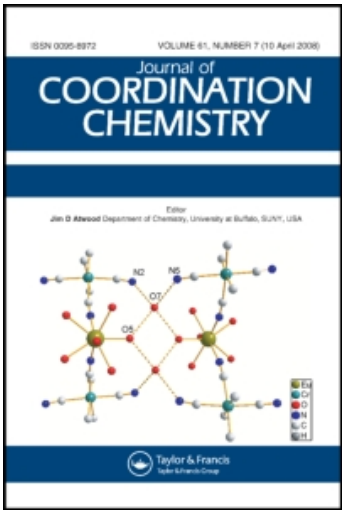


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

INTERACTION OF METAL IONS WITH TWO NEW CALIX[4, 8]ARENE DERIVATIVES

Zhifeng Ye[a]; Weijiang He[a]; Xianfa Shi[b]; Longgen Zhu[a]
[a] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu, P. R. China [b] Chemistry Department, Tongji University, Shanghai, P. R. China

To cite this Article Ye, Zhifeng , He, Weijiang , Shi, Xianfa and Zhu, Longgen(2001) 'INTERACTION OF METAL IONS WITH TWO NEW CALIX[4, 8]ARENE DERIVATIVES', Journal of Coordination Chemistry, 54: 2, 105 — 116
To link to this Article: DOI: 10.1080/00958970108027147
URL: http://dx.doi.org/10.1080/00958970108027147

J. Coord. Chem., 2001, Vol. 54, pp. 105–116
Reprints available directly from the publisher
Photocopying permitted by license only

INTERACTION OF METAL IONS WITH TWO NEW CALIX[4, 8]ARENE DERIVATIVES

ZHIFENG YE[a], WEIJIANG HE[a], XIANFA SHI[b] and LONGGEN ZHU[a,*]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu, 210093, P. R. China;* [b]*Chemistry Department, Tongji University, Shanghai 200092, P. R. China*

(Received 24 April 2000; In final form 12 October 2000)

Two new calixarene derivatives: 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis-(piperidinocarbonylmethyoxy)calix[4]arene (L^4) and 5,11,17,23,29,35,41,47-octa-*t*-butyl-49,50,51,52,53,54,55,56-octa-(piperidinocarbonylmethoxy)calix[8]arene (L^8), which show good binding abilities to metal ions, were synthesized by the reaction of the corresponding calixarene derivatives with piperidine. The ligand L^4 is capable of separating a tight ion-pair formed by Pb^{2+} and the picrate anion in THF. The interactions of the new ligands (L^n n = 4, 8) with Na^+, Pb^{2+} and Cd^{2+}, in the presence or absence of picrate, were investigated by ^1H NMR and electrospray mass spectrometry. It is found that L^4 reacts with these metal ions to form a unique complex which can be described as $[M^{m+}L^4]^{m+}$ while L^8 forms a variety of complexes depending on whether there are picrate anions in solution. $[M^{m+}L^8]^{m+}$ is formed in the absence of the picrate, and two complexes, $[PbL^8]\cdot CH_3CN\cdot H_2O$ and $[PbNaL^8]^{3+}$, are formed in the presence of the picrate. The higher conformational flexibility and larger macro-ring size of L^8 account for the fact that it forms a variety of complexes as compared with L^4.

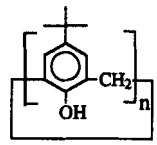
Keywords: Calixarene derivatives; Metal ions; Complexes; Electrospray mass spectrometry

INTRODUCTION

Although many examples of synthetic receptors which show unique coordination abilities with respect to metal ions are known [1], research in this field is still very active with the aim of achieving improved selectivity. Recently, several aspects of the chemistry of calixarenes (**I**),

*Corresponding author. e-mail: zhulg@public1.ptt.js.cn

Calix[n]arene I



I

which are a family of synthetic macrocyclic receptors consisting of cyclic arrays of phenol moieties linked by methylene groups have been examined [2]. Beside their inclusion abilities toward neutral organic molecules [3], the calixarenes are of interest in regard to their structures and binding abilities to metal ions [4–7]. They are lipophilic in nature and contain several hydroxyl groups ordered in cyclic arrays of different sizes which could be functionalized with suitable cation-binding units to build up new lipophilic ligands. They can also be modified at the lower rim to produce a variety of ionophores [8]. While reports on calixarenes functionalized with donor atoms appropriate for binding soft metal ions are increasing [9–11], most examples of such systems involve the introduction of extra oxygen donor atoms, producing ionophores known to bind alkali metal, alkaline-earth metal and lanthanide ions [12, 13]. In particular, the tetrasubstituted calix[4]arenes have been found to form stable complexes with alkali metal ions, and the observed selectivity depends on the conformation of the calixarene [10, 14, 15]. In addition, such ligands may provide unusual coordination environments for cations such as those of the transition metals, producing complexes that may have novel catalytic properties. Furthermore, their bonding abilities to toxic metal ions may have potential applications in environmental protection [7].

Electrospray mass spectrometry (ESMS) as introduced by Fenn and co-workers [16–18], has been shown to be a powerful technique for analyzing multiply-charged ions, primarily applied to large biomolecules such as proteins, peptides, nucleic acids, carbohydrates, drug metabolites, and other biologically active species [19, 20]. In recent years, the technique has been used to elucidate the structural and solution properties of inorganic complexes in solution [21–27].

In the present article, we report the synthesis of two new calix[n]arene derivatives L^n ($n = 4, 8$) and their interaction with Na^+, Pb^{2+} and Cd^{2+} investigated by ^1H NMR and ESMS. Precise determination of molecular masses and simulation of the isotopic distribution patterns have yielded structural information.

EXPERIMENTAL

Materials

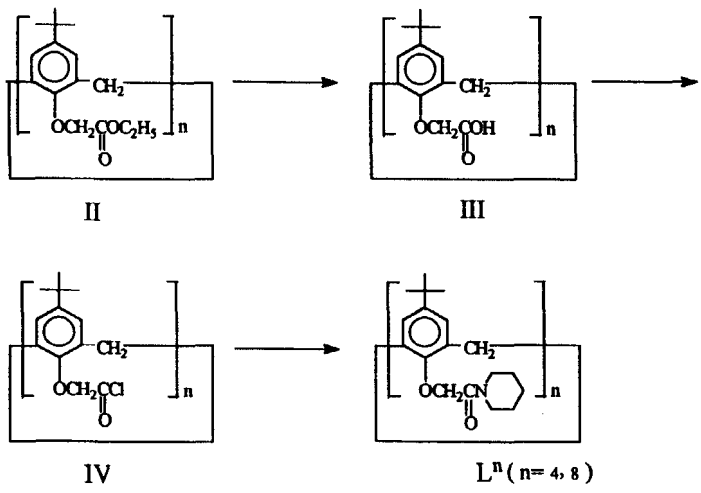
THF was distilled over $LiAlH_4$ and stored over sodium pellets. Picrate salts were obtained by neutralizing picric acid with the appropriate base in aqueous ethanol and recrystallizing twice from the same solvent; the product was then dried *in vacuo* at ambient temperature for several days. Methyl cyanide was distilled from 3 Å Linde Molecular Sieves and stored over the same sieves. Dichloromethane was distilled over P_2O_5. Triethylamine was distilled over $(CH_3CO)_2O$ and piperidine was dried over KOH pellets. All other chemicals were of reagent grade and used without further purification.

Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded at 500 MHz using an AM500 spectrometer in $CDCl_3$ with TMS as an internal standard. The chemical shifts of ^1H and ^{13}C NMR are expressed in ppm. IR spectra were recorded on a Nicolet FT-IR170SX spectrometer and the most relevant absorption peaks were reported. UV-visible spectra were recorded in THF solution on a Shimadzu UV-240 spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 240 instrument. An LCQ electrospray mass spectrometer (ESMS, Finnigan) was employed for molecular mass determination of the complexes of calixarene derivatives.

Synthesis of the Two Calix[n]arene Derivatives (L^n) (n = 4, 8)

Compounds **II** and **III** were synthesized according to the procedure described in the literature [28, 29]. Compound **III** (1.2 g) was dissolved in dichloromethane (20 mL), and thionyl chloride (6 mL) was then added dropwise under heating and stirring. The reaction mixture was refluxed under N_2 for 12 h and then most of the solvent was removed. After the residue **IV** was treated with anhydrous THF(10 mL), 4 mL diethylamine and 4 mL piperidine were added to the solution under stirring. After 24 h, all volatile material was removed and the mixture poured into water. A white precipitate formed, was filtered off and dried at 120°C overnight. The precipitate was recrystallized from dichloromethane containing 50% ethanol.

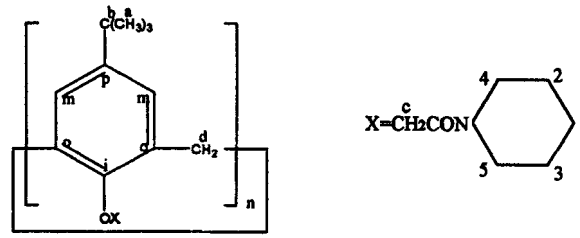


SCHEME 1 The synthesis route of the two calix[n]arene derivatives (L^n) (n = 4, 8).

For L^4: m.p. 284–286°C. IR (KBr, in cm^{-1}) 1658(—CO—), 1356(—$C(CH_3)_3$). ^1H NMR ($CDCl_3$, in ppm) 6.71 (8H, s, ArH), 4.99–5.01 (4H, d, endo–Ar–CH_2–Ar), 4.92 (8H, s, O—CH_2—CO), 3.35–3.44 (16H, m, N—$(CH_2)_2$), 3.09–3.13 (4H, d, exo–Ar–CH_2–Ar), 1.45–1.54 (24H, m, —$(CH_2)_3$—), 1.00 (36H, s, —$C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) 24.69(C^1), 25.63(C^2), 26.32(C^3), 31.41(C^a), 32.13(C^dH_2), 33.75(C^b), 42.47(C^4), 45.68(C^5), 71.73(C^cH_2), 125.26(C^m), 133.56(C^o), 144.34(C^p), 153.76(C^i), 168.41(C=O). Elemental analysis: Calc. for $C_{72}H_{100}N_4O_8$(%): C, 75.26; H, 8.71; N, 4.88. Found: C, 75.32; H, 8.66; N, 5.06.

For L^8: IR (KBr, in cm^{-1}) 1658(—CO—), 1356(—$C(CH_3)_3$). ^1H NMR ($CDCl_3$ in ppm) 6.84 (16H, br m, ArH), 4.16 (16H, br m, O—CH_2—CO), 3.42 (48H, br m, N—$(CH_2)_2$ and $ArCH_2Ar$), 1.35 (48H, br m, —$(CH_2)_3$), 1.01 (72H, br m, —$C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) 24.21(C^1), 25.43(C^2), 26.22(C^3), 29.87(C^dH_2), 31.45(C^a), 34.17(C^b), 42.49(C^4), 45.88(C^5), 71.74(C^cH_2), 126.02(C^m), 132.60(C^o), 146.10(C^p), 153.55(C^i), 166.12(C=O); Elemental analysis: Calc. for $C_{144}H_{200}N_8O_{16}$(%): C, 75.26; H, 8.71; N, 4.88. Found: C, 74.70; H, 8.22; N, 5.60. The deviation of the results from the calculated ones may be caused by encapsulation of organic solvent. As shown later, ESMS determinations of the complexes formed by reaction of L^8 with metal ions yield molecular masses that are exactly equal to the expected values.

Calix[n]arene derivatives II



II

Synthesis of Metal Complexes of L^4 with Pb^{2+} and Cd^{2+}

The metal complexes of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis-(piperidinocarbonylmethyoxy)calix[4]arene (L^4) with Pb^{2+} and Cd^{2+} were prepared by the following procedure. A slurry of L^4 (0.11 g, 0.1 mmol) in acetonitrile (CH_3CN, 5 mL) was reacted with an appropriate metal(II) perchlorate hydrate in excess (0.3 – 0.5 mmol). After filtration, the filtrate was evaporated to yield a solid. The product was recrystallized from chloroform and dried *in vacuo*. Both Pb^{2+} and Cd^{2+} yield white products. Elemental analysis and ESMS determined their compositions. Elemental analysis: Calc. for $C_{72}H_{100}Cl_2N_4O_{16}Pb$ ($[PbL^4][ClO_4]_2$) (%); C, 55.59; H, 6.43; N, 3.60. Found C, 55.58; H, 6.24; N, 3.52. Its m/z values are listed in Table I. Elemental analysis: Calc. for $C_{72}H_{100}Cl_2N_4O_{16}Cd$ ($[CdL^4][ClO_4]_2$) (%): C, 58.21; H, 6.85; N, 3.84. Found C, 58.17; H, 6.68; N, 3.91. Its m/z values are also listed in Table. I.

UV-visible Spectra

From a stock solution (10^{-3} M) of L^4 in THF, aliquots of the solution were withdrawn and added to 350 µl THF solution ($\sim 10^{-3}$ M) of a picrate salt,

TABLE I The observed m/z (z) values and calculated molecular masses for complexes of L^4 with metal ions

Species	*Observed m/z (z)*	*Calculated m/z**
L^4+Pb^{2+}	677.0, 678.0, 678.5, 679.0 (2)	676.9 (^{204}Pb)
L^4+Cd^{2+}	627.8, 628.8, 629.9, 630.4, 630.9, 631.5, 631.9, 632.8 (2)	627.8 (^{106}Cd)
L^4+Na^+	1171.8, 1172.7, 1173.7, 1174.9, 1175.8 (1)	1171.7, 1172.7, 1173.7, 1174.7, 1175.7

* The remaining of m/z values can be deduced based on isotopic abundance of Pb and Cd.

and then diluted to 5 mL with THF. The UV-visible spectra were recorded at 25°C.

^{1}H NMR Complexation Experiments

From stock solutions (1.2 M) of the metal salts in CD_3OD, aliquots were withdrawn and directly added to a $CDCl_3$ solution (10^{-2} M) of the ligand in a NMR tube. The spectra were registered after addition and the temperature of the NMR probe was kept at 25°C.

ESMS Measurement

An LCQ electrospray mass spectrometer (ESMS, Finnigan) was employed for molecular mass determination of the samples. A sample was dissolved in acetonitrile and diluted to 100 μmol·l^{-1} with methanol. 1.0 μl of this solution was loaded into the injection valve of the LCQ unit and then injected into the mobile phase solution and carried through the electrospray interface into the mass analyzer at a rate of 200 μl min^{-1}. The employed voltage at the electrospray needles was 5 kV and the capillary was heated to 200°C. A maximum ion injection time of 200 msec along with 10 scans was set. Positive ion electrospray mass spectra were obtained. Zoom scan was used in these experiments. Predicted isotope distribution patterns for each of complexes were calculated by IsoPro 3.0 program.

RESULTS AND DISCUSSION

UV-visible Study of Ion-pair Separation by L^4 Ligand

An interesting property of the L^4 ligand is its ability to separate ion-pairs in a medium of low polarity. This separation can be studied with UV-visible spectrometry and a similar phenomenon was also observed with crown ethers [30–32]. As shown in Figure 1, addition of variable amounts of L^4 into a 10^{-3} M THF solution of $Pb(Pi)_2$ (Pi = picrate), causes a bathochromic shift of absorption maximum from 330 to 380 nm (isosbestic point at 348 nm). The aqueous solution of picric acid has a peak at 380 nm. The shift is associated with a transformation from a tight ion-pair (Pb^{2+}, $2pic^-$) to a L^4 separated one (Pb^{2+}, L^4, $2pic^-$), which has a longer interionic distance between the lead ion and picrate anion. The molar extinction

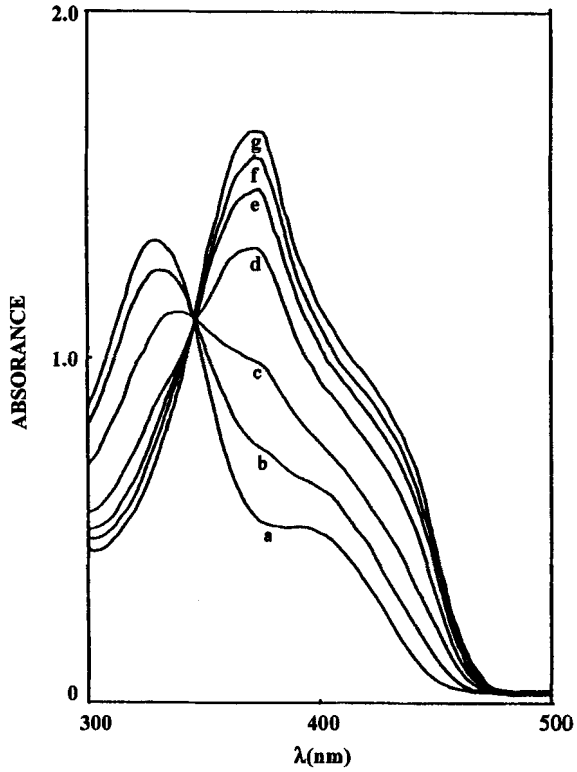


FIGURE 1 UV-visible spectrum of a 0.93×10^{-3} M THF solution of Pb(II) picrate with different amounts of L^4 ligand at 25°C. Molar ratio of L^4 to picrate: (a) = 0; (b) = 0.25; (c) = 0.5; (d) = 0.9; (e) = 1.2; (f) = 1.7; (g) = 2.5.

coefficients of the two species, (Pb^{2+}, $2pic^-$) and (Pb^{2+}, L^4, $2pic^-$) were obtained from UV-visible spectra, which are $3.8 \times 10^4\,M^{-1}\,cm^{-1}$ at 330 nm and $1.4 \times 10^5\,M^{-1}\,cm^{-1}$ at 380 nm, respectively. The complex formation constant, K_f of (Pb^{2+}, L^4, $2pic^-$) in THF, as shown in Eq. (1), can then be calculated to be $3.6 \times 10^3\,M^{-1}$. This value is not very high, but it is evident that the tight ion-pair is separated by the L^4 ligand.

$$Pb^{2+}, 2pic^- + L^4 \rightleftharpoons Pb^{2+}, L^4, 2pic^- \qquad (1)$$

We also measured the UV-visible spectrum of a mixture of $EtCOOCH_2$–substituted calixarene with (Pb^{2+}, $2pic^-$). There is no obvious difference before and after adding $EtCOOCH_2$–substituted calixarene. It indicates that piperidinated calixarene is more useful as a metal complexing agent compared with the initial $EtCOOCH_2$–substituted calixarene.

Interaction of Ligand L^4 with Pb^{2+}, Cd^{2+} and Na^+

A solution prepared by mixing L^4 with Pb^{2+} in a 1:1 mole ratio was measured by ESMS. The m/z values obtained are the same as that listed in Table I which is determined with the synthesized complex, $[PbL^4](ClO_4)_2$. The four isotopic peaks of Pb^{2+}, which are separated by 0.5 m/z unit, are attributed to a doubly charged cationic complex. The molecular mass observed is in exact agreement with that calculated for $[PbL^4]^{2+}$. Based on the same procedure described above, we studied the interaction of L^4 with Cd^{2+}. The m/z values are also shown in Table I. There are eight isotopic peaks of Cd^{2+}, separated by 0.5 m/z unit, that are attributed to a doubly charged cationic complex. The molecular mass observed is precisely equal to that calculated for $[CdL^4]^{2+}$. It reveals that Cd^{2+} reacts with L^4 only to form a $[CdL^4]^{2+}$ complex. The ^1H NMR spectra of free L^4 (Fig. 2, a) and of its complexes with Pb^{2+} and Cd^{2+} (Figs. 2b and c) also show that the chemical shifts migrate upfield or downfield upon coordination of the L^4 with Pb^{2+} (or Cd^{2+}): 0.65(0.75) ppm upfield for the endo protons H^A, 0.47 (0.41) ppm downfield for the exo protons H^B, 0.22 (0.21) ppm upfield for the methylene protons of the acetate moieties, 0.03 (0.02) ppm upfield and 0.38 (0.35) ppm downfield for the two kinds of protons on $N(CH_2)_2$, 0.56 (0.55)

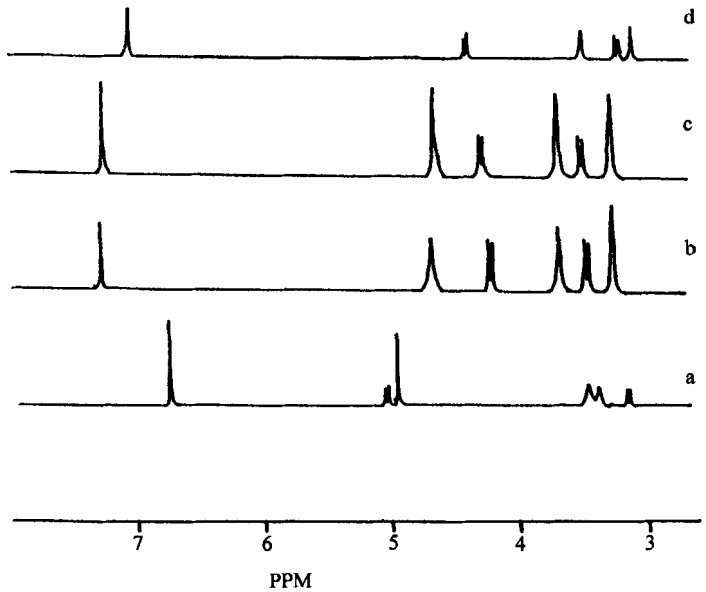
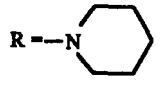


FIGURE 2 ^1H NMR spectra of free L^4 (a) and of its complex with Pb^{2+} (b), Cd^{2+} (c) and Na^+ (d).

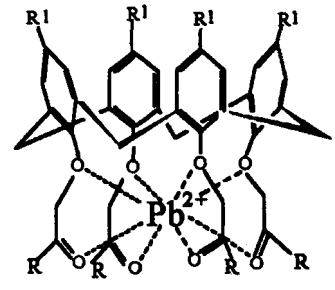
ppm downfield for the aromatic protons. All these are due to coordination of the Pb^{2+} (Cd^{2+}) ion, which induces downfield shifts of protons adjacent to the binding sites, and conformational changes. The upfield shift of protons from the methylene unit of the acetate group can be explained by assuming that all of these groups, upon coordination, adopt a *trans*-conformation that brings the methylene protons away from the hydrophilic oxygen region and above the aromatic ring, where they experience a shielding effect [33]. As pointed out by Cram and Coll in explaining the complexing ability of spherands [34], the proper organization of the oxygens can usually compensate for the negative electronic effect. In the case of the L^4 ligand, this seems to be an important factor too. The preorganization of binding sites in a structure with limited conformational freedom results in remarkable abilities for binding. Based on the ESMS spectrum, ^1H NMR and literature precedence [33], a proposed binding mode of L^4 with Pb^{2+} is shown in the scheme below.

All of these results show that the L^4 ligand has good binding ability to the metal ions used. As Pb^{2+} and Cd^{2+} are toxic metal ions, this property may be of interest in environmental protection.

From the ESMS of L^4, it is found that Na^+ is easily encapsulated by the L^4 ligand, even Na^+ that is present in contaminants. The behavior of L^4 toward Na^+ is similar to that of other calix[4]arene derivatives [33] and powerful complexing agents, such as cryptands [35, 36], and spherands [34], which have low exchange rates and high stability constants with alkali ions. The ^1H NMR spectra of free L^4 (Fig. 2a) and its complex with Na^+ (Fig. 2d) also show that the chemical shifts migrate upfield or downfield upon coordination of L^4 with Na^+: 0.57 ppm upfield from 4.99 to 4.42 for the endo protons H^A, 0.17 ppm downfield from 3.09 to 3.26 for the exo protons H^B, 0.37 ppm upfield from 4.92 to 4.55 for the methylene protons, 0.19 ppm upfield from 3.35 to 3.16 and 0.13 ppm downfield from 3.42 to 3.55 for the



R1 = Bu^t



SCHEME 2 The structure of the complex of Pb^{2+} with ligand (L^4).

two kinds of protons on $N(CH_2)_2$, 0.32 ppm downfield from 6.71 to 7.03 for the aromatic protons. All these, as mentioned above, are due to the contributions of the coordinated sodium ion and conformational changes.

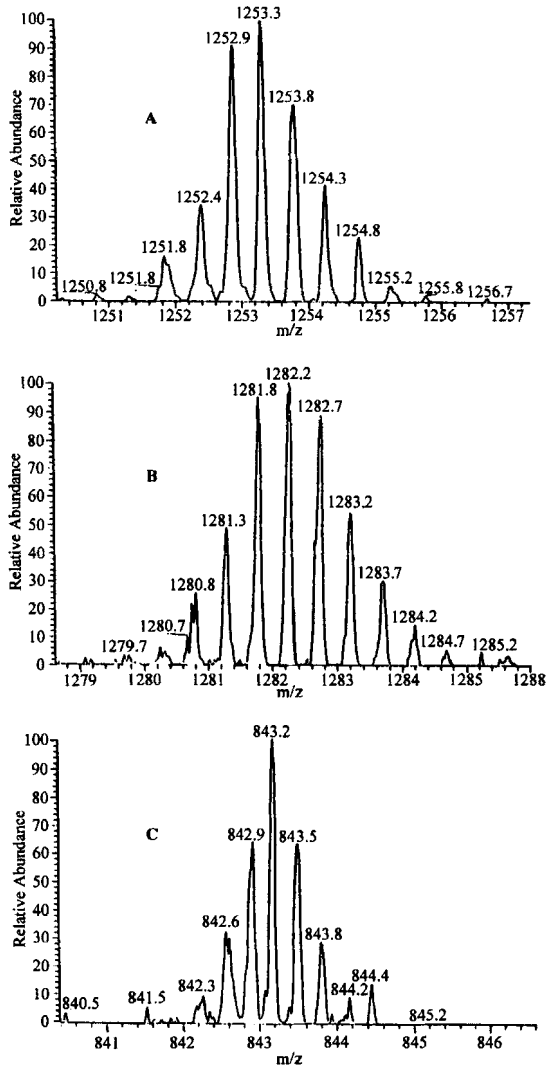


FIGURE 3 ESMS spectra measured ten minutes after mixing of Pb^{2+} and L^8 with or without an equi-molar quantity of picrate. (A) Measured m/z values (in the absence of picrate): 1251.9, 1252.7, 1253.3 and 1253.7; calculated m/z values for $[PbL^8]^{2+}$: 1251.7(^{204}Pb), 1252.7(^{206}Pb), 1253 .3(^{207}Pb) and 1253.7(^{208}Pb). (B) Measured m/z values (in the presence of picrate): 1281.3, 1282.2, 1282.7 and 1283.2; calculated for $[PbL_8]^{2+} \cdot CH_3CN \cdot H_2O$: 1281.3(^{204}Pb), 1282.3(^{206}Pb), 1282.8(^{207}Pb) and 1283.3 (^{208}Pb). (C) Measured m/z values (in the presence of picrate): 842.3, 842.9, 843.2 and 843.5; calculate m/z values for $[Pb \cdot Na \cdot L^8]^{3+}$: 842.2(^{204}Pb), 842.8(^{206}Pb), 843.2(^{207}Pb) and 843.5(^{208}Pb).

Interaction of Pb^{2+} with L^n (n = 4, 8) in the Presence of Picrate

In order to obtain detailed structural information on a solution in which Pb^{2+}, L^n and picrate are mixed in a 1 : 1 : 1 mole ratio, and ESMS measurements were carried out ten minutes after mixing. As for L^4, only the $[PbL^4]^{2+}$ species is detected, except for $[NaL^4]^+$. No other species containing picrate was detected in this case. These results are consistent with the above-mentioned ion-pair separation studies. As compared with the picrate, L^4 has stronger binding ability to Pb^{2+} and coordinates to Pb^{2+} directly, resulting in separation of the tight ion-pair (Pd^{2+}, $2pic^-$).

In contrast to L^4, as shown in Figure 3 (B and C), L^8 reacts with Pb^{2+} to form two complexes. One is $[PbL^8]^{2+}\cdot CH_3CN\cdot H_2O$ in which solvents CH_3CN and H_2O are tightly bound to L^8. The other one is $[PbNaL^8]^{3+}$ in which both Pb^{2+} and Na^+ are recognized and bound to L^8. On the other hand, L^8 reacts with Pb^{2+}, in the absence of picrate, only to form $[PbL^8]^{2+}$, as shown in Figure 3(A). These results clearly reveal that the presence of the picrate makes the species formed in solution more complicated, although the picrate does not participate in coordination with Pb^{2+}. Compared with L^4, the L^8 ligand has greater conformational flexibility and a bigger macro-ring size, which seem to be mainly responsible for L^8 forming more complicated complexes in the presence of the picrate ion.

CONCLUSION

Two new calix[n]arene derivatives (n = 4, 8), L^4 and L^8, show good binding ability toward Na^+, Pb^{2+} and Cd^{2+}. Ligand L^4, which can separate a tight ion-pair, coordinates to Na^+, Pb^{2+} and Cd^{2+} to form a unique type of complex, $[M^{m+}L^4]^{m+}$, regardless of the presence or absence of the picrate ion. However, interaction of L^8 with Pb^{2+} and Cd^{2+} is more complicated and forms several species depending on whether picrate is in solution. The interesting properties of these calixarene derivatives inspire us to synthesize a variety of powerful and selective complexing agents using calixarenes as a starting material and investigate their binding abilities to various metal ions.

Acknowledgement

We thank the National Natural Science Foundation of China (Grant Nos. 29871017 and 29823001) for financial support.

References

[1] (a) M. Hiraoka, "*Crown Compounds*" Kodanska, Tokyio (1982); (b) "Host Guest Complex Chemistry", Vol. I-III (Ed. F. Vogtle), *Top. Curr. Chem.* p. 98 (1981); p. 101 (1982); p. 121 (1984); (c) R. C. Hayward, *Chem. Soc. Rev.* **12**, 285 (1983); (d) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.* **85**, 271 (1985).

[2] C. D. Gutsche, *Calixarenes: Monographs in Supramolecular Chemistry*, Vol. 1, Ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge (1989).

[3] R. Ungaro, A. Pochini, G. D. Andreetti and P. Domiano, *J. Chem. Soc. Perkin Trans.* **2**, 197 (1985) and references therein.

[4] M. A. McKervey, E. M. Seward, G. Ferguson and B. L. Ruhl, *J. Chem. Soc. Chem. Commun.* p. 388 (1985).

[5] S. K. Chang and I. Cho, *Chem. Lett.* p. 477 (1987).

[6] S. K. Chang and I. Cho, *J. Chem. Soc., Perkin Trans.* **1**, 211 (1986).

[7] F. Arnaud-Neu, G. Barrett and S. J. Harris, *Inorg. Chem.* **32**, 2644 (1993); *J. Chem. Soc., Perkin Trans.* **2**, 575 (1997).

[8] Topics in Inclusion Science: Calixarenes: a Versatile Class of Macrocyclic Compounds, Ed. J. Vicens and V. Bohmer, Kluwer, Dordrecht (1990).

[9] C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Organomet. Chem.* **47**, 297 (1994).

[10] J. M. Harrowfield, M. Mocerino, B. W. Skelton, C. R. Whitaker and A. H. White, *Aust. J. Chem.* **47**, 1185 (1994).

[11] X. Delaigue, J. M. Harrowfield and M. W. Hosseini, *J. Chem. Soc., Chem. Commun.* p. 1579 (1994).

[12] M. J. Schwing and M. A. McKervey, Ref. 2, p. 149.

[13] F. Arnaud-Neu, *Chem. Soc., Rev.* **23**, 235 (1994).

[14] A. Ikeda and S. Shinkai, *J. Am. Chem. Soc.* **116**, 3102 (1994).

[15] K. Iwamoto and S. Shinkai, *J. Org. Chem.* **57**, 7066 (1992).

[16] M. Yamashita and J. B. Fenn, *J. Phys. Chem.* **88**, 4671 (1984).

[17] J. B. Fenn, M. Mann, C. K. Meng, S. K. Wong and C. Whitehouse, *Science* **246**, 64 (1989).

[18] J. B. Fenn, M. Mann, C. K. Meng and S. K. Wong, *Mass. Spectr. Rev.* **9**, 37 (1990).

[19] R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Barinaga and H. R. Udsetch, *Anal. Chem.* **62**, 882 (1990).

[20] C. M. Fenwick and A. M. English, *J. Am. Chem. Soc.* p. 12236 (1996).

[21] R. Colton, B. D. James, I. D. Potter and J. C. Traeger, *Inorg. Chem.* **32**, 2626 (1993).

[22] V. Katt, S. K. Chowdhury and B. T. Chait, *J. Am. Chem. Soc.* **112**, 5348 (1990).

[23] A. Marrquis-Rigault, A. Dupont-Gervais, P. N. Baxler, A. Van Dorsselaer and J. M. Lehn, *Inorg. Chem.* **35**, 2307 (1996).

[24] B. Psascal, F. Silvana, L. Christophe, C. Catherne, B. Jean and M. Bernard, *Bull. Soc. Chin. Fr.* **133**, 679 (1996).

[25] S. F. Ralph, M. M. Sheil, L. A. Hick, R. J. Geue and A. M. Sargeson, *J. Chem. Soc. Dalton Trans.* p. 4417 (1996).

[26] C. Moucheron and A. K.-D. Mesmaeker, *J. Am. Chem. Soc.* **118**, 12834 (1996).

[27] A. D'Agostino, F. Colton, J. C. Traeger and A. J. Canty, *Eur. Mass Spectrom.* **2**, 273 (1996).

[28] S. J. Harri, M. A. McKervey, D. P. Melody, J. Woods and J. M. Rooney, *United States Patent No. 4556700.*

[29] (a) S. J. Harri, *European Patent No. 237265*; (b) S. J. Harri, J. Guthrie, M. Mucmanus, C. Mcardle and M. A. McKervey, *European Patent No. 432989.*

[30] K. H. Wong, K. Yagi and J. Smid, *J. Membr. Biol.* **18**, 379 (1974).

[31] I. Ikeda, T. Katayama, M. Okahara and T. Shono, *Tetrahedron Lett.* p. 1573 (1981).

[32] T. Maeda, M. Ouchi, K. Kimura and T. Shono, *Chem. Lett.* p. 1533 (1981).

[33] A. Arduint, A. Pochini, S. Reverberi and R. Ungaro, *Tetrahedron* **42**, 2089 (1986).

[34] J. M. Lehn, *Acc. Chem. Res.* **11**, 49 (1978), and references therein.

[35] B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.* **103**, 1054 (1981).

[36] (a) D. J. Cram and K. N. Trueblood, *Top. Curr. Chem.* **98**, 431 (1981); (b) D. J. Cram, T. Kaneda, R. C. Helgeson, S. B. Brown, C. B. Knobler, E. Maverick and K. N. Trueblood, *J. Am. Chem. Soc.* **107**, 3645 (1985); (c) D. J. Cram and G. M. Lein, *J. Am. Chem. Soc.* **107**, 3657 (1985).