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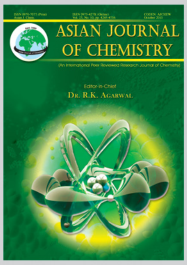

Spectroscopic and Structural Studies on the Complex of Benzoic Acid Azo PhenylCalix[4]arene (BAPC) with Ce^{4+}

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In the previous work, a reaction of Ce(IV) with (benzoic acid)(azo)phenylcalixarene (BAPC) at pH 6-7 has been studied. (Benzoic acid)(azo)phenylcalixarene reacted with Ce(IV) to form a 1:1 complex with maximum absorption at 515 nm and molar absorptivity of 7.81×10^4 L mol^{-1} cm^{-1}. Beer's law was obeyed in the range of 5.0×10^{-6}-2.0×10^{-5} mol L^{-1} of Ce(IV) and the detection limit was found to be 2.5×10^{-6} mol L^{-1}. Based on complex formation, a new method has been built to determine cerium in soil samples. The sand samples are decomposed by mixed acid (conc. H_2SO_4 and HF) in platinum crucible, after cooling, the residue was dissolved in dilute HCl and cerium is separated together with the lanthanides in the form of oxalate from zirconium, iron and the phosphate ion. The oxalate precipitate is dissolved in concentration nitric acid. In this work, the FT-IR, MS, UV-VIS spectroscopy were used to provide the existence of complex and the molecule mechanics was also studied for structural optimization and calculating the energy of system, bonding lengths, bonding angles. Combining all data, the mechanism of the complex formation between BAPC and Ce^{4+} could be explained.

Key Words: Azocalixarene, Spectroscopic, Cerium, Molecule mechanics.

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[1,2]. They are currently used in the design of chemical sensors, catalysts and selective ligands for the complexation of *d* and *f* metal ions, as well as for the self-assembly, through π-stacking, H-bonding or coordination interactions, of elaborate supramolecular structures[3-9]. 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: calixarenes bridging phenylazo moieties on the upper rim and lower rim, double azocalixarenes, azocalixcrowns[8-10].

Azocalix[4]arenes are especially attractive for their efficient ionophoric properties towards some of important guest ions such as Ca^{2+} or K^+ ion[11,12]. There were relatively few reports on the design of sensor for transition metal ions as Cu^{2+}, Pb^{2+}, Ni^{2+} [13-15] or Fe^{3+} [16] or made a lead ion-selective electrode based on a calixarene carboxyphenyl azo derivative[17]. Besides, the extraction procedures were developed based on calixarenes for metal cations like Ag^+, Zn^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}. Moreover, spectroscopic methods also built for determination of Pb^{2+}, Rh^{3+}, Cu^{2+} [11,18]. 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 Pankaj[12]. Recently, we had also reported that 5,11,17,23-tetra[(2-ethyl acetoethoxyphenyl) (azo)phenyl] calix[4]arene formed selective complexation with Th^{4+} ion in weak acid solution[19] and 5,11,17,23-tetra[(2-benzoic acid)(azo)phenyl]calix[4]arene formed selective complexation with Pb^{2+} ion in alkali solution[20]. 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 4.01[21] 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 degasified water was used throughout; MeOH, MeCN; $Pb(NO_3)_2$; $Cr(NO_3)_3$; $Ni(NO_3)_2$; CH_3COOH; NaOH; $NaNO_3$; $Ce(NO_3)_4$, $Th(NO_3)_4 \cdot 5H_2O$; $UO_2(NO_3)_2$, $La(NO_3)_3$, $Sm(NO_3)_3 \cdot 6H_2O$ (Merck); 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).

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[22]. Charges were calculated according to charge equilibration (QEq) method[23]. 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[24,25], 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^{4+} complex are shown in Fig. 1.

RESULTS AND DISCUSSION

Spectroscopy: The absorption spectra of the reagent BAPC and its BAPC-Ce^{4+} complex under the optimum conditions are shown in Fig. 2. In the figure, the spectra of BAPC and BAPC-Ce^{4+} 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[13,14] whereas the absorption peak of the BAPC-Ce^{4+} 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^{4+} appeared only 10 s after the addition of Ce^{4+} 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^{4+} 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^{4+} even other ions are present (Fig. 2).

We next investigated the FT-IR of BAPC and BAPC-Ce^{4+} 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

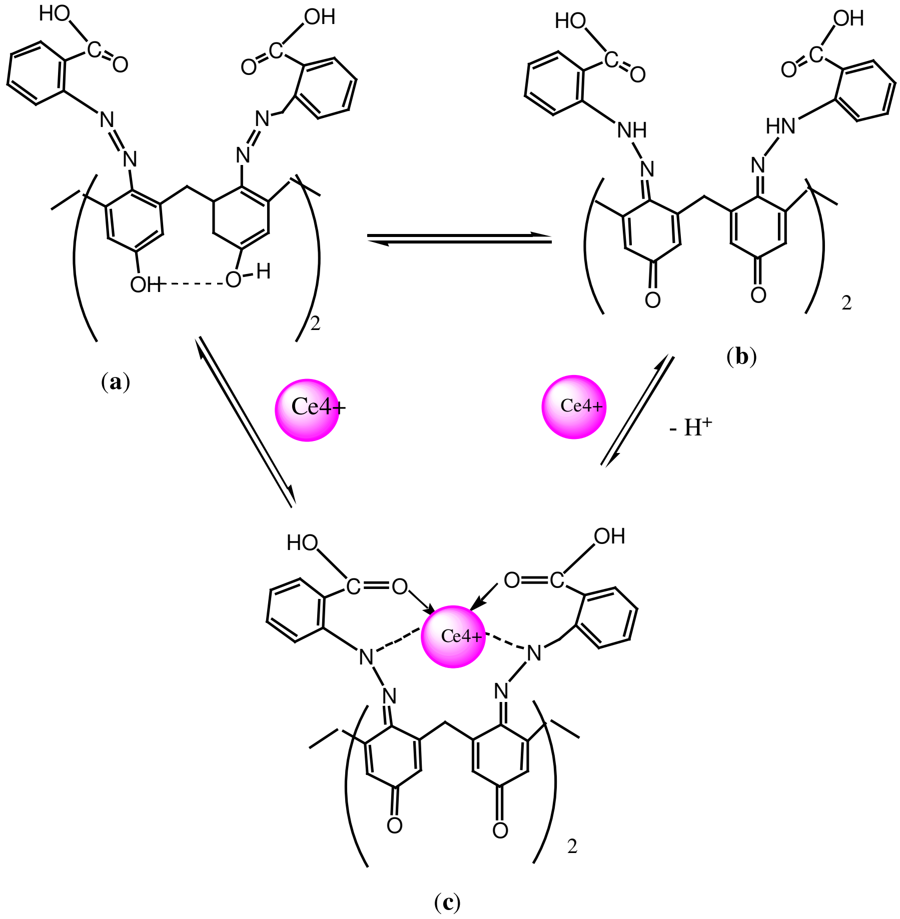

Fig. 1. Structures of BAPC and its complex (a) azophenol conformation; (b) keto-hydazo; (c) BAPC- Ce^{4+} complex

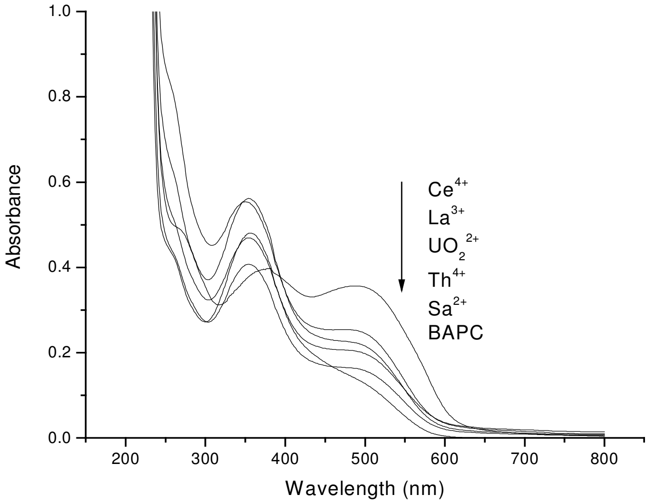

Fig. 2. Absorption spectra of BAPC-Mn$^+$ against water blank ([BAPC] = [Mn$^+$] = 2 × 10^{-5} M)

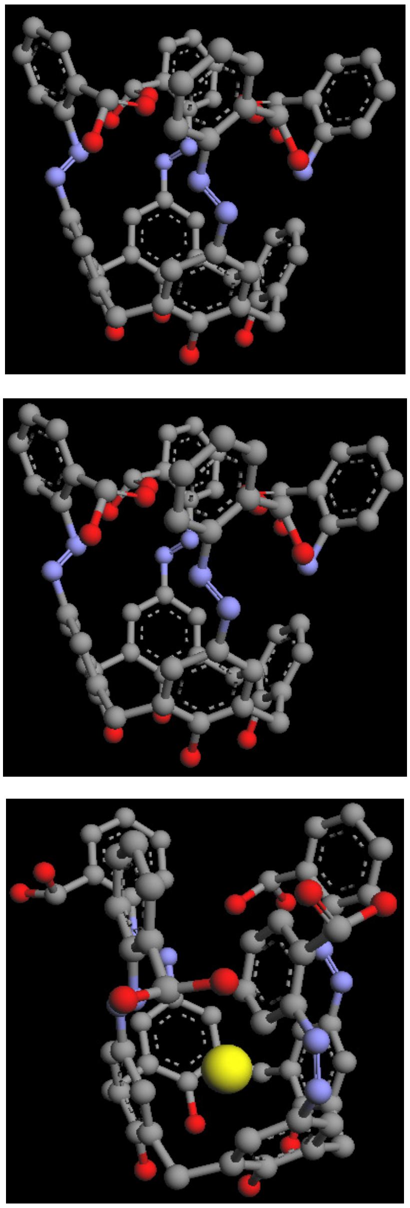

Fig. 3. Optimized geometry by the ArgusLab 4.01 program for BAPC and Its complex. (a) Azophenol; (b) Keto-hydazo; (c) BAPC-Ce^{4+} complex

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[3] 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.

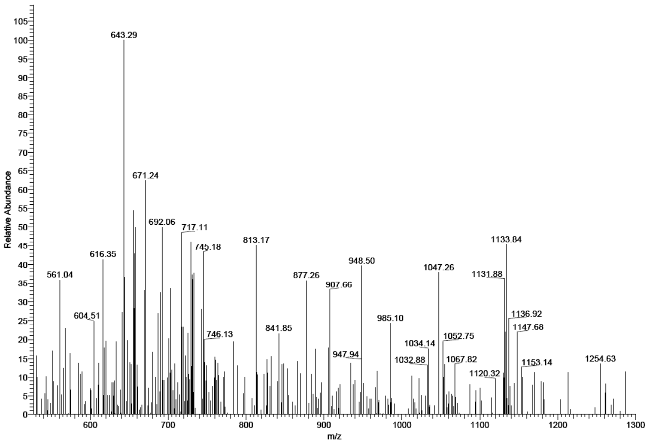

Fig. 4. ESI-MS spectrum of the complex BAPC-Ce (IV) in solvent MeOH

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 [$C_{56}H_{41}N_8O_{12}$ + 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
SPECTRA IR (cm^{-1}) IN KBr OF BAPC AND ITS COMPLEX

Frequency	BAPC	BAPC-Ce^{4+}
ν (OH)	3412; 3072	3460
ν(C-H)aro	2929	2933
ν_{alip}(C=C)	1720	1664
ν(N=N)	1506	1556
ν(C=O)	1589	1562
ν(Ce-N)	–	594

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

1153.14 with a piece of metal ions with azocalixarene and 1134.84 piece also is likely to lose the entire molecule a water molecule.

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 acetonitrile, this compound showed two peak at 354 and 470 nm[15], 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 azo groups, the N=N bonds (1.4039 Å) are longer than the values usually found (1.24-1.27 Å)[16]. The reason can be attributed formation of bonding Ce-N which extended the bond of N=N. While the C(17)-N(3) bonds (1.41 Å) is shorter than it in azophenol tautomer (1.48 Å) because in the complex, BAPC may exist at keto-quinone, so the bond changed from single bonds to double bonds. The distances between Ce^{4+} 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 (1.379 Å) in azophenol (a) and next is complex and minimum in ketoquinon (b). The reason could be explained the bonding C(6)-O(36) is simple bond in tautomeric (a) and double bond in ketoquinon (b). In the complex, Ce^{4+} ion attracted electrons to form bonding with Nitrogen atom, so the density of electrons of -C=O groups decreased, so endurance of these bondings was less stable. While the bonds distance of N-N bondings were different 1.234 Å in (a) and 1.400 Å in (b) and 1.401 Å in complex. A good agreement was found when we compared these values with the same azo compound which was reported[17]. As we had present, BAPC existed azophenol in solid state, hence the data of (a) is very suitable with crytal azocalixarene. The distances between Ce^{4+} 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[26]. 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[27]. Based on this intramolecular hydrogen, a second ring will be formed and made conformation was better stable. In the ketoquinon tautomeric, protons H were transformed to -N=N- and constituted -NH-N=, these 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, Ce^{4+} 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-4
SOME ATOMS CHARGE EQUILIBRATION OF BAPC

Atom	(a)	(b)
N (5)	-0.189	-0.184
N(6)	-0.173	-0.15
N(7)	-0.194	-0.204
N(1)	-0.197	-0.187
N(2)	-0.177	-0.152
N(3)	-0.233	-0.204
N(4)	-0.194	-0.152
O (1)	-0.393	-0.393
O (4)	-0.368	-0.382
O (3)	-0.382	-0.392
O (2)	-0.392	-0.382
C (56)	0.53	0.534
O (12)	-0.562	-0.525
O (11)	-0.474	-0.493
C (35)	0.585	0.534
O (6)	-0.514	-0.539
O (5)	-0.429	-0.482
C (42)	0.621	0.534
O (7)	-0.418	-0.494
O (8)	-0.532	-0.527
N (8)	-0.241	-0.154

TABLE-2
SELECTED BOND DISTANCES OF BAPC VÀ BAPC- Ce^{4+}

Bonds	Azophenol (a)	Ketoquinon (b)	BAPC-Ce	Reference (Noelle Ehlinger *et al* 1993)
C(22)-C(23)	1.379	1.458	1.458	1.378
C(1)-C(25)	1.379	1.323	1.323	1.376
C(25)-O(1)	1.408	1.279	1.279	1.398
C(5)-N(3)	1.418	1.302	1.301	1.402
N(1)-N(2)	1.243	1.400	1.401	1.247
N(6)-C(36)	1.419	1.435	1.435	1.402
N(2)-Ce(1)	–	–	4.260	–

TABLE-3
DISTANCE BETWEEN SOME SELECTED ATOMS (Å)

Distances	Azophenol (a)	Ketoquinon (b)	BAPC- Ce^{4+}	Reference (Noelle Ehlinger *et al.* 1993)
O(1)…O(4)	2.965	3.045	3.020	2.885
O(4)…O(3)	2.958	3.039	2.945	2.693
O(3)… O(2)	2.920	2.946	2.936	2.647
O(2)… O(1)	2.911	2.934	2.880	2.622
N(2)…N(6)	10.113	8.485	7.496	–
N(4)…N(8)	9.754	8.462	7.533	–

TABLE-5
SELECTED BOND ANGLES (º)

Atom 1	Atom 2	Atom 3	Angles (º)	Atom 1	Atom 2	Atom 3	Angles (º)
C(22)	C(23)	C(24)	120.00	N(3)	N(4)	Ce(1)	109.74
C(22)	C(23)	O(1)	120.00	C(50)	N(2)	Ce(1)	124.86
C(1)	C(25)	N(1)	120.00	C(56)	O(12)	C(51)	110.06
C(18)	C(14)	C(13)	109.47	O(12)	C(56)	O(11)	109.47
C(11)	N(5)	N(6)	106.70	N(6)	Ce(1)	N(4)	86.71
N(5)	N(6)	C(36)	106.70	N(6)	Ce(1)	N(2)	129.62

TABLE-6
ESI-MS ANALYSIS OF THE COMPLEX SPECTRUM BAPC-Ce (IV) IN SOLVENT MeOH

Sequence number	Piece	Fragment (m/z)	Intensity (%)	Ratio BAPC:Ce:MeOH
1	$C_{56}H_{44}N_8O_{12}$	1016.53	40	–
2	$[C_{56}H_{40}N_8O_{12}+Ce]^+$	1153.14	10	1:1
3	$[C_{56}H_{40}N_8O_{12}Ce\text{-}HOH]^+$	1133.84	45	1:1

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 showed 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 complexation-induced release of protons from the azophenols 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).

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