Spectrophotometric Studies for Complex Formation of Diammonium 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-bis(*N*-carbodithioate) with Transitional Metal Ions under Coexistence of Alkali Metal Ion and Alkali Earth Metal Ion

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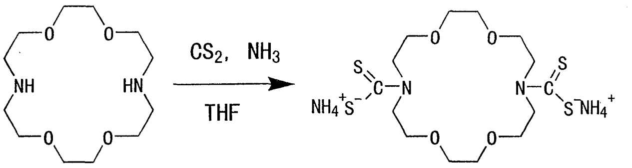
A new bifuntional ligand, Diammonium 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-bis(N-carbodithioate), has been synthesized. The UV-spectra of Ni(II)-chelate of the ligand was changed by addition of Na^+, K^+, Rb^+, Cs^+ and Mg^{2+}. The composition of Pb(II)-chelate was changed from 1:1 (metal:ligand) to 1:2 by addition of Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+} and Sr^{2+}. These changes were produced by the change in the conformation of the diaza-crown ring in the ligand.

Crown compounds have promising potentials as analytical reagents to trap and to sense alkali metal ions and alkaline earth metal ions.[1-7] We attempted to introduce chelating functional groups into a crown ring to develop a new use of crown compounds. A crown compound which has chelating functional groups and a crown ring could become a new bifunctional chelating agent whose coordinating abilities respond to transition metal ion and alkali metal ions and alkaline earth metal ions, respectively.

Diammonium 1,4, 10, 13- tetraoxa- 7, 16-diazacyclooctadecane- bis (*N*- carbodithioate) (DA18CC) was synthesized, as a model compound for our attempt. DA18CC has one 18-diaza-crown ring and two carbodithioate groups. The conformation change in DA18CC was easy for complex formation because the 18-diaza-crown ring consists of only single bonds and it has a highly symmetrical structure. Therefore, the conformation of the 18-diaza-crown ring is expected to be changed by forming complexes with alkali and alkaline earth metal ions or transition metal ions. This paper describes our study on the complex formation of DA18CC with transition metal ions in coexistence with alkali metal ions and alkaline earth metal ions spectrophotometrically.

Diammonium 1, 4, 10, 13- tetraoxa- 7, 16-diazacyclooctadecane-bis(N-carbodithioate) (DA18CC) was synthesized by a modification of the procedure described by King and Fritz.[8] 0.1 g (3.8 x 10^{-3} mol) of 4,13-diaza-18-crown-6-ether was dissolved into 1 cm^3 of methanol. 3 cm^3 of tetrahydrofuran and 0.2 cm^3 of concentrated ammonium hydroxide were added into the solution. The mixture was then cooled in an ice bath, and 0.1 cm^3 of carbon disulfide was added in drops to the mixture while it was stirred. The mixture was stood for one day in the ice bath to crystallize the product. The product, comprising white needlelike crystals, was filtered, then washed with tetrahydrofuran and dried in a vacuum at ambient temperature. The yield was 85%. The elemental analysis is as follows: C,36.91; H,6.91; and N, 11.96%, calculated for C,37.48; H,7.19; and N,12.49%. The identity of DA18CC was confirmed by IR, NMR and mass spectrometry. The melting point of DA18CC could not be determined because of the decomposition of DA18CC. The reaction is shown in Scheme 1.



DA18CC

Shceme 1.

The testing solutions of metal-DA18CC chelates were made as follows: To a 10 cm^3 volumetric flask, 1 cm^3 of 5 x 10^{-4} mol dm^{-3} standard solution of transition metal ion [Ag(II), Bi(III), Cd(II), Co(II), Fe(II),(III), Hg(II), In(III), Ni(II), Pb(II), Pd(II), Pt(II), U(VI) and Zn(II)], 1 x 10^{-2} mol of alkali metal chloride (or 5 x 10^{-3} mol of alkaline earth metal chloride), 1 cm^3 of 1.0 mol dm^{-3} tris(hydroxymethyl) aminomethane buffer (pH 8.0), 1 cm^3 of 1 x 10^{-3} mol dm^{-3} DA18CC were added. The solution was then diluted to 10 cm^3 with water. After 30 min, the UV-VIS spectra of the solutions were measured.

DA18CC was water-soluble due to the hydration of the ether oxygen and carbodithioate groups. Therefore, a solubilizer was unnecessary for spectrophotometric studies in an aqueous media. The UV-spectrum of DA18CC solution had absorption maxima of carbodithioate groups at 275 nm and 286 nm, which was similar to other carbodithioates.[9] Transition metal ions which we tested [Ag(II), Bi(III), Cd(II), Co(II), Fe(II),(III), Hg(II), In(III), Ni(II), Pb(II), Pd(II), Pt(II), U(VI) and Zn(II)] reacted with DA18CC as well as other carbodithioates[9] commonly used such as diethylamine-N-carbodithioate and pyrrolidine-N-carbodithioate. Among the transition metal ions tested (see above), Fe(III), Co(II), Pd(II) and Ni(II) formed colored chelates with DA18CC. All transition metal-DA18CC chelates we tested (see above) precipitated when their concentrations were over 5 x 10^{-5} mol dm^{-3}. The precipitates were not dissolved by the solubilizers (methanol, ethanol, dimethylfolmamide, tetrahydrofuran and 1,4-dioxane). However, ammonium 1, 4, 10, 13- pentaoxa-16-azacyclooctadecane-(N-carbodithioate), which has a mono-aza-crown ring and one carbodithioate group, forms water soluble chelates with transition metal ions over 5 x 10^{-5} mol dm^{-3} of transition metal ions. These results suggest that the transition metal-DA18CC chelates precipitated not due to poor hydrophilisity but due to some other reasons. One possible reason is the formation of a polynuclear complex comprising repeated units of DA18CC and transition metal ion.

While the UV-spectra of DA18CC were not influenced by addition of alkali and alkaline earth metal ions, those of the transition metal-DA18CC chelates tested (see above) were. The change in spectra of Ni(II)- DA18CC chelate is shown in Figure 1, as a typical case. The addition of Mg^{2+} or Na^+ ion made the formation of the Ni(II) chelate advantageous.

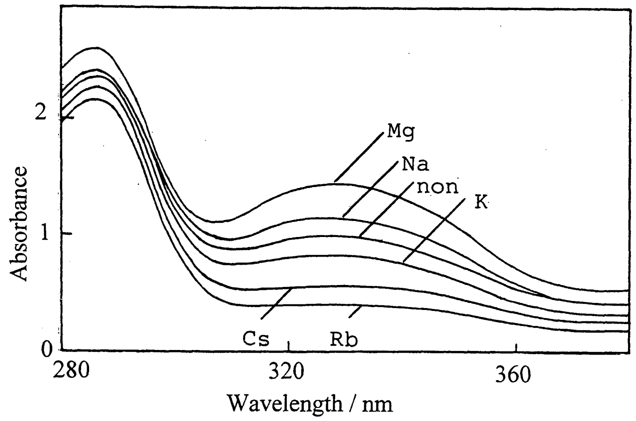
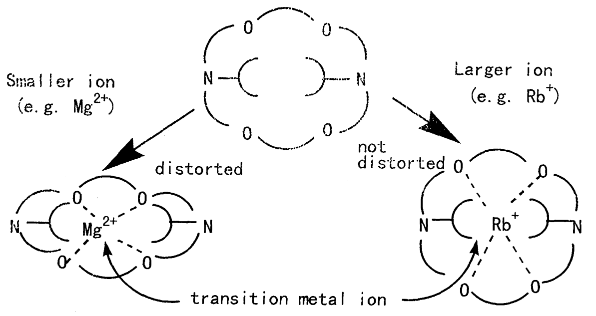


Figure 1. UV spectra of Ni(II)-DA18CC chelate in the presence of alkali metal, alkali earth metal ion. [Ni(II)]=5 x 10^{-5} mol dm^{-3}, [DA18CC]= 1 x 10^{-4} mol dm^{-3}, [alkali chloride]= 1 mol dm^{-3} or [alkali earth chloride]=0.5 mol dm^{-3}, pH 8.0.

However, the addition of K^+, Cs^+ and Rb^+ ion interfered with the formation of the Ni(II) chelate. We guessed that those phenomena were produced by the change of conformation in the diaza-crown ring. To fit the smaller ion (Mg^{2+} and Na^+), the conformation of the diaza-crown ring changes, as the four oxygen atoms were located closer. This change results in expanding the cavity formed by the two carbodithioate groups in DA18CC and makes Ni(II) chelate advantageous. In the absence of alkali metal ions and alkaline earth metal ions, the diaza-crown ring must distort its conformation by itself to form the Ni(II) chelate. Fitting the larger ions (K^+, Rb^+ and Cs^+) prevents changing the conformation and makes the formation of Ni(II) chelate disadvantageous. The influence of alkali metal ions and alkaline earth metal ions is shown in Scheme 2.



Scheme 2.

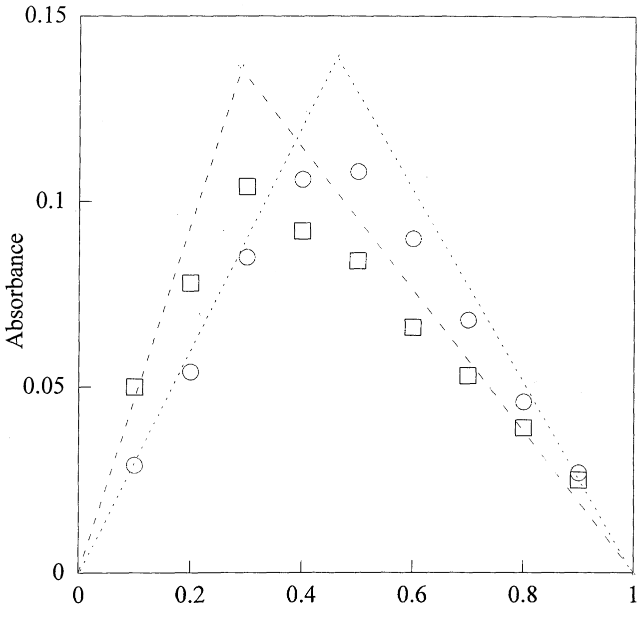


Figure 2. Plots of contenious variation method of Pb(II)-DA18CC chelate. [Pb]+[DA18CC]=2x10^{-5} mol dm^{-3}, pH 8.0. ○:[Mg^{2+}]=0 mol dm^{-3}, □:[Mg^{2+}]=0.5 mol dm^{-3}.

Coexisting alkali metal ions and alkaline earth metal ions also affected the composition ratio (transition metal to ligand) of DA18CC chelates. Figure 2 shows the plots of the continuous variation method of Pb(II)-DA18CC chelate in the presence or absence of Mg^{2+} ion, as a typical case. The addition of Mg^{2+} ion altered the composition rate of the Pb(II)-DA18CC chelate. The addition of Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+} showed the similar effects. We guess that there were several species of transition metal-DA18CC chelate in the solution, which equilibrated one another. Addition of alkali metal ions and alkaline earth metal ions may control the equilibriums of the chelates through change in conformation of the diaza-crown ring. From investigation of the other transition metal-DA18CC chelates, it was observed that Cd(II), Co(II), Cu(II), In(III), Ni(II), Pd(II), Pt(II) and Zn(II) - DA18CC chelates showed the similar behavior to Pb(II) chelate.

It was thus shown that coexisting alkali metal ions and alkali earth metal ions could control the reactivity of DA18CC and the composition of transition metal-DA18CC chelates. The easiness of the conformation change of the diaza-crown ring produced these phenomena.

Reference and Notes

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