Synthesis of Crosslinked Chitosan-Crown Ethers and Evaluation of These Products as Adsorbents for Metal Ions

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ABSTRACT: Two new crosslinked-crown ethers (CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6) were synthesized by the reaction of crosslinked chitosan (CCTS-NH$_2$) with 4′-formyl benzo-15-crown-5 and 4′-formyl benzo-18-crown-6. Their structures were confirmed with elemental analysis, infrared spectra analysis, solid-state ^{13}C NMR analysis, X-ray diffraction analysis, and differential scanning calorimetry thermogram analysis. In the infrared spectra of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, the characteristic peak of C=N stretch vibration appeared at 1650 cm^{-1}. The X-ray diffraction analysis showed that the peak at $2\theta = 20°$ decreased greatly in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6. In the ^{13}C NMR spectra of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, the characteristic peak of aromatic carbon appeared at 128-ppm, the characteristic peak of carbon in the C=N group appeared at 151 ppm. The adsorption and selectivity properties of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag$^+$, Pd^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{3+} were studied. The experimental results showed that the two crosslinked chitosan-crown ethers have not only good adsorption capacities for Ag$^+$ and Pd^{2+}, but also high selectivity for the adsorption of Ag$^+$ or Pd^{2+} with the coexistence of Pb^{2+} and Cr^{3+}. The selectivity coefficients of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were $K_{Pd^{2+}/Pb^{2+}} = 9.9$, $K_{Ag^+/Pb^{2+}} = 9.8$, $K_{Pd^{2+}/Cr^{3+}} = \infty$, $K_{Pd^{2+}/Pb^{2+}} = 11.5$, $K_{Ag^+/Pb^{2+}} = 7.1$, $K_{Pd^{2+}/Cr^{3+}} = \infty$, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 501–506, 1998

Key words: crosslinked chitosan; crosslinked chitosan-crown ethers; synthesis; adsorption properties; metal ions

INTRODUCTION

Chitin is a liner polymer mainly obtained from the cuticle of a marine crustacean. Chitosan, which is easily derived from chitin by *N*-deacetylation, has recently aroused great interest in its industrial and medical application, owing to its specific structures and properties. Chitosan appeared to be more useful than chitin, because it has hydroxyl and amino groups that can be modified easily.[1–3] This polymer has been the object of continued study for several decades, and recent review articles outline much of the broad-ranging research on this polymer to date.[4] In particular, its adsorption properties have attracted much attention as a potential hazardous waste remediation material, because chitosan has a demonstrated ability to bind transition metal ions especially heavy or precious metal ions.[5–10]

For its particular molecular structure, crown ethers have good complex selectivity for many metal ions, but they are expensive and unrecycled easily after used; therefore, its application was limited. If crown ethers were grafted in chitosan chain to give chitosan-crown ethers containing double structures and properties of chitosan and crown ethers, it can be predicated that these novel chitosan derivatives have wide-rang-
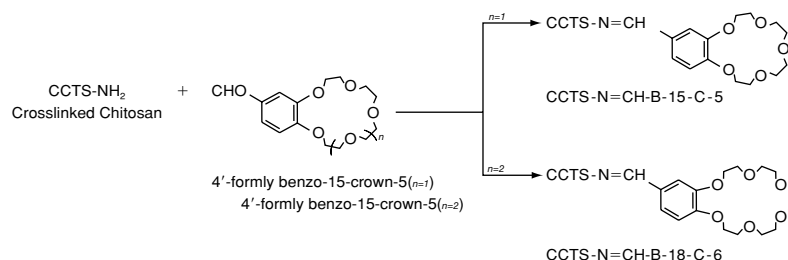
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Figure 1 Reaction scheme for the synthesis of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6.

ing applications for the separation and concentration of heavy or precious metal ions.

However, the amino group responsible for dissolution of chitosan in acid media, which is one serious disadvantage from the practical viewpoint. Thus, in this research, chitosan was first crosslinked with epichlorohydrin to give crosslinked chitosan (CCTS-NH$_2$) and 4′-formyl benzo-crown ethers were prepared also. Then, the N-Schiff base type CCTS-NH$_2$-crown ethers (CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6) were obtained through the reaction of CCTS-NH$_2$ with 4′-formyl benzo-crown ethers. Their structures were confirmed with elemental analysis, infrared spectra analysis, solid-state ^{13}C NMR analysis, X-ray diffraction analysis, and differential scanning calorimetry (DSC) thermogram analysis. The adsorption properties and selectivity of them for Ag$^+$, Pd^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{3+} were studied.

EXPERIMENTAL

Material

Chitosan, whose degree of deacetylation was calculated to be 80% from the amino contents,[11] was prepared by *N*-deacetylation of chitin from shrimp shells. CCTS-NH$_2$ was prepared according to the procedure reported previously[12] and was used after it was sieved using a 200 mesh size. 3,4-Dihydroxy benzoldehyde was purchased from the First Chemical Factory in Shanghai (China). 1,11-Dichloro-3,6,9-trioxaundecane was prepared by the general methods reported[13] (yield, 90%), and 1.14-dichloro-3,6,9,12-tetraoxatetradecane was prepared by the method reported[14] (yield, 45%). 4′-Formyl benzo-15-crown-5 and 4′-formyl benzo-18-crown-6 were prepared by the reaction of 3,4-dihydroxy benzoldehyde with 1,11-dichloro-3,6,9-trioxaundecane or 1.14-dichloro-3,6,9,12-tetraoxatetradecane according to the procedure as described previously.[15] All

inorganic compounds were reagent grade, and all solvents and available organic material were commercial products used without purification.

Synthesis of CCTS-NH$_2$-Crown Ethers

Figure 1 showed the synthetic routes of CCTS-NH$_2$-crown ethers.

Preparation of CCTS-NH$_2$-benzo-15-crown-5 (CCTS-N=CH-B-15-C-5)

Powdered CCTS-NH$_2$ (1.0 g) was swelled in 40 mL ethanol overnight, then 4′-formyl benzo-15-crown-5, which was dissolved in 20 mL ethanol, was slowly dropped into the CCTS-NH$_2$ solution under nitrogen. The mixture was refluxed with good agitation for 24 h, filtered, and washed completely by a Soxhlet's extraction with ethanol to remove any unreacted 4′-formyl benzo-15-crown-5 and dried to give 1.7 g light yellow CCTS-N=CH-B-15-C-5 (85%).

Preparation of CCTS-NH$_2$-benzo-18-crown-6 (CCTS-N=CH-B-18-C-6)

This compound was prepared from CCTS-NH$_2$, with 4′-formyl benzo-18-crown-6 by the same procedure as described for CCTS-N=CH-B-15-C-5. The product was obtained in 80% yield.

Adsorption Procedure for CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6

The Ability to Absorb Metal Ions of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6

To 25 mL of an aqueous solution of metal ion (5.0 × 10^{-4} mol · dm^{-3}) was added 25 mg of CCTS-NH$_2$ derivative sample. After stirring 12 h at room temperature, the mixture was centrifuged and filtered. The metal ion concentration in the filter was determined by automatic adsorption spectrophotometry, and the quantity of metal ion

absorbed by CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 was calculated as follows:

$$Q = \frac{V \cdot (C_0 - C)}{W}$$

where Q is the adsorption capacities of crosslinked derivatives (mg metal ion/g adsorbent), V is the volume of metal ion solution (ml), C_0 is the concentration of metal ion before adsorption (mg $\cdot$ mL^{-1}), C is the concentration of metal ion after adsorption (mg $\cdot$ mL^{-1}), and W is the weight of CCTS-NH$_2$ derivatives (g).

Adsorption Selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Precious Metal Ions

A 5.0×10^{-4} mol $\cdot$ dm^{-3} solution of desired metal ions was prepared; 25 mg of CCTS-NH$_2$-crown ethers sample was added to 25 mL of the solution and stirred for 12 h at room temperature. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for the metal ions by atomic adsorption spectrophotometer. The quantity of metal ion absorbed by CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 was obtained by subtracting concentration in the supernatant solution from the initial concentration. The selectivity coefficient of CCTS-N=CH-B-15-C-5, and CCTS-N=CH-B-18-C-6 was calculated the same way as reported.[16]

Measurement

Elemental analysis was determined with a Perkin–Elmer automatic instrument. Infrared spectra was measured on a Nicolet 5DX FT-IR spectrophotometer. Solid-state ^{13}C NMR spectra was conducted using Bruker MSL-400 model NMR spectrometer; proton and carbon frequencies were 400 MHz and 100 MHz, respectively. Wide-angle X-ray diffraction (WAXD) patterns were obtained with the use of nicklet-filtered CuKα ratication produced by a Rigaku (D/MAX 111A) diffractometer. Thermal properties of materials were measured using a differential scanning calorimeter (Dupont model 910), with a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Characterization of Structure of CCTS-NH$_2$-Crown Ethers

CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were successfully prepared by the reaction of

Table I   Elemental Analysis Results of CCTS-NH$_2$, CCTS-N=CH-B-15-C-5, and CCTS-N=CH-B-18-C-6

	C%	H%	N%
CCTS-NH$_2$	38.26	6.49	5.39
CCTS-N=CH-B-15-C-5	37.43	6.51	5.36
CCTS-N=CH-B-18-C-6	37.44	6.52	5.37

Schiff base reaction between —NH$_2$ in CCTS-NH$_2$ and —CHO in 4′-formyl benzo-crown ethers. CCTS-N=CH-B-15-C-5 was light yellow in color and did not dissolve in solvents such as dimethysulfoxide, chloroform, formamide, and dimethylformamide. CCTS-N=CH-B-18-C-6 was yellow in color and did not dissolve in organic solvents such as dimethylsulfoxide, chloroform, formamide, and dimethylformamide. They all were rather swollen in acetic acid solution.

Elemental Analysis

The elemental analysis results of CCTS-NH$_2$, CCTS-N=CH-B-15-C-5, and CCTS-N=CH-B-18-C-6 were showed in Table I.

It could be seen that the content of nitrogen in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 was a little lower than that in CCTS-NH$_2$. It was thought that the decrease was attributed to the presence of the Schiff base type benzo-crown ethers groups produced in the reaction of CCTS-NH$_2$ with 4′-formyl benzo-crown ethers.

Infrared Spectra Analysis

The Fourier transform infrared spectras of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were shown together with that of CCTS-NH$_2$ in Figure 2.

Although marked differences were not observed in the Fourier transform infrared spectra between CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, the characteristic peak of C=N stretch vibration appeared at 1650 cm^{-1} and the characteristic peak of aromatic backbone vibration appeared at 1560 cm^{-1}. It was also seen that CCTS-NH$_2$, CCTS-N=CH-B-15-C-5, and CCTS-N=CH-B-18-C-6 have the characteristic peak of pyanyl vibration at 900 cm^{-1} caused by the presence of CCTS-NH$_2$-crown ethers backbone chain. All of this evidence supported the reaction of —CHO in 4′-formyl benzo-crown ethers with CCTS-NH$_2$ at amino groups.

Solid-State ^{13}C NMR Analysis

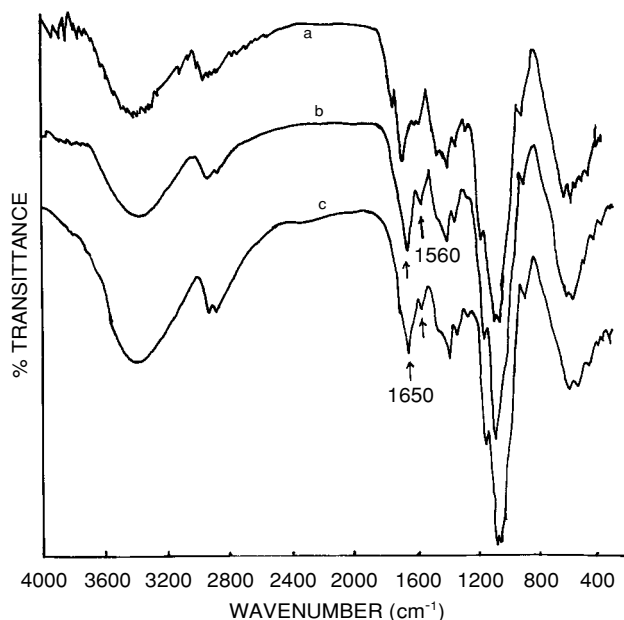The solid-state ^{13}C NMR spectras of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6

Figure 2 Infrared spectra of (a) CCTS-NH$_2$, (b) CCTS-N=CH-B-15-C-5, and (c) CCTS-N=CH-B-18-C-6.

were shown together with that of CCTS-NH$_2$ in Figure 3.

The ^{13}C NMR studies of CCTS-NH$_2$, CCTS-N=CH-B-15-C-5, and CCTS-N=CH-B-18-C-6 were done as solid samples, because these compounds could not easily be dissolved. Figure 3 compared the CCTS-NH$_2$ spectra with that of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6. It could be seen that the characteristic aromatic carbon appeared at 128 ppm and the char-
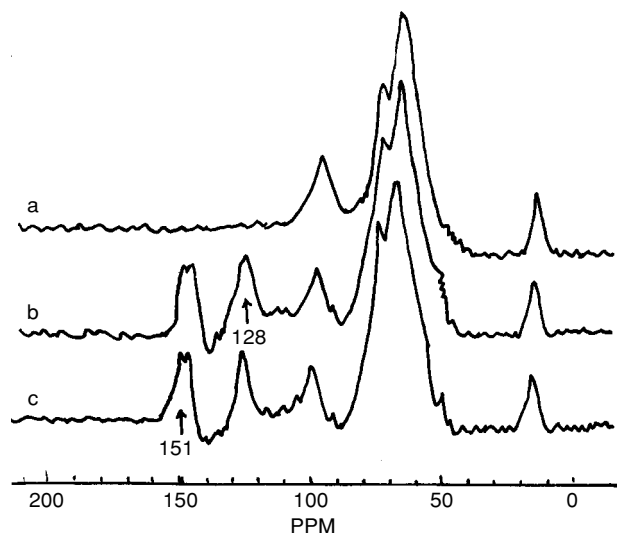

Figure 3 ^{13}C NMR spectra of (a) CCTS-NH$_2$, (b) CCTS-N=CH-B-15-C-5, and (c) CCTS-N=CH-B-18-C-6.
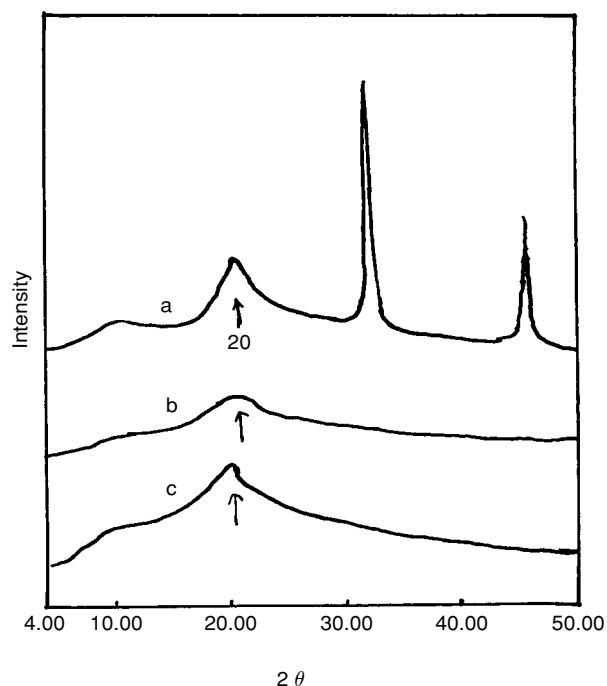

Figure 4 X-ray diffraction patterns of (a) CCTS-NH$_2$, (b) CCTS-N=CH-B-15-C-5, and (c) CCTS-N=CH-B-18-C-6.

acteristic peak of carbon in the C=N group appeared at 151 ppm in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, noting that these peaks did not appear in the spectra of CCTS-NH$_2$. Changes in intensity were also noticeable for carbon in the —CH$_2$O— groups at 70 ppm, owing to the presence of crown ether groups in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6.

X-ray Diffraction Analysis

The X-ray diffraction patterns of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were shown together with that of CCTS-NH$_2$ in Figure 4.

Figure 4 showed the WAXD patterns of CCTS-NH$_2$ and its derivatives. The WAXD pattern of CCTS-NH$_2$ showed the characteristic peaks at 2θ = 10°, 20°, 32°, and 46°.[17] Noting that the peaks at 2θ = 32°, 46° disappeared and the peak at 2θ = 10° decreased greatly in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6. It was thought that the decrease in crystallinity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 was attributed to deformation of the strong hydrogen bond in the CCTS-NH$_2$ backbone as the amino groups were substituted by 4′-formyl benzo-crown ethers. The two CCTS-NH$_2$ derivatives gave a low crystallinity, indicating that
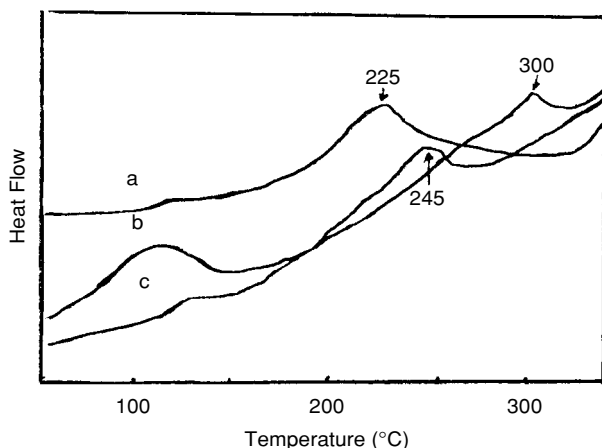
Figure 5 DSC thermograms of (a) CCTS-NH$_2$, (b) CCTS-N=CH-B-15-C-5, and (c) CCTS-N=CH-B-18-C-6.

they were considerably more amorphous than CCTS-NH$_2$.

Thermal Properties Analysis

DSC thermograms of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were shown together with that of CCTS-NH$_2$ in Figure 5.

Figure 5 exhibited the DSC thermograms of CCTS-NH$_2$ and its derivatives. CCTS-NH$_2$ showed an exothermic peak at around 300°C due to the degradation of the main chain.[17] CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 showed decreased exothermic peaks. In general, it is known that hydrogen bonds between polymer chains contribute to raising the degradation temperature, whereas the degradation temperature of the polymer substituted by the benzo-crown ether groups may be decreased owing to the loss of hydrogen bonding. Therefore, if the amino groups were replaced by 4′-formyl benzo-crown ethers groups, hydrogen bonding in the polymer chains might be diminished, resulting in the smaller exothermic peak. These data coincide well with X-ray analysis.

Evaluation of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 as Adsorbents for Metal Ions

Adsorption Capacities of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6

The adsorption experimental results of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag$^+$, Pd^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{3+} were shown together with that of CCTS-NH$_2$ in Table II.

From Table II, it could be seen that the adsorption capacity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag$^+$, Pd^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{3+} was lower than that of CCTS-NH$_2$ owing to the decrease of nitrogen in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6. It also could be seen that the adsorption capacity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag$^+$ and Pd^{2+} was much higher than that of them for Pb^{2+}, Cd^{2+}, and Cr^{3+} due to the presence of crown ether groups in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, which demonstrated that the selectivity of them were greatly improved.

Adsorption Selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6

The experimental results of the adsorption selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were shown in Tables III and IV.

It could be seen that CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 have good adsorption selectivity for Pd^{2+} with the coexistence of Pb^{2+} and Cr^{3+}. This could be applied in the separation or concentration of Pd^{2+} in the aqueous system containing Pb^{2+} and Cr^{3+}.

The value in Table IV demonstrated that the adsorption of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag$^+$ was prior to Pb^{2+}, and the adsorption effect of CCTS-N=CH-B-15-C-5 for Ag$^+$ was better than that of CCTS-N=CH-B-18-C-6, because the crown-ether ring radius of benzo-15-crown-5 was smaller than that of benzo-18-crown-6. This

Table II   Ability of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 to Absorb Metal Ion (mg, metal ion/g, adsorbent pH 2.0–6.5)

	Ag$^+$ pH 6.2	Pd^{2+} pH 2.0	Pb^{2+} pH 5.9	Cd^{2+} pH 6.5	Cr^{3+} pH 3.9
CCTS-N=CH-B-15-C-5	52.5	38.7	4.1	4.0	3.9
CCTS-N=CH-B-18-C-6	28.2	33.2	4.4	5.4	3.6
CCTS-NH$_2$[7]	54.4	48.8	34.0	32.2	30.1

Table III   Adsorption Selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for the Aqueous System Containing Pd^{2+}, Pb^{2+}, and Cr^{3+} (pH 4.0)

	Quantity of Adsorption (mg · g^{-1})			
	Pd^{2+}	Pb^{2+}	Cr^{3+}	Selectivity/Coefficients
CCTS-N=CH-B-15-C-5	38.7	3.9	0.0	$K_{Pd^{2+}/Pb^{2+}} = 9.9$, $K_{Pd^{2+}/Cr^{4+}} = \infty$
CCTS-N=CH-B-18-C-6	36.8	3.2	0.0	$K_{Pd^{2+}/Pb^{2+}} = 11.5$, $K_{Pd^{2+}/Cr^{4+}} = \infty$

also could be applied in the separation of Ag^{+} in aqueous system containing Pb^{2+}.

CONCLUSIONS

CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were synthesized via Schiff-base reaction between amino groups in CCTS-NH$_2$ and 4′-formyl benzo-15-crown-5 or 4′-formyl benzo-18-crown-6, whose structures were confirmed with elemental analysis, infrared spectra analysis, solid-state ^{13}C NMR analysis, X-ray diffraction analysis, and DSC thermograms analysis. The adsorption properties selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 were determined. Owing to the presence of benzo-crown ethers in CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6, the adsorption capacity of them for Ag^{+}, Pd^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{3+} was lower than that of CCTS-NH$_2$, but the selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for Ag^{+} and Pd^{2+} with the coexistence of Pb^{2+} and Cr^{3+} was greatly improved. Therefore, we could predict

Table IV   Adsorption Selectivity of CCTS-N=CH-B-15-C-5 and CCTS-N=CH-B-18-C-6 for the Aqueous System Containing Ag^{+} and Pb^{2+} (pH 5.0)

	Quantity of Adsorption (mg · g^{-1})		Selectivity/Coefficients
	Ag^{+}	Pb^{2+}	
CCTS-N=CH-B-15-C-5	23.4	2.4	$K_{Ag^{+}/Pb^{2+}} = 9.8$
CCTS-N=CH-B-18-C-6	16.4	2.3	$K_{Ag^{+}/Pb^{2+}} = 7.1$

that they would have broad applications in wastewater treatment.

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