conformation symmetry

the SCCS dihedral angles deviate from that of conformation **1** of 173° by not more than 7°, but the CSCC dihedral angles deviate from that of conformation **1** of 72° by as much as 30°. This indicates that a SCCS dihedral angle of 180° requirement is more important than a gauche CSCC dihedral angle requirement. This can be considered as a correction of the previous prediction that the gauche angle is the reference of the stability of free 12t4 and all other free thiacrown ethers [18]. Study of the other free thiacrown ethers, as 15t5 and 18t6, is not the subject of the current study. It is simple to see that in conformation **105**, one of the highest energy conformations of free 12t4 according to the MP2/6-311G**//B3LYP/6-311G** energy order, four of the SCCS dihedral angles are close to 60°, but four of the eight CSCC dihedral angles are close to the 60° requirement of the gauche conformation.

Compared to the experimental geometry reported in Refs. [18] and [19], among all the methods used in this work using the 6-311G** basis set, Table 2, the MP2 method has the best agreement with the experimental geometry. The B3LYP functional has the worst agreement, worse than even that at the HF level. This is in agreement with the known overestimation of the bond lengths calculated by the B3LYP method especially those containing the S atom [24–29, 82]. At the MP2 level, the C–S bond length is predicted exactly and the C–C bond length is overestimated by about 0.01 Å. The calculated C–S bond length by B3LYP functional is overestimated by about 0.03 Å, and the C–C bond length is overestimated by about 0.02 Å. This is compared to an overestimation of about 0.01 and 0.01 Å for the same C–S and C–C bond lengths, respectively, at the HF level. The other group of four M06, M06HF, M06L and M062x functionals and the CAM-B3LYP functional perform qualitatively the same, with that using the local M06L functional performing better than the other four functionals. This group of five functionals is performing in between the MP2 and B3LYP levels.

## 3.6 Structure of the ground state conformations of 12t4–cation metal complexes

The calculated S–C and C–C bond lengths by all methods for the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$ and $Cu^+$ complexes are predicted to be too long, Tables 9, 10, 11 and 12. This is with the exception of the C–C bond of the 12t4–$Cd^{2+}$ and $Cu^+$ complexes with the M06 and M06L methods which are predicted to be too short by not more than 0.01 Å. The calculated S–C and C–C bond lengths by the B3LYP method have the highest overestimation. Most important is how the different levels of theory used in the current study predict the metal–S bond length. In fact, there is no preference of one method over the other. The four Ag–S, Bi–S, Cd–S and Cu–S bonds are predicted to be too short by all methods. This is with the exception of the Ag–S bond length by the HF and M062x methods and the Cu–S bond length by the HF, M062x and M06HF methods.

**Table 9** Geometry of the $C_4$ conformation of the 12t4–$Ag^+$ complex using the 6-311G** basis set

| Coord. | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 | Exp. [49] |
|---|---|---|---|---|---|---|---|---|---|
| Ag–$S_1$ | 2.832 | 2.703 | 2.676 | 2.685 | 2.705 | 2.748 | 2.705 | 2.613 | 2.732 |
| $C_{12}$–$S_1$ | 1.827 | 1.847 | 1.829 | 1.834 | 1.830 | 1.828 | 1.827 | 1.819 | 1.817 |
| $S_1$–$C_2$ | 1.823 | 1.843 | 1.826 | 1.831 | 1.827 | 1.826 | 1.827 | 1.818 | 1.789 |
| $C_3$–$C_4$ | 1.536 | 1.532 | 1.527 | 1.519 | 1.521 | 1.528 | 1.536 | 1.531 | 1.519 |
| $S_1C_2C_3S_4$ | 66.4 | 64.7 | 64.7 | 66.0 | 67.1 | 67.1 | 66.4 | 64.9 | 67.9 |
| $C_2C_3S_4C_5$ | 68.6 | 69.8 | 69.9 | 68.7 | 67.7 | 67.8 | 68.6 | 69.9 | 67.4 |
| $C_3S_4C_5C_6$ | −162.0 | −159.6 | −160.1 | −160.6 | −160.7 | −161.0 | −162.0 | −161.3 | −161.9 |

Atom numbering is according to Fig. 8. Bond lengths in Å and angles in degrees. Coord. stands for coordinate. CAM stands for the CAM-B3LYP functional. Values of each coordinate reported in Ref. [49] are calculated as the average of these coordinates in the CSD, hit QAHNET

**Table 10** Geometry of the $C_s$ conformation of the 12t4–$Bi^{3+}$ complex using the 6-311G** basis set

| Coord. | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 | Exp. [51] |
|---|---|---|---|---|---|---|---|---|---|
| Bi–$S_1$ | 2.755 | 2.803 | 2.761 | 2.797 | 2.805 | 2.764 | 2.690 | 2.729 | 2.996 |
| Bi–$S_4$ | 2.737 | 2.782 | 2.742 | 2.770 | 2.790 | 2.748 | 2.676 | 2.717 | 3.029 |
| Bi–$S_7$ | 2.729 | 2.769 | 2.732 | 2.776 | 2.775 | 2.742 | 2.669 | 2.713 | 3.205 |
| $S_1$–$C_2$ | 1.842 | 1.860 | 1.840 | 1.848 | 1.841 | 1.839 | 1.838 | 1.831 | 1.817 |
| $C_2$–$C_3$ | 1.525 | 1.524 | 1.519 | 1.510 | 1.512 | 1.521 | 1.531 | 1.524 | 1.499 |
| $C_3$–$S_4$ | 1.834 | 1.849 | 1.831 | 1.836 | 1.831 | 1.831 | 1.832 | 1.822 | 1.787 |
| $S_4$–$C_5$ | 1.837 | 1.855 | 1.836 | 1.842 | 1.840 | 1.836 | 1.834 | 1.827 | 1.800 |
| $C_5$–$C_6$ | 1.526 | 1.527 | 1.522 | 1.513 | 1.515 | 1.524 | 1.533 | 1.527 | 1.496 |
| $C_6$–$S_7$ | 1.844 | 1.862 | 1.842 | 1.848 | 1.842 | 1.841 | 1.844 | 1.831 | 1.815 |
| $C_{12}S_1C_2C_3$ | 149.8 | 148.8 | 149.4 | 149.0 | 149.2 | 150.0 | 151.3 | 150.0 | 146.9 |
| $S_1C_2C_3S_4$ | −58.0 | −59.9 | −59.5 | −61.4 | −61.3 | −60.3 | −59.5 | −61.5 | −60.6 |
| $C_2C_3S_4C_5$ | −63.3 | −61.9 | −61.9 | −58.5 | −58.9 | −59.5 | −61.1 | −58.6 | −57.4 |
| $C_3S_4C_5C_6$ | 166.4 | 164.8 | 165.7 | 168.1 | 166.8 | 167.7 | 168.1 | 167.7 | 170.5 |
| $S_4C_5C_6S_7$ | −57.4 | −58.0 | −58.0 | −61.4 | −61.0 | −60.2 | −57.9 | −60.2 | −62.0 |
| $C_5C_6S_7C_8$ | −89.1 | −87.7 | −88.1 | −85.1 | −85.8 | −86.6 | −89.00 | −86.9 | −82.7 |

See corresponding footnote in Table 9. Values of each coordinate reported in Ref. [51] are calculated as the average of these coordinates in the CSD, hit VOSTEC

**Table 11** Geometry of the $C_4$ conformation of the 12t4–$Cd^{2+}$ complex using the 6-311G** basis set

| Coord. | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 | Exp. [45] |
|---|---|---|---|---|---|---|---|---|---|
| Cd–$S_1$ | 2.664 | 2.650 | 2.616 | 2.631 | 2.655 | 2.653 | 2.614 | 2.584 | 2.836 |
| $C_{12}$–$S_1$ | 1.836 | 1.856 | 1.838 | 1.844 | 1.841 | 1.837 | 1.835 | 1.828 | 1.813 |
| $S_1$–$C_2$ | 1.833 | 1.851 | 1.833 | 1.839 | 1.834 | 1.834 | 1.835 | 1.825 | 1.810 |
| $C_3$–$C_4$ | 1.531 | 1.532 | 1.527 | 1.519 | 1.520 | 1.529 | 1.537 | 1.532 | 1.525 |
| $S_1C_2C_3S_4$ | 62.9 | 63.0 | 62.8 | 64.5 | 65.6 | 65.2 | 64.4 | 63.9 | 64.7 |
| $C_2C_3S_4C_5$ | 71.5 | 71.2 | 71.5 | 69.9 | 68.9 | 69.3 | 70.3 | 70.6 | 70.1 |
| $C_3S_4C_5C_6$ | −159.6 | −158.7 | −159.2 | −159.7 | −159.9 | −160.2 | −161.2 | −160.4 | −162.9 |

See corresponding footnote in Table 9. Values of each coordinate reported in Ref. [45] are calculated as the average of these coordinates in the CSD, hit KEMYIL

The deviation of the calculated metal–S bond length from the experimental value is much higher than that for the other S–C and C–C bond lengths. The calculated bond lengths by the Coulomb-attenuating method (CAM) hybrid exchange–correlation functional that combines the hybrid qualities of B3LYP and the long-range correction, the CAM-B3LYP functional [83], have better agreement with the experimental bond lengths than the bond lengths calculated by B3LYP method. The calculated bond lengths by the CAM-B3LYP method generally perform similar to the

**Table 12** Geometry of the $C_4$ conformation of the 12t4–$Cu^+$ complex using the 6-311G** basis set

| Coord. | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 | Exp. [43] | Exp. [43] |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu–$S_1$ | 2.600 | 2.481 | 2.459 | 2.456 | 2.458 | 2.538 | 2.545 | 2.400 | 2.535 | 2.538 |
| $C_{12}$–$S_1$ | 1.826 | 1.846 | 1.829 | 1.833 | 1.832 | 1.828 | 1.827 | 1.818 | 1.818 | 1.816 |
| $S_1$–$C_2$ | 1.823 | 1.841 | 1.824 | 1.829 | 1.824 | 1.825 | 1.826 | 1.816 | 1.815 | 1.811 |
| $C_3$–$C_4$ | 1.530 | 1.531 | 1.526 | 1.517 | 1.518 | 1.527 | 1.535 | 1.530 | 1.524 | 1.517 |
| $S_1C_2C_3S_4$ | 62.1 | 58.3 | 58.6 | 59.5 | 60.0 | 62.7 | 63.1 | 58.1 | 58.3 | 58.3 |
| $C_2C_3S_4C_5$ | 72.4 | 76.0 | 75.8 | 74.8 | 74.4 | 71.9 | 71.6 | 76.4 | 76.3 | 76.3 |
| $C_3S_4C_5C_6$ | −160.6 | −160.5 | −161.0 | −161.3 | −161.7 | −161.8 | −162.7 | −162.5 | −162.8 | −162.6 |

See corresponding footnote in Table 9. Values of each coordinate reported in Ref. [43] are calculated as the average of these coordinates in the CSD, hits QITZAU and QITZEY

**Table 13** Geometry of the $C_4$ conformation of the 12t4–$Sb^{3+}$ complex using the 6-311G** basis set

| Coord. | HF | B3LYP | CAM | M06 | M06L | M062x | M06HF | MP2 |
|---|---|---|---|---|---|---|---|---|
| Sb–$S_1$ | 2.649 | 2.703 | 2.663 | 2.697 | 2.708 | 2.664 | 2.604 | 2.641 |
| $C_{12}$–$S_1$ | 1.833 | 1.855 | 1.836 | 1.840 | 1.838 | 1.835 | 1.833 | 1.826 |
| $S_1$–$C_2$ | 1.836 | 1.854 | 1.834 | 1.840 | 1.834 | 1.834 | 1.836 | 1.826 |
| $C_3$–$C_4$ | 1.531 | 1.525 | 1.520 | 1.511 | 1.512 | 1.521 | 1.531 | 1.524 |
| $S_1C_2C_3S_4$ | 59.9 | 60.3 | 60.0 | 62.4 | 62.3 | 61.2 | 59.9 | 61.9 |
| $C_2C_3S_4C_5$ | 74.9 | 74.0 | 74.4 | 72.0 | 72.1 | 73.4 | 74.9 | 72.7 |
| $C_3S_4C_5C_6$ | −163.0 | −160.5 | −161.2 | −161.9 | −161.5 | −162.1 | −163.0 | −162.3 |

See corresponding footnote in Table 9

calculated bond lengths by the group of the M06 functionals. To the best of our knowledge, there is no experimental geometry of the 12t4–$Sb^{3+}$ complex available to compare with (Table 13).

The calculated metal–O bond length of the 12c4–alkali metal cations at the MP2/6-31+G* level is in the range from 2.02 Å for the 12c4–$Li^+$ complex to 3.14 Å for the 12c4–$Cs^+$ complex [5]. By comparing these values with the calculated metal–O bond length at the MP2/6-311G** level for the 12t4–metal complexes considered in the current work, the calculated metal–O bond length of the complexes considered in the current work has a narrower range, between 2.54 Å for the 12t4–$Cu^+$ complex and 2.73 Å for the 12t4–$Bi^{3+}$ complex. The ionic radii of the considered metal cations in this work range from 0.73 Å for $Cu^+$ cation to 1.26 Å for the $Ag^+$ cation. It is clear that the ionic radii of the five metal cations considered in the current work have little effect on the geometry of the 12t4 cation metal complexes. Notice that the alkali metal cation radii range from 0.76 Å for the $Li^+$ cation to 1.67 Å for the $Cs^+$ cation.

For almost all the predicted conformations of the 12t4 cation metal complexes considered in this work, the metal cation lies out of the 12t4 ring plane. The existence of the metal cation out of the ring plane is a result of the larger ionic radii of the $Ag^+$, $Bi^{3+}$, $Cu^+$, $Cd^{2+}$ and $Sb^{3+}$ cations than the ring cavity. This similar to the case of the 12c4–alkali metal cation complexes [5]. Notice that, as was mentioned by Armentrout and coworkers [84], the existence of the metal cation out of the ring plane in the $C_4$ conformation allows the existence of optically active enantiomers.

## 3.7 Binding energy

The binding enthalpies, BEs, were calculated similar to those in Ref. [5]. The counterpoise correction according to the Boys and Bernardi [85, 86] was employed including the zero point energy correction using unscaled B3LYP/6-311G** correction to enthalpy. The calculated BEs of the 12t4–cation metal complexes for the $C_4$ conformation in addition to the ground state conformation, if has symmetry different from the $C_4$ symmetry, are shown in Table 14. There is no experimental BEs available we know of for the studied complexes in this work for comparison with these calculated BEs. The calculated BEs for the 12t4–cation metal complexes are comparable to those for the 12c4–alkali metal cation complexes reported in Ref. [5] with the same +1 charge of about 90 kcal/mol. The calculated BEs show little dependence on the level of theory used. For example, for the 12t4–$Ag^+$ complex, the calculated BE after the inclusion of the MP2 energy correction is in the 91–94 kcal/mol range but without the MP2 correction, the BE vary in the 97–100 kcal/mol range. Excluded from this is the BE calculated at the HF level where smaller values of

**Table 14** Binding enthalpies, kcal/mol, of the 12t4 cation metal complexes using the 6-311G** basis set

| Metal cation | $Ag^+$ | $Bi^{3+}$ | | $Cd^{2+}$ | $Cu^+$ | | $Sb^{3+}$ |
|---|---|---|---|---|---|---|---|
| Sym. | $C_4$ | $C_4$ | $C_s$ | $C_4$ | $C_4$ | $C_{2v}$ | $C_4$ |
| HF | 67.20 | 435.34 | 435.25 | 223.94 | 84.71 | 80.62 | 485.80 |
| B3LYP | 96.08 | 477.55 | 480.38 | 269.51 | 121.99 | 130.61 | 526.36 |
| CAM | 97.96 | 470.43 | 474.32 | 268.96 | 124.29 | 133.41 | 521.20 |
| M06 | 99.47 | 472.76 | 473.73 | 266.25 | 128.00 | 137.87 | 523.29 |
| M06L | 98.99 | 467.38 | 470.94 | 260.78 | 133.21 | 143.30 | 521.43 |
| M062x | 97.20 | 452.95 | 458.84 | 262.04 | 117.71 | 119.30 | 502.53 |
| M06HF | 99.97 | 470.68 | 479.94 | 268.32 | 113.21 | 112.08 | 518.97 |
| MP2//HF | 88.76 | 472.01 | 471.57 | 254.74 | 109.75 | 120.87 | 520.58 |
| MP2//B3LYP | 93.39 | 459.11 | 472.66 | 257.10 | 115.51 | 130.74 | 521.08 |
| MP2//CAM | 92.88 | 457.17 | 471.45 | 255.95 | 115.39 | 129.68 | 520.27 |
| MP2//M06 | 92.45 | 456.17 | 469.70 | 254.96 | 114.41 | 127.54 | 518.13 |
| MP2//M06L | 92.14 | 456.63 | 469.71 | 254.22 | 113.98 | 128.61 | 518.27 |
| MP2//M062x | 91.32 | 456.13 | 470.08 | 254.32 | 111.86 | 123.47 | 519.26 |
| MP2//M06HF | 91.77 | 453.30 | 469.33 | 254.70 | 111.58 | 123.09 | 519.13 |
| MP2 | 91.48 | 453.94 | 468.92 | 254.32 | 115.12 | 129.71 | 517.96 |

See corresponding footnote in Table 3

the BEs are calculated. Notice that for the 12t4–$Bi^{3+}$ and the 12t4–$Cu^+$ complexes where the calculated ground state conformation is different from the experimental conformation, the calculated BEs for the $C_s$ conformation of the 12t4–$Bi^{3+}$ complex are higher than those for the $C_4$ conformation. But for the 12t4–$Cu^+$ complex, the calculated BEs of the $C_{2v}$ conformation are higher than those for the $C_4$ conformation.

## 4 Conclusions

This study is the fourth in our series of studies about the conformational analysis and structure of crown ethers and their metal complexes [3–5, 14, 16]. These previous studies included the conformational analysis of free 12c4 and its alkali metal cation complexes and free 18c6. In the present study, conformational search was performed for one of the most important crown ethers, free 12t4. In this conformational search, 156 conformations were predicted using the CONFLEX method and the MMFF94S force field. The method demonstrated its efficiency by predicting all previously predicted conformations of free 12t4 by either conformational search or experimentally for free 12t4 or its metal complexes. The study predicted, in agreement with the X-ray results [18, 19], and the previous conformational search [20, 21], that the $D_4$ conformation is the global minimum conformation of free 12t4.

To test some of the new DFT functionals for the prediction of the geometries, energy order and vibrational spectra, computations were performed in the current work using the CAM-B3LYP, M06, M06L, M06HF and M062x functionals and the 6-311G** basis set. Computations were also done at the G3MP2 level to compare between the predicted energy order at the other levels used in the current study. Surprisingly, none of the methods used, including that at the MP2 level, had the same or very close energy order to that at the G3MP2 level. The B3LYP, CAM-B3LYP, M06, M06L, M062x, M06HF and MP2 methods performed qualitatively similar. Similarly, compared to the experimental bond lengths, the calculated bond lengths of the ground state $D_4$ conformation of free 12t4 at the CAM-B3LYP, M06, M06L, M062x and M06HF levels performed qualitatively the same, whereas that at the MP2 level had the best agreement and that at the B3LYP level had the worst agreement with the experimental bond lengths.

The methods used in the current study correspond to the single-reference method. Since these computations could not reproduce the energy order at the G3MP2 level, it remains to suggest the use of the multireference methods and other levels of the ab initio theory as the CCSD method. This is in light to what was reported that the Mukherje’s state-specific multireference coupled cluster (MkMRCC) method was able to reproduce the singlet–triplet energy gap for trimethylenemethane and the oxyallyl diredical and relates species where single-reference methods fail [87]. Similar observation was made also for antiaromatic molecules [88]. The subject of these studies can be addressed in a different publication.

The current study predicts that a SCCS dihedral angle of 180° requirement is more important factor for the stability of free 12t4 conformations than the gauche angle requirement. This is contrary to the previous conclusion that the gauche CSCC dihedral angle is the factor that affects the conformational stability of thiacrown ethers [18].

The current conformational analysis was extended to include the 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$, $Cu^+$ and $Sb^{3+}$ cation metal complexes. The predicted global minimum conformations of these five 12t4–cation metal complexes are the $C_4$, $C_4$, $C_4$, $C_{2v}$ and $C_4$ conformations, respectively. This is in agreement with the experimental X-ray data for the 12t4–$Ag^+$ [49] and $Cd^{2+}$ [45] cation metal complexes, but experimentally by X-ray the 12t4–$Bi^{3+}$ [51] and $Cu^+$ [43, 44] cation metal complexes have $C_s$ and $C_4$ structures, respectively. To the best of our knowledge, there is no experimental geometry available for the 12t4–$Sb^{3+}$ complex. The energy order of the predicted conformations of the four 12t4–$Ag^+$, $Bi^{3+}$, $Cd^{2+}$ and $Sb^{3+}$ cation metal complexes showed little dependence on the level of theory used. But for the 12t4–$Cu^+$ complex, the experimental $C_4$ conformation was predicted to be the ground state conformation at the HF, M062x and M06HF levels.

The computations performed in the present work were done at the B3LYP, CAM-B3LYP and the four M06, M06L, M062x and M06HF levels. The later five functionals were developed to correct for problems with the popular B3LYP functional for the transition metals and its failure to account for weak interactions. The CAM-B3LYP [83] functional as a modification of the B3LYP functional accounts for the long-range interactions as those present in the metal complexes considered in the current study. The M06 and M062x functionals are two hybrid meta exchange–correlation functionals. The former functional is parameterized for transition metals and the later is parameterized for nonmetals. The M06L functional is a local functional and the M06HF functional is a Hartree–Fock functional [89–91]. The poorer performance of the B3LYP functional compared to the CAM-B3LYP functional and the other M06 group of functionals is in agreement with what was observed in the DFT study of the isomerization energy [92]. In that study, the authors concluded that a combination of long-range corrected DFT and local response dispersion are required to produce accurate reaction energies.

For either free 12t4 or 12t4–cation metal complexes considered in the current work, in terms of the optimized geometries and energies, the CAM-B3LYP method probably performs better than the B3LYP method but performs relatively the same as the group of the four M06, M06L, M062x and M06HF functionals. There was no preference between the later group of the four M06 functionals.

It is surprising, according to the best of our knowledge, that there are no previous studies of the vibrational spectra of 12t4. It is interesting to see how the scaled force field at the different levels of theory would be able to reproduce the experimental spectra. Such study, since 12t4 is relatively small molecule of high $D_4$ symmetry, of how the assignment of the calculated to the experimental bands would depend on not only on the symmetry and frequency order but also on the intensity is being planned in our laboratory. This is in regard to the interesting finding of Jalkanen and Stephens of the importance of considering the absorption intensity as well [93]. For 18c6, it is known that the molecule may exist in different conformations according to the solvent [94]. It is interesting to consider in the vibrational spectral study to be done in our laboratory to include such solvent effects taking into consideration the recent computational and experimental results by Jalkanen et al. [95] of the role of hydration in the determination of the structure and vibrational spectra.

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