INTRODUCTION

Calixarenes act as versatile building blocks in supramolecular and coordination chemistry, since both their lower and upper rims may be derivatized to induce specific functionalities of rate supramolecular structures. π-stacking, H-bonding or coordination interactions, of elaborate supramolecular structures. Azocalix[n]arenes are one of the most useful and widely employed ligands for transition metal ions, as well as for the self-assembly, through π-stacking, H-bonding or coordination interactions, of elaborate supramolecular structures. Azocalix[n]arenes are one of the most useful and widely employed ligands for transition metal complexes. Many of which display excellent activity and selectivity in homogenous catalytic reactions. Among these works, azocalixarenes have been mainly studied: azicalixarenes bridging phenylazo moieties on the upper rim and lower rim, double azocalixarenes, azocalixcrown ethers.

Azocalix[4]arenes are especially attractive for their efficient ionophoric properties towards some of important guest ions such as Ca
+2, Sr
+2 or Ba
+2. However, there were relatively few reports on the design of sensor for transition metal ions as Cu
+2, Pb
+2, Ni
+2 or Fe
+3 which is made a lead ion-selective electrode based on a calixarene carboxyphenyl azo derivative. Besides, the extraction procedures were developed based on calixarenes for metal cations like Ag
+1, Zn
+2, Cu
+2, Fe
+3, Al
+3. Moreover, spectroscopic methods also built for determination of Pb
+2, Rh
+3, Cu
+2. 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 by Pankaj12. Recently, we had also reported that 5,11,17,23-tetra[(2-ethyl acetooxyphenyl)] (azo)phenyl calix[4]arene formed selective complexation with Th
+2 ion in alkali solution20. In this report, we would like to introduce 5,11,17,23-tetra[(2-benzoic acid)(azo)phenyl]calix[4]arene formed selective complexation with Ce
+4 ion in weak acid solution and spectroscopic data combined with mechanism molecular method in ArgusLab program 4.0121 for predicting the mechanism of the complex formation between metal ion and azocalixarene.

EXPERIMENTAL

All chemicals and solvents used were of analytical grade and used without further purification unless otherwise mentioned. Doubles distilled and deaggregated water was used throughout; MeOH, MeCN; Pb(NO
+3); Cr(NO
+3); Ni(NO
+3); CH
+3COOH; NaOH; NaNO
+3; Ce(NO
+3); Th(NO
+3); 5H
+2O; UO
+3(NO
+3); La(NO
+3); Sm(NO
+3); 6H
+2O (Merck); UV-VIS Lambda 25 (Perkin Elmer), FT-IR: Bomen DA 8 spectrometer.
as KBr pellets (Canada) and 1H NMR spectroscopy: AVANCE-600FT-MNR 600 MHz (Germany).

We carried out molecular mechanics method calculation using the Arguslab 4.01 program. Molecular mechanics method are well adapted for geometrical optimizations and investigated different charge models in a force-field approach for calculating structural data of organic reagent as bond lengths, bond angles. Charges were calculated according to charge equilibration (QEq) method. A fluctuating charge model, based on QEq approach, for describing polarization effects was developed. These Hamiltonians have been revealed to provide an accurate description of supramolecular compounds as proteins, so we thought molecular mechanics method may be suitable for the same compounds as azophenylcalixarene derivatives. The optimized geometries were calculated setting the gradient in the hypersurface of energy to be lower (in module) than 0.05 kcal/mol. The max step taken 20000 cycles for energy and recalculated QEq charge every 20 steps. Structures of BAPC and its Ce complex are shown in Fig. 1.

RESULTS AND DISCUSSION

Spectroscopy: The absorption spectra of the reagent BAPC and its BAPC-Ce complex under the optimum conditions are shown in Fig. 2. In the figure, the spectra of BAPC and BAPC-Ce complex were showed, respectively against water blank. As the observation, the maximum absorption peak of the reagent BAPC lies at 365 nm, corresponding $\pi \rightarrow \pi^*$ transition of the -N=N- bond, which are in accordance with typical diazo spectra as observed by other worker whereas the absorption peak of the BAPC-Ce complex is located at 515 nm. Hence, a very large wavelength change ($\Delta \lambda = 150$ nm) is obtained. We also investigated the effect of pH on absorbance and the result showed that the maximum of absorption spectra of the complex at pH condition of 6.0, which was chosen for the following experiments. The absorption peak at 515 nm of BAPC-Ce appeared only 10 s after the addition of Ce to the BAPC reagent, the equilibrium was attained in ca. 2 min and the Job’ plot method was used to find the ratio of complex, a 1:1 complex was determined at chosen conditions. And after that, we had studied the selectivity of BAPC reagent with Ce ions at presence other metal ions in the same condition. The absorption spectra were recorded and played on Fig. 2. Its result showed that BAPC possesses good selectivity towards Ce even other ions are present (Fig. 2).

We next investigated the FT-IR of BAPC and BAPC-Ce complex. From results on Table-1, the structure was confirmed by the appearance of an azo band at 1506 cm$^{-1}$ in the FT-IR spectra of this compound. The FT-IR spectra showed a weak band within the range 3097 cm$^{-1}$ corresponding to -OH. The low value reveals that the -OH group was involved in intra molecular H-bonding. The FT-IR spectra also shows a weak band or shoulder located at 2989 cm$^{-1}$ which was assigned to aromatic C-H and stretching vibration of the C=O group leading

![Fig. 1. Structures of BAPC and its complex (a) azophenol conformation; (b) keto-hydazo; (c) BAPC-Ce complex](image-url)
to the band located at 1589 cm$^{-1}$, asymmetrical stretching vibration of the N=N group leading to the band located in the 1589 cm$^{-1}$ region. The BAPC may exist in two possible tautomeric forms, namely an azo-enol and keto-hydrazo$^{1}$ deprotonation of the two tautomers leads to a common anion. The infrared spectra of all compounds (in KBr) showed broad -OH bands at 3341-3072 cm$^{-1}$ and C-O bands at 1132-1116 cm$^{-1}$. It can be suggested that these compounds do not exist in the keto-hydrazo form in the solid state.

While the stretching vibration of the N=N groups in BAPC-Ce$^{4+}$ increased with formation of the complex BAPC-Ce$^{4+}$ (1556 cm$^{-1}$), this phenomenon showed an important evidence to provide the interaction of BAPC with Ce$^{4+}$ at azo region of compound which could be attributed to the metal-azo back bonding.

**Fig. 3.** Optimized geometry by the ArgusLab 4.01 program for BAPC and Its complex. (a) Azophenol; (b) Keto-hydrazo; (c) BAPC-Ce$^{4+}$ complex

**Fig. 4.** ESI-MS spectrum of the complex BAPC-Ce (IV) in solvent MeOH

**ESI-MS:** We carried out mass spectrometry of the complex to seek the parent ion of the complex with the desired information on mass spectrometry. There are also few evidences to confirm the components of the complex. Results are presented in Table-6 and Fig. 4.

By analyzing the pieces of the complex ions with ESI-MS technique, we found that complexing ratio between BAPC and Ce was 1:1; this is consistent with the works published previously. The emergence ion fragments $[C_{56}H_{41}N_{8}O_{12} + Ce]$ mass of 1153.14 when complexing BAPC show has completely eliminated 4 the H$^+$ ion of the aromatic hydroxyl groups. Meanwhile, reagents converted to keto-hydrazo and Ce ions form electrostatic links with four atoms of azo groups.

**Table-1**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>BAPC</th>
<th>BAPC-Ce$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (OH)</td>
<td>3412, 3072</td>
<td>3460</td>
</tr>
<tr>
<td>$\nu$(C-Har)</td>
<td>2929</td>
<td>2933</td>
</tr>
<tr>
<td>$\nu_{\text{adv}}$ (C=C)</td>
<td>1720</td>
<td>1664</td>
</tr>
<tr>
<td>$\nu$(N=N)</td>
<td>1506</td>
<td>1556</td>
</tr>
<tr>
<td>$\nu$(C=O)</td>
<td>1589</td>
<td>1562</td>
</tr>
<tr>
<td>$\nu$(Ce-N)</td>
<td>–</td>
<td>594</td>
</tr>
</tbody>
</table>

Table-6 and Fig. 4 can be seen that the fragments m/z corresponding to 1016.53, 1153.14, 1133.84 are evidence to show the existence of Ce in the complex molecule; where m/z
ArgusLab 4.01 (Fig. 3). The final geometry energy (MM Bond, MM Angle, MM Dihedral, MM ImpTor, MM vdW, MM compound) was calculated using MM method based on molecule. 

1134.84 piece also is likely to lose the entire molecule a water with a piece of metal ions with azocalixarene and Vol. 24, No. 5 (2012) Studies on the Complex of Benzoic Acid Azo PhenylCalix[4]arene (BAPC) with Ce⁴⁺. 2327

Optimized the complex model: Optimized geometry for compound was calculated using MM method based on ArgusLab 4.01 (Fig. 3). The final geometry energy (MM Bond, MM Angle, MM Dihedral, MM ImpTor, MM vdW, MM Coulomb) of two tautomeric forms of BAPC and its complex were calculated and arranged as below: complex (c) (91.17 kcal/mol) < conformation (b) (87.48 kcal/mol) < conformation (a) (122.48 kcal/mol). The energy of systems demonstrated an equation mixture of two tautomers. However, the absorption spectra of BAPC at pH condition of 6.0 only appeared one peak at 365 nm. In acetone, this compound showed two peak at 354 and 470 nm, this reason could be explained by the effect solvent.

In Table-2, the bond length between important atoms is showed. It can be seen that C(5)-C(6) is 1.4580 Å and in the aro compounds, the N=N bonds (1.379 Å) in azophenol (a) and next is complex and minimum in ketoquinone (b). The reason could be explained the bonding Ce-N which extended the bond in azocalixarene. The distances between Ce⁴⁺ atom and nitrogen atoms are about 4.17-4.35 Å.

Table-2 showed some important bonding lengths of two tautomeric form (a), (b) and BAPC-complex. From these results we could remark that: the length of C(6)-O(36) is maximum in ketoquinone (b) and double bond in tautomeric (a) and simple bond in tautomeric (a) and double bond in ketoquinone (b). In the complex, Ce⁴⁺ ion formed bonds with -NH-N=, hence the distances N(33)…N(30), N(49)…N(35) in are the shortest and next is in (b) and the last is in (a). Some of important bond angles were showed in Tables-5.

As we had present, BAPC existed azophenol in solid state, hence the data of (a) is very suitable with crystal azocalixarene. The distances between Ce⁴⁺ atom and nitrogen atoms are about 3.91-4.58 Å.

At lower rim in conformation (a), it showed the intramolecular hydrogen between hydroxyl groups. These values are in good agreement with intramolecular H-bonds between the hydroxy groups usually found in calix[4]arenes except the value 2.681-2.765 Å. Based on this intramolecular hydrogen, a second ring will be formed and made conformation was better stable. In the ketoquinone tautomeric, protons H were transformed to -N=N- and constituted -NH-N=, hence the H-bondings disappeared. So distances between O…O as O (36)...O (37) in (b) is larger than its in (a). Moreover, in the complex, Ce⁴⁺ ion formed bonds with -NH-N=, hence the distances N(33)…N(30), N(49)…N(35) in are the shortest and next is in (b) and the last is in (a). Some of important bond angles were showed in Tables-5.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(a)</th>
<th>(b)</th>
</tr>
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<tbody>
<tr>
<td>N (5)</td>
<td>-0.189</td>
<td>-0.184</td>
</tr>
<tr>
<td>N(6)</td>
<td>-0.173</td>
<td>-0.155</td>
</tr>
<tr>
<td>N(7)</td>
<td>-0.194</td>
<td>-0.204</td>
</tr>
<tr>
<td>N(1)</td>
<td>-0.197</td>
<td>-0.187</td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.177</td>
<td>-0.152</td>
</tr>
<tr>
<td>N(3)</td>
<td>-0.233</td>
<td>-0.204</td>
</tr>
<tr>
<td>N(4)</td>
<td>-0.194</td>
<td>-0.152</td>
</tr>
<tr>
<td>O (1)</td>
<td>-0.393</td>
<td>-0.393</td>
</tr>
<tr>
<td>O (4)</td>
<td>-0.368</td>
<td>-0.382</td>
</tr>
<tr>
<td>O (3)</td>
<td>-0.382</td>
<td>-0.392</td>
</tr>
<tr>
<td>O (2)</td>
<td>-0.392</td>
<td>-0.382</td>
</tr>
<tr>
<td>C(56)</td>
<td>0.53</td>
<td>0.534</td>
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<tr>
<td>O (12)</td>
<td>-0.562</td>
<td>-0.525</td>
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<tr>
<td>O (11)</td>
<td>-0.474</td>
<td>-0.493</td>
</tr>
<tr>
<td>C (35)</td>
<td>0.585</td>
<td>0.534</td>
</tr>
<tr>
<td>O (6)</td>
<td>-0.514</td>
<td>-0.539</td>
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<tr>
<td>O (5)</td>
<td>-0.429</td>
<td>-0.482</td>
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<tr>
<td>C (42)</td>
<td>0.621</td>
<td>0.534</td>
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<tr>
<td>O (7)</td>
<td>-0.418</td>
<td>-0.494</td>
</tr>
<tr>
<td>O (8)</td>
<td>-0.532</td>
<td>-0.527</td>
</tr>
<tr>
<td>N (8)</td>
<td>-0.241</td>
<td>-0.154</td>
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<table>
<thead>
<tr>
<th>Bonds</th>
<th>Azophenol (a)</th>
<th>Ketoquinone (b)</th>
<th>BAPC-Ce⁴⁺</th>
<th>Reference (Noelle Ehlinger et al. 1993)</th>
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</thead>
<tbody>
<tr>
<td>C(22)-C(23)</td>
<td>1.379</td>
<td>1.458</td>
<td>1.458</td>
<td>1.378</td>
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<tr>
<td>C(1)-C(25)</td>
<td>1.379</td>
<td>1.323</td>
<td>1.323</td>
<td>1.376</td>
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<tr>
<td>C(25)-O(1)</td>
<td>1.408</td>
<td>1.279</td>
<td>1.279</td>
<td>1.398</td>
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<tr>
<td>C(5)-N(3)</td>
<td>1.418</td>
<td>1.302</td>
<td>1.301</td>
<td>1.402</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.243</td>
<td>1.400</td>
<td>1.401</td>
<td>1.247</td>
</tr>
<tr>
<td>N(6)-C(36)</td>
<td>1.419</td>
<td>1.435</td>
<td>1.435</td>
<td>1.402</td>
</tr>
<tr>
<td>N(2)-Ce(1)</td>
<td>–</td>
<td>–</td>
<td>4.260</td>
<td>–</td>
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</table>

<table>
<thead>
<tr>
<th>Distances</th>
<th>Azophenol (a)</th>
<th>Ketoquinone (b)</th>
<th>BAPC-Ce⁴⁺</th>
<th>Reference (Noelle Ehlinger et al. 1993)</th>
</tr>
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<tbody>
<tr>
<td>O(1)...O(4)</td>
<td>2.965</td>
<td>3.045</td>
<td>3.020</td>
<td>2.885</td>
</tr>
<tr>
<td>O(4)...O(3)</td>
<td>2.958</td>
<td>3.039</td>
<td>2.945</td>
<td>2.693</td>
</tr>
<tr>
<td>O(3)...O(2)</td>
<td>2.920</td>
<td>2.946</td>
<td>2.936</td>
<td>2.647</td>
</tr>
<tr>
<td>O(2)...O(1)</td>
<td>2.911</td>
<td>2.934</td>
<td>2.880</td>
<td>2.622</td>
</tr>
<tr>
<td>N(2)...N(6)</td>
<td>10.113</td>
<td>8.485</td>
<td>7.496</td>
<td>–</td>
</tr>
<tr>
<td>N(4)...N(8)</td>
<td>9.754</td>
<td>8.462</td>
<td>7.533</td>
<td>–</td>
</tr>
</tbody>
</table>
The charge equilibration (QEq) method was applied to BAPC. The QEq parameters are optimized for BAPC to represent the atomic charges by quantum chemical calculations with atom types for H, C, N and O atoms. These results were shown in Table-5. The total QEq charges of azo region in tautomer (a) and (b) are -1.598, -1.387, respectively. This significant can provide formation ability ionic bonding of nitrogen atoms with Pb ion via electrostatic.

**Conclusion**

The complex formation of Ce$^{4+}$ with BAPC was investigated. Combined data from HNMR, IR, Raman, UV-VIS spectra and used MM method for calculating energy. QEq, distance bonds, we could explain the mechanism of complex. This reagent shows elective colour changes to Ce$^{4+}$ metal ion over other metal ions from yellow to red; which is mainly due to metal ion complexion-induced release of protons from the azoophenols to the quinone-hydrazone tautomer followed by internal complexation of the metal ion with aid of nitrogen atoms and ortho-ester carbonyl groups by 1:1 complexation event (Fig. 1).

**ACKNOWLEDGEMENTS**

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**REFERENCES**