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ORIGINAL ARTICLE

Syntheses of novel calix[4]arene hydrazone-based receptors and their cooperative complexation with soft and hard metal ions

Fafu Yang · Zhisheng Huang · Jianwei Xie · Xiaoyi Zhang · Hongyu Guo

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Abstract Four novel calix[4]arene hydrazone-based receptors **3a–d** were prepared in yields of 69–87% by condensating formylated calix[4]arene ester (**2**) with salicylyl hydrazine, 2,4-dinitrophenyl hydrazine, nicotinyl hydrazine or phenyl thiosemicarhazide, respectively. New compounds were characterized through elemental analysis, IR, ESI–MS, ^{1}H NMR studies. Compounds **3a–d** containing two binding sites had the complexation abilities for hard and soft cations concurrently. The noncompetitive extracting experiments showed compounds **3a–d** were excellent receptors for hard and soft metal cations. The competitive extracting experiments exhibited the cooperative complexation in binding hard and soft metal cations and compound **3a** possessed outstanding selectivity for Na^+ and Hg^{2+}. The IR spectra of compound **3a** before and after complexation revealed that the soft metal cation was binded in the cavity composed of hydrazone groups and azo groups at the upper rims of calix[4]arene units and hard metal cations was binded in cavity composed of ester groups and phenolic hydroxyl groups at the lower rims of calix[4]arene units.

Keywords Calix[4]arene · Hydrazone · Synthesis · Complexation · Cooperative

Introduction

The ability of multiple recognition and the mutual effects of binding subunit occupation has been paid much attention in supramolecular chemistry [1]. Calixarenes were excellent building blocks to construct the polytoptic systems combining two or more binding sites within the same architecture, such as calixarene-based co-receptors for hard and soft metal cations [2]. Up to now, two methods were reported to prepare calixarene-based co-receptors for hard and soft metal cations. One was the calix-biscrowns in 1,3-alternate conformation with full-oxygen crown and heteroatom crown at lower rims [3–5]. For examples, Vicens etc. reported series calix[4]biscrowns with complexation abilities for hard and soft metal cations [6, 7]. The another method was calix[4]arene derivatives or biscalixarene with oxygen and heteroatom containing functional groups at lower rims, which could bind hard and soft metal cations at different binding sites [8–11]. For examples, the calix[4]arene derivatives with $EtS(CH_2)_nNHCOCH_2O$- or $RCH{=}NNHCOCH_2CO$- groups exhibited binding capabilities for hard and soft metal cations [10, 11]. Our groups also reported several calix[4]arene derivatives or biscalix[4]arene with two binding sites for hard and soft metal cations [11–14]. Lately, some research concerned on the selectively formylated calixarene ethers with special complexation abilities [15–18]. Moreover, from the view of molecular design, this kind of compound was an excellent platform to construct the new calixarene derivatives with binding abilities for hard and soft cations, because the two separate binding sites and cone conformation might be favorable for producing excellent cooperative complexation abilities for different cation concurrently, which were not studied by far, however. In this paper, we wish to report the synthesis of four novel calix[4]arene hydrazone-based receptors derivatived from formylated calixarene ethers as well as their cooperative complexation abilities for hard and soft metal cations.

F. Yang (✉) · Z. Huang · J. Xie · X. Zhang · H. Guo
College of Chemistry and Materials, Fujian Normal University, Fuzhou 350007, People's Republic of China
e-mail: yangfafu@fjnu.edu.cn

Experimental

Melting points were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument, using TMS as reference. ESI–MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. The UV–Vis measurements were performed on Varian UV–Vis spectrometer. Cation concentrations in competitive extracting experiments were measured with Thermo Intrepid XSP Radial ICP-OES. IR spectra were recorded on a Thermo Nicollet AVATAR 5700 FTIR spectrometer using KBr pellets in spectral range 4000–400 cm^{-1}. The picrate salts were prepared according to literature [19, 20]. Compound **1** was prepared according to literature [11]. The organic and inorganic reagents were analytical grade or chemical grade without further purification.

Synthesis of calix[4]arene 1,3-diformyl derivative **2**

With the method in literature [18], a mixture of compound **1** (0.5 g, 0.6 mmol) and hexamethylenetetramine (3.4 g, 24 mmol) was stirred in 16 mL TFA solution for 5 h at room temperature. Then 40 g ice was added in the solution. After the unfreeze of ice, the solution was extracted by 3 × 10 mL $CHCl_3$. The $CHCl_3$ solution was washed by 10 mL distilled water, dried by $MgSO_4$, concentrated. The residue was purified by chromatographic column (50 cm × 3 cm, SiO_2 100–200 mesh, acetone/CH_2Cl_2 (1:2, *V*/*V*) as eluant, 400 mL), then compound **2** was obtained as white powder in yield of 68%. m.p.: 173–175 °C;IR(KBr, cm^{-1}): 1746(C=O), 1700 (HC=O); ^{1}HNMR(400, MHz, $CDCl_3$) δ: 1.03(s, 18H, $C(CH_3)_3$), 1.35(t, 6H, CH_2CH_3), 3.47(d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.34 (q, 4H, CH_2CH_3), 4.47 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.75 (s, 4H, $ArOCH_2$), 6.91(s, 4H, ArH), 7.60(s, 4H, ArH), 8.53(s, 2H, CHO), 9.77(s, 2H, OH); ESI–MS m/z (%): 763.4 (M^+, 100); Anal.calcd for $C_{46}H_{52}O_{10}$: C, 72.23; H, 6.85; found C, 72.14; H, 6.94.

Synthesis of calix[4]arene hydrazone derivative **3a**

Under N_2 atmosphere, a mixture of compound **2** (0.22 g, 0.3 mmol) and 0.5 mL glacial acetic acid was stirred and refluxed in 15 mL $CHCl_3$ and 10 mL MeOH solution containing salicylyl hydrazine (0.097 g, 0.64 mmol) was added by dropwise in 1 h. The solution was stirred and refluxed in 10 h and some precipitation appeared. TLC analysis revealed that the starting materials were disappeared. After distilling off the solvent by reduced pressure, 10 mL methanol was added and the precipitation was separated, and then recrystallized in $CHCl_3$/MeOH. Compound **3a** was obtained as maple powder in yield of 82%. m.p.: 189–191°C: IR(KBr, cm^{-1}): 1748(C=O), 1634 (C=O), 1604 (C=N); ^{1}HNMR(400, MHz, $CDCl_3$) δ: 1.04(s, 18H, $C(CH_3)_3$), 1.25(t, 6H, CH_2CH_3), 3.47(d, J = 12.0 Hz, 4H, $ArCH_2Ar$), 4.32 (bs, 4H, CH_2CH_3), 4.43 (d, J = 12.0 Hz, 4H, $ArCH_2Ar$), 4.73 (s, 4H, $ArOCH_2$), 6.84–7.62(m, 16H, ArH), 7.83, 8.09, 9.79, 11.94(s, each, 2H, each, CH, OH and NH); ESI–MS m/z (%): 1032.1 (M^+, 100); Anal.calcd for $C_{60}H_{64}N_4O_{12}$: C, 69.75; H, 6.24; N, 5.42; found C, 69.63; H, 6.36; N, 5.30.

Synthesis of calix[4]arene hydrazone derivative **3b**

Under N_2 atmosphere, a mixture of compound **2** (0.22 g, 0.3 mmol) and 0.2 mL glacial acetic acid was stirred and refluxed in 15 mL $CHCl_3$ and 15 mL MeOH solution containing 2,4-dinitrophenyl hydrazine (0.13 g, 0.64 mmol) was added by dropwise in 1 h. The solution was stirred and refluxed in 6 h and some precipitation appeared. TLC analysis revealed that the starting materials were disappeared. After distilling off the solvent by reduced pressure, 10 mL methanol was added and the precipitation was separated, and then recrystallized in $CHCl_3$/MeOH. Compound **3a** was obtained as red powder in yield of 87%. m.p.: 274–276°C: IR(KBr, cm^{-1}): 1744 (C=O), 1616 (C=N); ^{1}HNMR(400, MHz, $CDCl_3$) δ: 1.25(s, 18H, $C(CH_3)_3$), 1.35(t, 6H, CH_2CH_3), 3.46(d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.35 (q, 4H, CH_2CH_3), 4.55 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.82 (bs, 4H, $ArOCH_2$), 6.94–8.38(m, 16H, ArH and CH), 9.13, 11.20(s, each, 2H, each, OH and NH); ESI–MS m/z (%): 1147.1 (MNa^+, 100); Anal.calcd for $C_{58}H_{60}N_8O_{16}$: C, 61.91; H, 5.38; N, 9.96; found C, 61.88; H, 5.47; N, 9.87.

Synthesis of calix[4]arene hydrazone derivative **3c**

Under N_2 atmosphere, a mixture of compound **2** (0.22 g, 0.3 mmol), 0.2 mL glacial acetic acid was stirred and refluxed in 15 mL $CHCl_3$ and 10 mL MeOH solution containing nicotinyl hydrazine (0.088 g, 0.64 mmol) was added by dropwise in 1 h. TLC analysis revealed that the starting materials were disappeared in 6 h. After distilling off the solvent by reduced pressure, 10 mL methanol was added and the precipitation was separated, and then recrystallized in $CHCl_3$/MeOH. Compound **3c** was obtained as straw yellow powder in yield of 69%. m.p.: 159–162°C: IR(KBr, cm^{-1}): 1744 (C=O), 1666(C=O), 1633(C=N); ^{1}HNMR(400, MHz, $CDCl_3$) δ: 1.23(s, 18H, $C(CH_3)_3$), 1.36(t, 6H, CH_2CH_3), 3.43(d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.34 (q, 4H, CH_2CH_3), 4.56 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.79 (bs, 4H, $ArOCH_2$), 6.96–7.88(m, 16H, ArH and CH), 7.85, 9.04, 11.12(s, each, 2H, each, CH, OH and NH); ESI–MS m/z (%): 1003.9 (M^+, 100); Anal.calcd

for $C_{58}H_{62}N_6O_{10}$: C, 69.39; H, 6.23; N, 8.37; found C, 69.26; H, 6.32; N, 8.25.

Synthesis of calix[4]arene hydrazone derivative **3d**

Under N_2 atmosphere, compound **2** (0.15 g, 0.2 mmol) was stirred and refluxed in 40 mL $CHCl_3$ and 10 mL EtOH solution containing phenyl thiosemicarhazide (0.07 g, 0.42 mmol) was added by dropwise in 1 h. TLC analysis revealed that the starting materials were disappeared in 5 h. After distilling off the solvent by reduced pressure, 10 mL methanol was added and the precipitation was separated, and then recrystallized in $CHCl_3$/MeOH. Compound **3d** was obtained as straw yellow powder in yield of 72%. m.p.: 218–219°C: IR(KBr, cm^{-1}): 1743 (C=O), 1599(C=N); ^{1}HNMR(400, MHz, $CDCl_3$) δ: 1.18(s, 18H, $C(CH_3)_3$), 1.34(t, 6H, CH_2CH_3), 3.42(d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.32 (q, 4H, CH_2CH_3), 4.48 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.77 (s, 4H, $ArOCH_2$), 6.93–7.66 (m, 18H, ArH), 7.73, 8.11, 9.15, 9.45(bs, each, 2H, each, CH, OH and NH); ESI–MS m/z (%): 1085.4 (MNa^+, 50); Anal.calcd for $C_{60}H_{66}N_6S_2O_8$: C, 67.77; H, 6.20; N, 7.90; found C, 67.66; H, 6.32; N, 7.79.

Noncompetitive extracting experiment of metallic picrates

According to the reported method [18], 3 mL of chloroform solution containing calixarene derivatives (2.0×10^{-5}M) and 3 mL of aqueous solution containing a metallic picrate (2.0×10^{-5}M) were placed in a flask. The mixture was shaken for 5 min and stored for 2 h at room temperature. The extraction ability was not affected by further shaking, indicating that the equilibrium had been attained within 2 h. The aqueous phase was separated and subjected to the analysis by UV absorption spectrometry in near 357 nm. The extracting percentage (E%) was determined by the decrease of the picrate concentration in the aqueous phase: $E\% = \{([Pic]_{blank}–[Pic]_{water})/[Pic]_{blank}\} \times 100$, where $[Pic]_{blank}$ denoted the picrate concentrations in the aqueous phase after extraction with pure chloroform, and $[Pic]_{water}$ denoted the picrate concentrations in the aqueous phase after extraction with chloroform solution containing calixarene derivatives as extractants. Average of two independent experiments was carried out. Control experiments showed that no picrate extraction occurred in the absence of the calixarene derivatives. The relative standard deviations from the mean were less than 5%. The test showed that the pH value in each aqueous phase were neutral (6.9–7.1) and the values made no change before and after extraction, which indicated the metallic picrates were extracted successfully.

Competitive extracting experiments of metallic cations

Competitive extraction experiments were performed with equal volumes (10 mL) of an aqueous solution of an equimolar mixture of picrate salts (Li^+, Na^+, K^+, Cs^+, Ag^+, Hg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}, 2.0×10^{-5} M each) and a $CHCl_3$ solution (10 mL) of the hosts (2.0×10^{-5} M) were mixed in a stoppered flask and vigorously shaken for 15 min. The solution was stored for 2 h. This was repeated three times. Then the solutions were left standing for 24 h until phase separation was complete. The relative concentrations of the cations in the aqueous phase were determined by ICP-OES. Quantification was made by using a standard solution containing a mixture of picrate salts (Li^+, Na^+, K^+, Cs^+, Ag^+, Hg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+},). Blank experiments without added hosts were carried out under same experimental conditions.

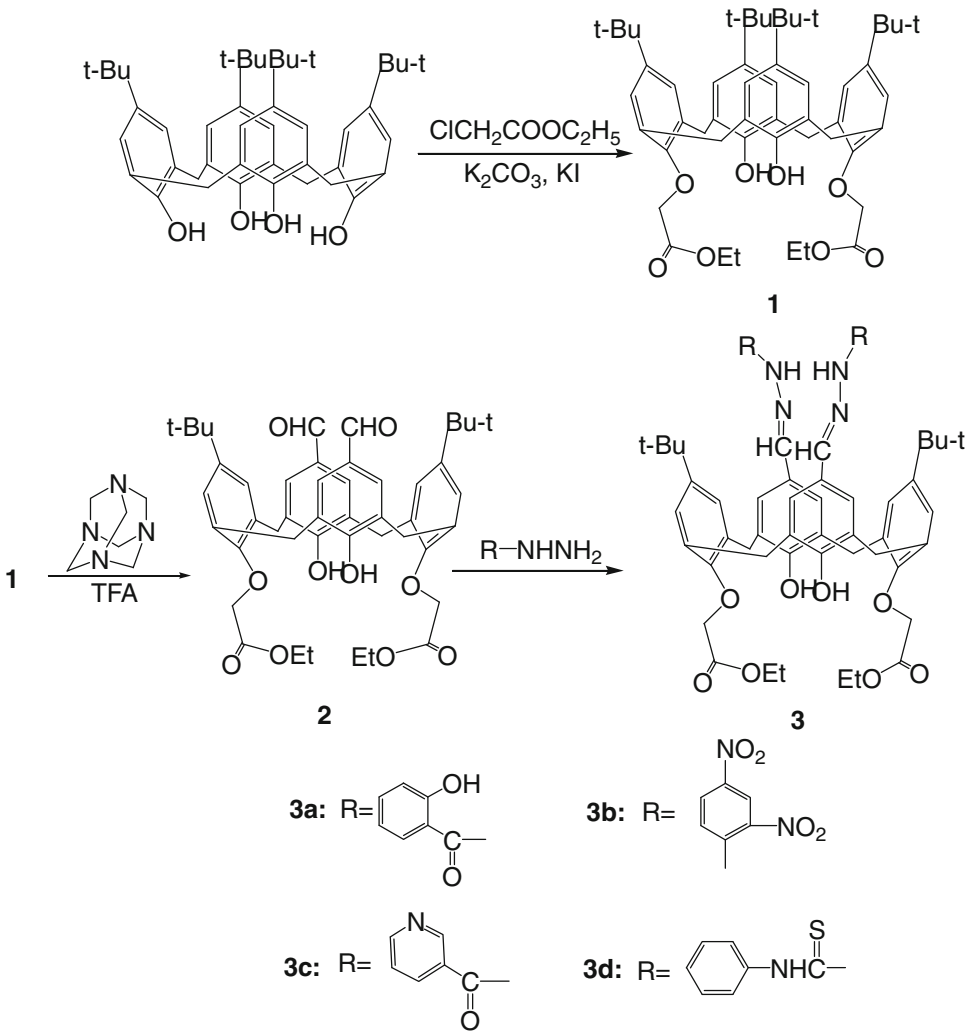
Results and discussion

Synthesis and characterization of novel calix[4]arene hydrazone derivatives **3a–d**

The synthetic route was shown in Scheme 1. Compound **1** was prepared according to literature [11]. According to the reference [18], compound **2** was obtained in low purity. We improved this method with chromatographic column and purified compound **2** was obtained in yield of 68%. It was well known that the formacyl group could react with hydrazino group easily. Thus, salicylyl hydrazine, 2,4-dinitrophenyl hydrazine, nicotinyl hydrazine and phenyl thiosemicarhazide was chosen to react with compound **2**. In order to avoid the reaction of hydrazino group and ester groups in compound **2**, the hydrazine derivatives were added by dropwise and glacial acetic acid was used as catalyst in preparing compounds **3a–d**. Also, the optimized mole ratio of compound **2** and hydrazine derivatives were 1:2 approximately. The excess hydrazine derivatives resulted in complicated products although the react times decreased greatly. The experimental results showed compounds **3a–d** were obtained conveniently by recrystallization in ideal yields of 69%–87%.

The structures of new compounds **3a–d** were confirmed by IR spectra, ESI–MS spectra, elemental analyses, ^{1}H NMR spectra. In the IR spectra, the adsorption peaks (1700 cm^{-1}) of formacyl groups of compound **2** was disappeared utterly and new adsorption peaks of C=N groups were appeared. The ESI–MS spectra of compounds **3a–d** showed clearly molecular base peaks (M^+ or MNa^+) at 1032.1, 1147.1, 1003.9, 1085.4, respectively, which indicated the "1 + 2" condensation were accomplished completely. As compound **2** was confirmed to adopt cone

Scheme 1 The synthetic routes of title compounds



conformation [18], it was reasonable to deduce that compounds **3a**–**d** were also in cone conformations, which were confirmed by ^{1}H NMR spectra. The ^{1}H NMR spectra of compounds **3a**–**d** showed one singlet for *tert*-butyl groups, one pair of doublets (1:1) for the methylene bridges of the calix[4]arene skeleton. All the spectral data were in accordance with the assigned structures and indicated that the calix[4]arene units adopt the cone conformation as showed in Scheme 1. As to the cis/trans conformers about C(O)–N bond and *E*/*Z* geometrical isomers respect to the C=N double bonds in these new compounds, it could be deduced that the mixed conformers and isomers were existed by comparing with the similar report[21]. However, in this paper, it was difficult to determine the percentage of different isomers due to the overlapped signal of NH and OH in IR spectra and the absence of CH_2 groups beside the C(O)–N bond and C=N double bond which were crucial to study the percentages of different isomers [21].

Noncompetitive extracting experiments of metallic cations

It could be seen that compounds **3a**–**d** possessed two binding sites for guests. One was the cavity composed of ester groups and phenolic hydroxyl groups at the lower rims of calix[4]arene units and the other was the cavity composed of hydrazone groups and azo- or sulfur- groups at the upper rims of calix[4]arene units. According to principle of "hard and soft acids and bases", the two cavities could bind hard and soft metal cations, respectively. Also, the stable cone conformations of compounds **3a**–**d** were favorable for producing complexation abilities. Thus, the binding abilities of compounds **3a**–**d** were studied for series of metal cations. There were two methods to study the extracting abilities. One was by using metallic picrates as extract directly in neutral solution and another was metal picrate in buffered solution [19, 22]. Due to the binding abilities of NH and OH were greatly influenced by

pH, the method of using metallic picrates as extract directly in neutral was employed in our extracting experiments to avoid the fall of complexation abilities in buffered solution. Thus, in our extracting experiment, the pH value in each aqueous phase were neutral (6.9–7.1) and the values made no change before and after extraction, which indicated the metallic picrate were extracted successfully.

Figure 1 showed the noncompetitive extraction results of compounds **3a–d** towards alkali metal cations. It could be seen that compounds **3a–d** exhibited good extraction percentage. For example, the extraction percentages of compound **3c** for Li^+, Na^+, K^+, Cs^+ were as high as 25.8%, 52.1%, 48.3%, and 44.9%, respectively. The low extraction selectivity might be attributed to the open chain structures of compounds **3a–d**. Moreover, comparing with the extraction abilities of precursor **2**, the extraction abilities of compounds **3a–d** made little changes. These results indicated that the binding sites for alkali metal cations were the same cavity composed of ester groups and phenolic hydroxyl groups at the lower rims of calix[4]arene units of compounds **2** and **3a–d**.

However, the extraction results of compounds **3a–d** towards soft metal cations were utterly different from that of compound **2**. In Fig. 2, compound **2** showed very low extraction percentage. But compounds **3a–d** exhibited very high extraction percentages for tested soft cations. For example, the Hg^{2+} extraction percentage increased from 0.8% of compound **2**–50.9% of compound **3a**. These results indicated that it was the cavity composed of hydrazone groups and azo- or sulfur- groups at the upper rims of calix[4]arene units played the crucial roles in binding soft metal cations. All these noncompetitive extracting experiments suggested that compounds **3a–d** were excellent receptors for soft and hard metal cations in two different binding sites as expected.

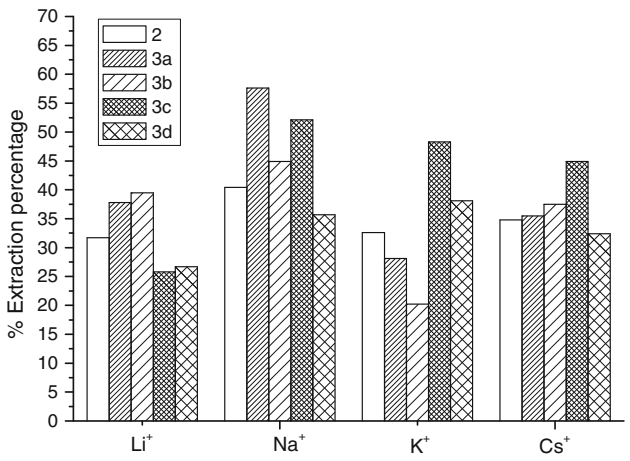


Fig. 1 The extraction percentages of receptors **3a–d** for hard metal cations

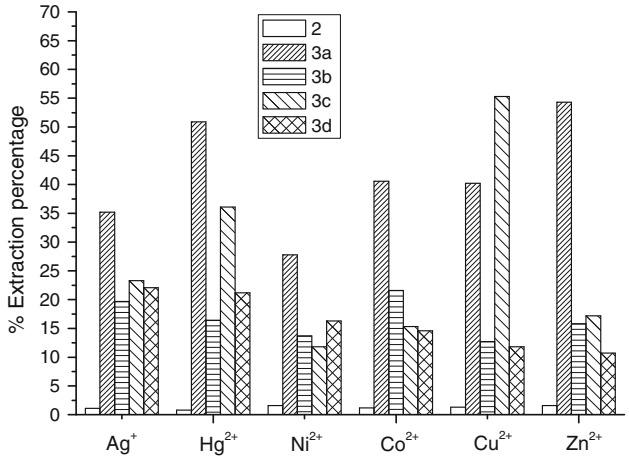


Fig. 2 The extraction percentages of receptors **3a–d** for soft metal cations

Competitive extracting experiments of metallic cations

Based on the noncompetitive extracting experiments, the competitive extracting experiments were carried out to investigate the cooperative complexation of two different binding sites. The competitive extraction percentages were summarized in Table 1. It can be seen that compounds **3a–d** showed good extraction abilities towards both hard and soft metal cations, which were in accordance with noncompetitive extracting experiments. It was worthy of noting that all of total extraction percentages (the addition of each extraction percentage) of compounds **3a–d** for metal cations exceeded 100%. The biggest total extraction percentage of compound **3a** was as high as 148.7%. These results could be explained that the two different complexing sites of compounds **3a–d** binded soft and hard metal cations concurrently. On the other hand, comparing with noncompetitive extracting experiments, the extraction selectivity was improved greatly in competitive extracting experiments, especially for compound **3a**. Compound **3a** exhibited high extraction selectivity for Na^+ among hard metal cations and for Hg^{2+} among soft metal cations, respectively. For example, the extraction ratio Na^+/Li^+ and Hg^{2+}/Ag^+ of compound **3a** were up to 8.44 and 7.09 in competitive extracting experiments, whereas it were only 1.52 and 1.45 in noncompetitive extracting experiments, respectively. These results suggested that the cooperative complexation exists between the two binding sites of compounds **3a–d**. The complexation in one cavity would influence the complexing behavior of another cavity for binding another guest, which improved or reduced the extraction percentages. To the best of our knowledge, this kind of cooperative complexation for hard and soft metal cations was reported for the first time in calixarene chemistry by far.

Table 1 Competitive extracting percentages (%E) of receptors **3a–d** for picrate salts

Cations	Li^+	Na^+	K^+	Cs^+	Ag^+	Hg^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}
3a	5.2	43.9	12.1	10.4	5.4	38.3	8.5	7.6	6.8	10.5
3b	8.4	23.8	11.5	8.9	10.2	22.9	11.7	14.4	9.4	11.3
3c	9.4	24.8	20.5	18.4	16.9	18.8	6.6	9.8	17.8	8.9
3d	11.6	18.6	9.7	17.3	8.6	10.9	12.4	11.7	8.4	7.5

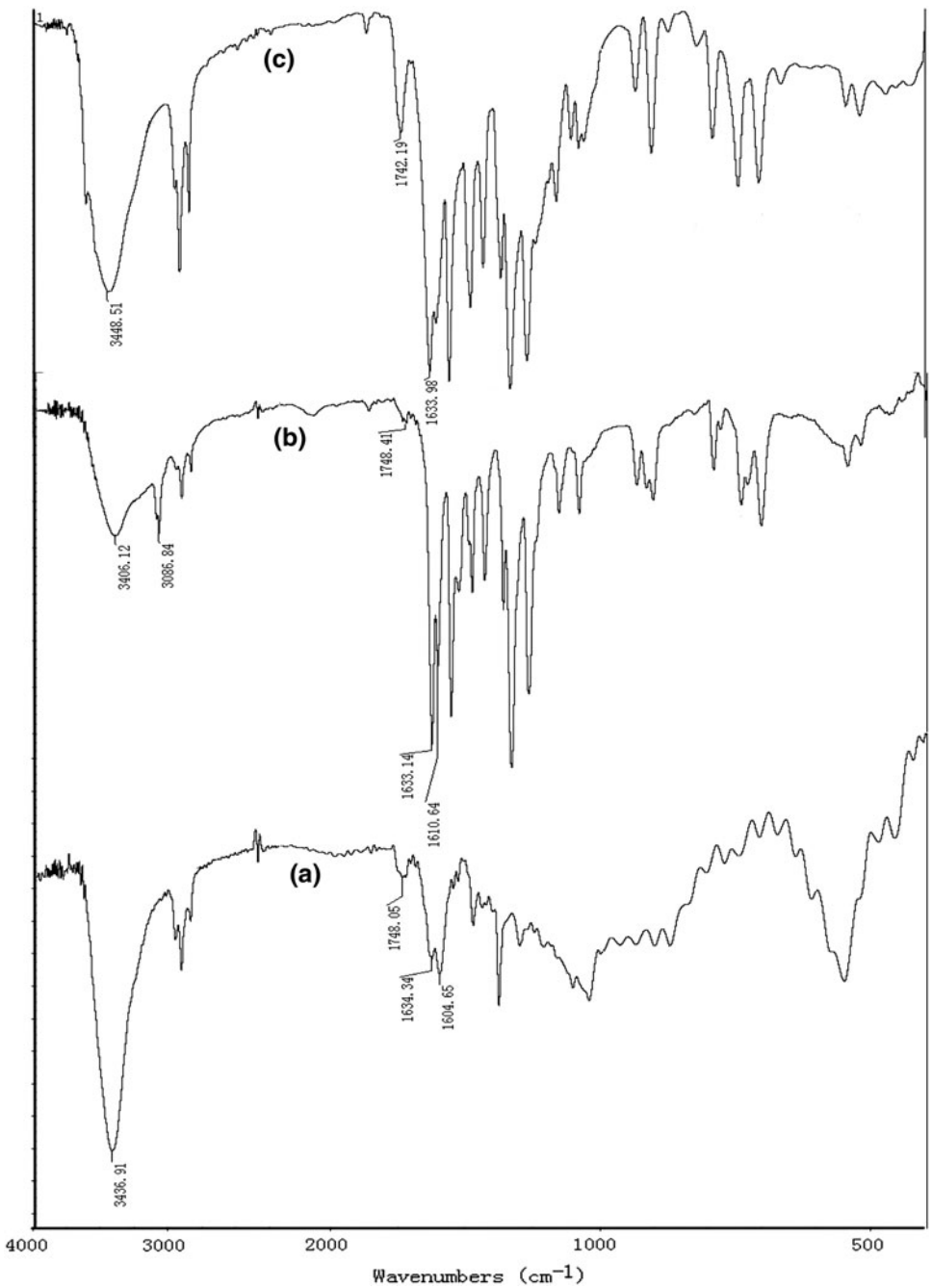


Fig. 3 IR studies of compound **3a** (**a**) and its complex with Hg^{2+} (**b**) and Na^+

The IR spectra of complexation studies

The IR spectra of compound **3a** before and after complexation with Hg^{2+} and Na^{+} picrate were employed to study the complexation behavior. The results were as showed in Fig. 3. After complexation with Hg^{2+}, the adsorption peaks of C=O (1748 cm^{-1} for ester group and 1634 cm^{-1} for amido group) made little shift. However, the peak at 3436 cm^{-1} moved to 3406 and 3086 cm^{-1}, which was attributed to the N–H peak (3086 cm^{-1}) split from the mixture peak of N–H and O–H after complexation. Also, the shifting of C=N peak from 1604 to 1610 cm^{-1} suggested C=N groups participated in the complexation. Thus, it could be concluded that the Hg^{2+} was binded in the cavity composed of hydrazone groups and azo groups at the upper rims of calix[4]arene units. However, the IR spectra of compound **3a** before and after complexation with Na^{+} picrate showed little shift of adsorption peaks of NH, NC=O and C=N groups except the shift of adsorption peaks of C=O in ester groups(from 1748 to 1742 cm^{-1}) and OH groups (from 3436 to 3448 cm^{-1}). This result indicated that the complexation mode of **3a** for Na^{+} were occurred in cavity composed of ester groups and phenolic hydroxyl groups at the lower rims of calix[4]arene units. These complexation results of IR spectra also indicated the hard and soft metal cations were binded in two different cavities, respectively, which was in accordance with the results of extracting experiments. These complexation results revealed that receptors **3a–d** with two different binding sites might possess multiple complexation capabilities for other complicated guests, such as ion pairs and amino acids, which will be studied in further work.

Conclusion

By reacting formylated calixarene ester (**2**) with salicylyl hydrazine, 2,4-dinitrophenyl hydrazine, nicotinyl hydrazine or phenyl thiosemicarhazide, four novel calix[4]arene hydrazone-based receptors **3a–d** were prepared in yields of 69–87%. The noncompetitive extracting experiments showed compounds **3a–d** were excellent receptors for hard and soft metal cations. The competitive extracting experiments exhibited the cooperative complexation in binding hard and soft metal cations for the first time in calixarene chemistry and compound **3a** possessed outstanding complexation selectivity for Na^{+} and Hg^{2+}. The IR spectra of before and after complexation revealed that the soft metal cation was binded in the cavity composed of hydrazone groups and azo groups at the upper rims of calix[4]arene units and hard metal cations was binded in cavity composed of ester groups and phenolic hydroxyl groups at the lower rims of calix[4]arene units, which also suggested that compounds **3a–d** containing two binding sites had the complexation abilities for hard and soft cations concurrently.

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