CHAPTER IV

CONCLUSION

Two calixarene-based receptors, 25,26,27-*N*, *N′*, *N″*-tris((2-ethoxy)benzyl) ethylenetetraamine-*p-tert*-butyl-calix[4]arene, **6a**, and 25,26,27-*N*, *N′*, *N″*-tris((4-ethoxy)benzyl)ethylenetetraamine-*p-tert*-butylcalix[4]arene, **6b**, were synthesized. The synthetic pathway for **6b** was started with a substitution reaction of 4-(2′-bromo ethoxy)benzaldehyde, **1b** with *p-tert*-butylcalix[4]arene in the presence of BaO as base in dry DMF for 7 days. Both dialdehyde calix[4]arene, **2b**, and trialdehyde calix [4]arene, **3b**, were obtained in 2% and 46% yields, respectively. The condensation reaction between **3b** and *tris*(2-aminoethyl)amine gave the Schiff base calix[4]arene, **4b**, in almost quantitative yield. The conversion of functional group from imine to amine was carried out by reduction of **4b** with $NaBH_4$ and subsequent protonation with dilute HCl in methanol afforded the ammonium derivative, **5b** (84%). Synthetic process of **5a** is similar to that of **5b**.[77] Both neutral derivatives, **6a** and **6b**, were obtained from the treatment of **5a** and **5b**, respectively, with NaOH in methanol. The yields of **6a** and **6b** were 72% and 74%, respectively.

The basicity and complexation properties of **6a** and **6b** were carried out by means of potentiometric titration using 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol as the inert background electrolyte. Both **6a** and **6b** exhibit 4 protonation reactions. The first and second protonation constants of **6a** were higher than that of **6b** while the third and fourth protonation reactions in **6a** gave lower equilibrium constants when compared with **6b**. LH_2^{2+} is the predominant species of **6a** in the solution, which is contrast to **6b** that expresses no main species. Upon the increase of pH, the amount of species in the solution was varied as follows: $LH_4^{4+} < LH_3^{3+} < LH_2^{2+} < LH^+ < L$. Free ligand species of **6a** and **6b** only exist in an alkaline solution.

Ligands **6a** and **6b** show the high tendency to form 1:1 complexes with Cu^{2+} ions. The stability constants of copper complex for **6a** is slightly higher than **6b**. The formation reaction can be completed even at the low concentration of free ligand. The same trend of formation constant is found in the presence of Zn^{2+} instead of Cu^{2+}. Both **6a** and **6b** can form both 1:1 and 1:2 ligand to metal ratio with Zn^{2+} ion. Zinc binuclear complexes of **6a** and **6b** appear in the neutral pH range. The introduction of the calix[4]arene framework to the **tren** unit leads to the possibility of binuclear complex formation. Only ZnL^{2+} complex of **6a** can undergo the hydrolysis reaction and hydroxo species $ZnL(OH)^{+}$ was obtained in a basic solution. CoL^{2+} species was noted as the main species of cobalt complexes of **6a** and **6b**. The stability constant of the cobalt mononuclear complex of ligand **6b** is greater than that of **6a** due to the effect of binding site cavity. Only the cobalt complex of **6b** can form the hydroxo species while that of **6a** is inert to the ligand substitution reaction.

The suggestion for future works:

From all aforementioned results and discussion, future works should be focused on:

1. X-ray crystal structures of both ligands **6a** and **6b** as well as their metal cation complexes should be obtained in order to understand the nature of coordination mode of synthetic receptors towards ions.
2. Complexation studies of the synthetic ligands **6a** and **6b** with Ni^{2+} by means of potentiometric titration, which will give valuable information about the trend of stability constants for divalent first-row transition metal ions.
3. Studies of extraction properties of both ligands should be investigated.
4. The possibility of employing calix[4]arene derivatives as basic structures for construction of Cu^{2+} ion sensor is also reasonable to explore.
5. The kinetic studies of both ligands should be carried out to identify the mechanism of complexation.
6. Complexation studies of both ligands with same metal ions by other techniques such as NMR-spectroscopy and UV-Visible titrations.