Structural Study on the Complex of Ortho-Ester Tetra Azophenylcalix[4]arene (TEAC) with Th(IV)

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Abstract

A new 1:1 complex between Ortho-Ester Tetra-Azophenylcalix[4]arene (TEAC) and Thorium(IV) was found in weakly acidic medium (pH =4-5), λ_{max} = 520 nm, Beer's law was obeyed in the range $2.5 \times 10^{-6} - 2.5 \times 10^{-5}$ mol.L^{-1} of Th(IV), the limit of detection was 1.0×10^{-6} mol.L^{-1} and linear regression equation was determined to be: absorbance (A) = $0,248 \times C(10^{-5}$ mol.L^{-1}) + $0,02$ (R^2 = 0,990, n =7). The FT-IR, HNMR, Raman spectroscopies were also used to provide the existence of this complex, and the Molecular Mechanics (MM) method in Arguslab software was applied to optimize the structure. The energy of the system, QEq charge, bond lengths and bond angles were also calculated by this program. Combining all data, the structure of complex TEAC - Th(IV) has been proposed.

Keywords: Azocalixarene, Spectroscopy, Thorium, Complex, Molecular Mechanics, Calculation

1. Introduction

Calixarenes, which are accessible by the base-catalyzed condensation of para-substituted phenols with formaldehyde, are ideal frameworks for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest since the incorporation of a suitable sensory group into the calixarene results in a tailored chromogenic receptor. Azocalixarenes, which have a conjugated chromophore azo (-N=N-) group in p-positions. These compounds belong to an important class of organic colorants and consist of at least a conjugated chromophore azo (-N=N-) group and two or more aromatic rings. Some investigations indicated that azocalix[4]arenes may exist in two possible tautomeric forms, namely an azophenol form and quinone–hydrazone (Karci, F., Sener, I & Delig˘oz, H. 2003, Kim,T.H et al. 2008). Many interesting aspects of complexation of alkali and alkaline earth metal ions were reported by studying the absorption behavior of chromophoric groups (Shinkai. 1991) Among the azophenolic supramolecules, azocalix[4]arenes are especially attractive for their efficient ionophoric properties towards some of important guest ions such as Ca^{2+}, Ba^{2+} (Kim, T.H et al 2008). There were relatively few reports on the design of sensor for transition metal ions as Cu^{2+}, Pb^{2+}, Ni^{2+} (Lua, L., Zhub, S., Liua, X., Xiec, Z., & Yanc, Xi. 2005, Ma, Q.L et al 2001). A lead ion-selective electrode was made from calixarene carboxyphenyl azo derivative (Lu, J., Chen, J & He, X. 2002). Besides, the extraction procedures were developed based on calixarene for metal cations like Cr^{3+},

Ag^+, Zn^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, (Deligoz, H & Erdem, E. 2008). Moreover, the spectroscopic methods were used for determination of Rh^{3+}, Cu^{2+} and Pb^{2+} in real samples (Kumar, A., Sharma, P., Chandel, L.K & Bhagwan, L.K. 2008; Tan, L.V & Le, N.T.N. 2010). In 2009, a new membrane containing p-(4-n-butylphenylazo)calix[4]arene as an electroactive material was used to fabricate a new cobalt(II)-selective sensor (Kumar, P. K & Yoon-Bo Shim. 2009). Recently, we had also reported that 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl)(azo)phenyl]calix[4]arene (TEAC) formed selective complexation with Thorium ion in weak acid solution, the complex ratio is 1:1, we found that the absorption peak at 520 nm of TEAC –Th(IV) appeared only 10s after the addition of Th(IV) to the TEAC reagent, the equilibrium was attained in ca. 2 min. The molar absorptivity coefficient (ε) is 2.5×10^4 L.mol⁻¹. cm⁻¹ (Hieu, T.Q., Tuan, N.N & Tan, L.V. 2010). In this report, we would like to introduce spectral data combined with Molecular Mechanics method (MM) in Arguslab program 4.01 (Rodica D. B. et al 2008) for predicting the mechanism and the structural of the complex formation between metal ion and azocalixarene.

2. Experiments

2.1 Apparatus and chemicals

Uv/Vis Lamda 25(Perkin Elmer), FT-IR: Bomen DA 8 spectrometer as KBr pellets (Canada) and ¹HNMR spectroscopy: AVANCE- 600FT-MNR 600 MHz (Germany). Fourier-transform Raman spectroscopy was carried out in the macroscopic mode with a specimen footprint of about 100 microns using a Bruker IFS 66 instrument with a FRA 106 Raman module (Korea).

All chemicals and solvents used were of analytical grade and used without further purification unless mentioned. Double-distilled and degasified water was used throughout HNO_3 65%, MeOH, MeCN, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $Ni(NO_3)_2$, CH_3COOH, NaOH, $NaNO_3$, $Th(NO_3)_4.5H_2O$; $UO_2(NO_3)_2$, $La(NO_3)_3$, $Sm(NO_3)_3.6H_2O$ were also used.

The reagent Ortho-Ester Tetraazophenyl Calixarene (TEAC) was synthesized and reported (Kim,T.H et al 2008) (Fig.1)

2.2 Calculation

The MM method is well adapted for geometrical optimizations and investigates different charge models in a force-field approach for calculating structural data of organic reagent as bond lengths, bond angles (Suwattanamala, A., Magalhaes, A & Gomes, N. F. 2005). The Hamiltonians have been used to provide an accurate description of supramolecular compounds such as proteins (Vreven. T et al 2002, Barbiric, D. J., Castro E. A & De Rossi R. H. 2000), so we thought MM method might be suitable for the same compounds as azophenylcalixarene derivatives.

The charge equilibration (QEq) procedure was developed and used in many applications on organic and inorganic systems (Rappé, A. K. & Goddard, W. A. 1991) and charges were also calculated according to charge equilibration method by other authors (Ersan, D & Goddard, W.A.1999, Zang, M & Fournier, R. 2009).

Herein, we carried out the MM method calculation by using the Arguslab 4.01 program. The optimized geometries were calculated to set the gradient in the hypersurface of energy to be lower (in module) than 0.1 kcal/mol. The max step taken 20000 cycles for energy and recalculated QEq charge every 20 steps.

3. Results and discussion

3.1 Spectroscopy

The absorption spectra of the reagent TEAC and TEAC–Th(IV) complex under the optimum conditions are shown in Fig. 2. In the figure, the spectra of TEAC and TEAC–Th(IV) complex were shown against water as blank. The absorption peak of the reagent TEAC is located at 385 nm, corresponding $\pi \rightarrow \pi^*$ transition of the -N= N- bond, which is in accordance with typical diazo spectra as observed by other workers (Karci, F et al 2003, Ma, Q.L et al 2001, Lilin Lua. L et al 2005) whereas the absorption peak of the TEAC–Th(IV) complex is located at 520 nm. Hence, a very large wavelength shift ($\Delta\lambda$= 135 nm) is obtained.

The results FT-IR spectra of TEAC showed a weak band within the range 3450 cm⁻¹ corresponding to -OH. The low value indicated that the -OH groups were involved intra molecular hydrogen bonds, a weak band or shoulder located at 3165 cm⁻¹ which was assigned to aromatic C-H, and stretching vibration of the C=O (ester groups) leading to the band located at 1720cm⁻¹, asymmetrical stretching vibration of the N=N group leading to the band located in the 1512 cm⁻¹ region. The TEAC may exist in two possible tautomeric forms, namely an azo-enol and keto-hydrazo. The infrared spectra of this compound (in KBr) showed broad -OH bands around 3450 cm⁻¹ and C-O bands at 1159–1120 cm⁻¹. It is suggested that this compound does not exist as the keto-hydrazo form in the solid state.

In the TEAC-Th complex, the stretching vibration of the N=N groups at 1512 cm^{-1} decreased and the new band observed at 1639 cm^{-1} (-C=N) to provide conclusive evidence concerning the bonding of nitrogen to the metal ion. So these phenomena were important evidences to provide the interaction of TEAC with Th(IV) at azo region.

The ^{1}HNMR spectrum of TEAC showed a deuterium exchangeable singlet at 10 ppm for -OH, multiplet for the aromatic protons of calixarene aryl σ – framework between 6.53-7.91 ppm (24 protons) two broad singlets at 4.07 and 2.40 ppm representing the methylene bridge protons and a broad singlet at 1.23 ppm representing proton of the methyl group. The structures of TEAC were examined in solution by high-resolution NMR. The HNMR spectrum measured in DMSO-d_6 at 25°C showed broad bands of hydroxyl (9.997 (OH)). The ^{1}HNMR spectrum of TEAC -Th(IV) showed a small downfield in the δ values of the peaks occurred in the aromatic region of the calixarene protons and the signal of protons in –OH groups disappeared. Because the interaction of TEAC with Th(IV) may happen at the central annulus of reagent compound.

The Raman spectra were studied in solution state against TEAC as blank in the range from 200 cm^{-1} to 800 cm^{-1}, because stretching frequency of the bonds between metal ions and function groups for example M^{n+}-N often appear in this range. After measurement, the spectra of TEAC with alkaline metal ions had two peaks around 460 cm^{-1} and 630 cm^{-1}. A new peak appeared at 405 cm^{-1} in the Raman spectra of TEAC-Th(IV) so this phenomenon was equal to the bonds of Th(IV) with nitrogen atoms in the reagent.

From results of ^{1}HNMR spectra we could remark that Th(IV) ion was located at central annulus (azo region) of the compound. A new band in the FT-IR appeared at 576 cm^{-1} and a new peak occurred at 405 cm^{-1} in the Raman spectra which could be attributed metal-azo back bonding.

The ESI-MS of TEAC-Th(IV) was recorded in solution. We used ionizing energy typically 70 eV to promote efficient ionization and to produce molecular and fragment ions used for chemical characterization and identification. Interestingly, in the MS spectra appeared the fragment ion TEAC-Th (m/z =1357). Thus, this information provided that the is a 1:1 complex of TEAC with Th(IV). Besides, some fragment ions with higher mass also appeared, this phenomenon can be explained that in TEAC has holes space so some of MeOH moleculars were fallen in to these spaces and interacted with TEAC via host-guest interaction.

3.2 Optimization of the complex model

3.2.1 Total energy

Optimized geometry for the compound was calculated by using the MM method based on ArgusLab 4.01. The final geometry energy (MM Bond, MM Angle, MM Dihedral, MM ImpTor, MM vdW MM Coulomb) of TEAC and its complex were calculated. The data on table 1 of four complex forms show the total energy of systems which were arranged as follows: TEAC-Th^{4+} (101.65 kcal/mol) < TEAC-$Th(OH)^{3+}$ (121.40 kcal/mol) < TEAC-$Th(OH)_2^{2+}$ (142.90 kcal/mol) < TEAC- $Th(OH)_3^{+}$ (162.01 kcal/mol)

3.2.2 Bond lengths and bond angles

The Fig 3 showed the numbering scheme of TEAC complex. The Tables 3 and 4 showed some important bonds lengths of two tautomeric form (**a**), (**b**) of TEAC and its complex. From these results, we could remark the following: the length of C(25)-O(1) is longer (1.407 A^0) than in azophenol (**a**) and in the complex (**c**) (1.279 A^0). Which could be explained that the bond C(6)-O(36) is single bond in conformation (**a**) and double bond in keto-hydrazo (**b**). In the complex, Thorium ion might attract electrons to form bonds with Nitrogen atom, so the density of electrons of –C=O groups decreased, so endurance of these bonds was less stable. The lengths of the bonds N-N were different 1.270 A^0 in (**a**) and 1.400A^0 in (**b**) and 1.401 A^0 in complex. We also compared these values with those of the same azo compound which was reported (Noelle, E., Lecocq, S., Perrin, R & Monique. 1993), and found a good agreement. The distances between Thorium atom and nitrogen atom are about 2.69 A^0-2.89 A^0.

The bond lengths between Th atom and N atoms, O atoms of TEAC-Th^{4+} complex are the shortest in the four possible complexes. These results could be used to explain the advantage in the complex formation of TEAC and Th^{4+}. Some selected bond angles were shown on Table 5, these data agree with previous work (Noelle, E., Lecocq, S., Perrin, R & Monique. 1993).

3.2.3 Intramolecular hydrogen bond

At the lower rim of the conformation (**a**), the intramolecular hydrogen bonds between hydroxyl groups appeared. Based on these intramolecular hydrogen bonds, a second ring was formed to make the conformation more stable. In the keto hydrazo (**b**), because of the transformation protons H^+ from hydroxyl groups to –N=N- groups, these

intramolecular hydrogen bonds were absent. So the distances O(1)…O(2) in (**b**) is larger than in (**a**). These data are in good agreement with another azo calix[4]arenes (Noelle. E et al 1993). In the complex, Thorium ion formed bonds with –NH-N=, hence the distances N(2)…N(6), N(4)…N(8) are the shortest in complex and next is in (**a**), and the last is in (**b**).

3.2.4 QEq charge

The QEq parameters were optimized for TEAC to represent the atomic charges by quantum chemical calculations with atom types for H, C, N and O atoms. The total QEq charge of azo region is -1.598. This significantly showed that Thorium could form ionic bonds with nitrogen atoms via electrostatic effect.

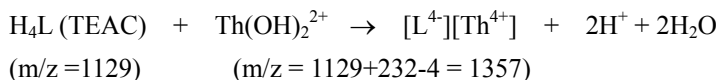### *3.3 The formation complex mechanism*

3.3.1 The ratio of complex

For the complexation ratio between the host and metal ions, the Job's plot experiment was carried out by varying the concentration of both host and metal ions. The maximum absorbance was observed at a mole fraction of [TEAC]/([TEAC]+[Th(IV)]) of about 0.5 corresponding to a TEAC–Th(IV) complex ratio of 1:1.

3.3.2 Effect of pH

The effect of pH on the absorbance of TEAC- Th(IV) at 520 nm was checked. The maximum absorbance of the complex is obtained in the range of pH=4-5, so this pH condition was chosen for the following experiments. Different pH values were obtained by varying the relative amounts of NaAc and HAc, and confirmed by a digital pH-meter.

In the pH range of acidic environment, thorium exists in many forms such as Th^{4+}(pH <3), $Th(OH)^{3+}$ (pH 3.0÷4.0), $Th(OH)_2^{2+}$ (pH 4.0÷5.0), $Th(OH)_3^+$ (5.0÷6.0) (Higashi & Shinnosuke. 1959). Which form of Th(IV) is involved the complex? The size of $Th(OH)_2^{2+}$ is more bulky than Th^{4+}. Moreover, its charge is lower than Th^{4+} and the total energy of TEAC-Th^{4+} (was calculated by Arguslab program ≈ 101.65kcal/mol) is the smallest in the four possible complexes. Combining information of mass spectra in the section 3.1 (a fragment ion TEAC-Th with m/z is 1357) and result of calculated energy we thought thorium might exist as Th^{4+} in complex. The reaction for the complex formation could be proposed in MeOH solvent as such(see more Fig.4):

$$H_4L \text{ (TEAC)} \quad + \quad Th(OH)_2^{2+} \quad \rightarrow \quad [L^{4-}][Th^{4+}] \quad + \quad 2H^+ + 2H_2O$$

(m/z =1129)   (m/z = 1129+232-4 = 1357)

Combining data from HNMR, IR, Raman, and UV-VIS spectra and using MM method for calculating energy, QEq charge, bonds length and bonds angels, we could recommend the mechanism of complex formation as follows: firstly, the $Th(OH)_2^{2+}$ ion was trapped in center of TEAC and then four protons of TEAC were abstracted to convert TEAC from azo-enol to keto-hydrazo tautomer. Finally, the ionic bonds between four nitrogen atoms in reagent with Th^{4+} were formed; this structure of system was stabilized by oxygen atoms in the ester groups to form four coordinate bonds.

3.3.3 The stability constant of complex

The stability constant was estimated by monitoring the decrease in the intensity of the absorbance at the peak with the data reduction being effected using Benesi-Hildebrand plots (Wang, R & Yu Z.W. 2007).

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{sat} - A_0)} + \frac{1}{(A_{sat} - A_0).K.[Guest]}$$

Where K is the stability constant, *A* the observed absorbance at each metal ion concentration tested, A_0 is the absorbance of TEAC in the absence of metal ion, A_{sat} is the absorbance at the point of saturation and *[Guest]* is the concentration of metal ion. The stability constant (*K*) was calculated to be 6.13×10^4 mol^{-1}.L by this method.

4. Conclusion

The formation complex mechanism between TEAC and Th(IV) was proposed based on spectral data and the structural of this complex was optimized and calculated by MM method in Arguslab 4.04 program. A method for determination of thorium in environment samples is being built which will report in next work.

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Table 1. Total energy calculating by MM for some forms of complex

N_0	Form of Th(IV) in complex	Total Energy (kcal/mol)
1	TEAC-Th^{4+}	101.65
2	TEAC-Th(OH)$^{3+}$	121.40
3	TEAC- Th(OH)$_2^{2+}$	142.90
4	TEAC- Th(OH)$_3^{+}$	162.01

Table 2. Bonds length of Th with N and O in four possible complex forms

Bond lengths	TEAC-Th^{4+}	TEAC-Th(OH)$^{3+}$	TEAC- Th(OH)$_2^{2+}$	TEAC- Th(OH)$_3^{+}$
Th(1)-N(2)	2.89	3.42	3.56	3.76
Th(1)-N(4)	2.76	3.54	3.68	3.69
Th(1)-N(6)	2.69	3.67	3.79	3.71
Th(1)-N(8)	2.75	3.34	3.41	3.63
Th(1)-O(5)	3.45	5.67	6.89	7.12
Th(1)-O(7)	3.32	5.32	7.32	7.62
Th(1)-O(9)	3.27	5.23	6.23	7.89
Th(1)-O(11)	3.31	5.82	6.82	7.21

Table 3. Selected bond distances of TEAC and TEAC-Th^{4+}

Bonds	(**a**)	(**b**)	TEAC-Th^{4+}	Reference (Noelle, E., Lecocq, S., Perrin, R & Monique. 1993)
C(6) - O(36)	1.407	1.279	1.279	1.398
C(23) - N(1)	1.434	1.302	1.301	1.402
N(1) -N(2)	1.270	1.400	1.401	1.247
N(2)-C(57)	1.434	1.434	1.434	1.402

Table 4. Distance between some selected atoms (A^0)

Distances	(**a**)	(**b**)	TEAC-Th^{4+}	Reference (Noelle, E., Lecocq, S., Perrin, R & Monique. 1993)
O(1)…O(2)	2.765	2.886	3.751	2.885
O(2)…O(3)	2.761	2.885	3.751	2.693
O(3)… O(4)	2.764	2.885	3.752	2.647
O(4)… O(1)	2.681	2.884	3.751	2.622
N(2)…N(6)	6.152	7.171	5.205	-
N(4)…N(8)	7.124	7.175	5.106	-

Table 5. Selected bond angles in complex (deg)

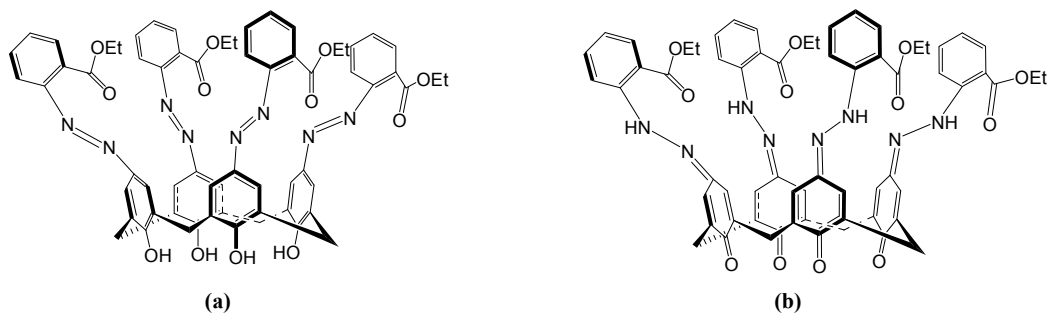| Atom 1	Atom 2	Atom 3	Angles(Deg)	Atom 1	Atom 2	Atom 3	Angles(Deg)
C(1)	C(24)	C(25)	120.00	N(1)	N(2)	C(57)	106.70
C(2)	C(1)	N(32)	120.00	N(1)	N(2)	Th(1)	106.70
C(23)	N(1)	N(2)	106.70	N(4)	Th(1)	N(6)	90.00

Figure 1. Two tautomeric forms of Ortho-Ester Tetraazophenyl Calixarene (TEAC): (**a**) azo-enol; (**b**) keto-hydrazo
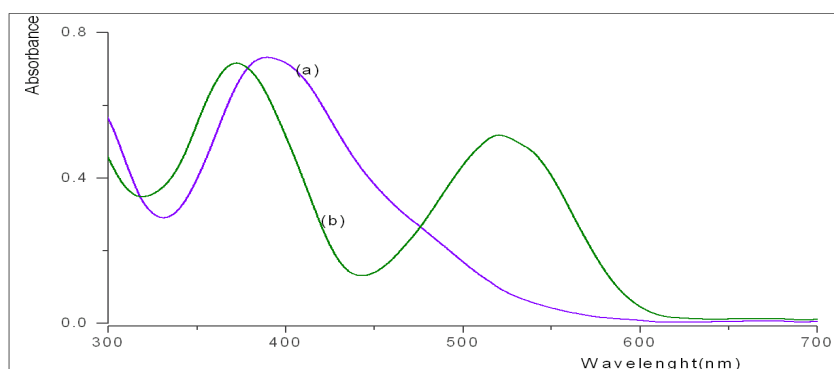

Figure 2. Absorption spectra of TEAC and its Th(IV) complex at pH 4.5

(a) 2.0×10^{-5} mol. L^{-1} of TEAC solution against water as blank;

(b) 2.0×10^{-5} mol. L^{-1} of TEAC and 2.0×10^{-5} mol .L^{-1} of Th(IV) against water as blank
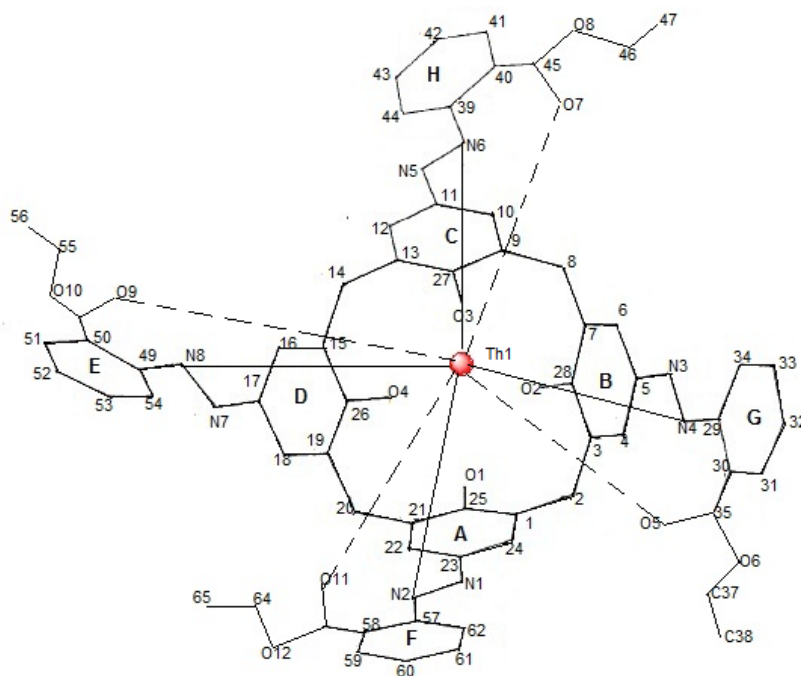

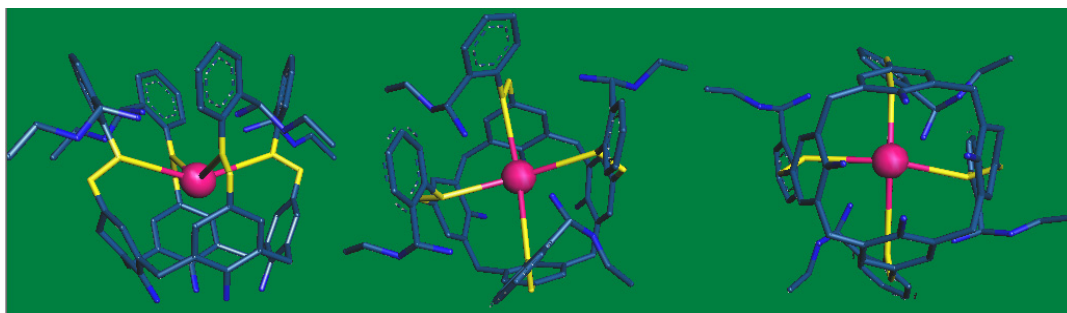Figure 3. The numbering scheme of TEAC-Th(IV) complex

Figure 4. Side view of 3-D structure of the TEAC-Th^{4+} complex (hydrogen atoms omitted for clarity)