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pH dependence of acetate coordination and intramolecular rearrangement of CyDTA metal complexes—^{1}H NMR study

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Abstract—The pH dependence of acetate coordination of Zn-, Cd- and Hg-CyDTA (cyclohexanediaminetetraacetate) complexes and the nitrogen inversion of Ca-, Sr and Ba-CyDTA complexes was studied by ^{1}H NMR. It was shown that the electron density on the out-of-plane coordinated carboxyl oxygens was more than that on the in-plane ones for Zn- and Hg-CyDTA, while no distinct difference of the electron density between the out-of-plane and in-plane coordinated carboxyl oxygens was observed for Cd-CyDTA. It was found that in the nitrogen inversion of Ca-, Sr- and Ba-CyDTA both H^+ and OH^- in solution would help the dissociation of the metal–nitrogen bond and decrease the activation energy of the process. © 1997 Elsevier Science Ltd

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For the aminopolycarboxylate metal complexes with octahedral configuration, three intramolecular processes are considered possible: (1) Δ, Λ conversion, i.e. the scrambling of the coordinated acetates followed by the substitution of the acetates out-of-plane consisting of N—M—N for those in the plane and meanwhile the acetates in the plane for those out-of-plane bound to another nitrogen; (2) nitrogen inversion, this is the coordination exchange between the out-of-plane and in-plane acetates bound to the same nitrogen by the lone-pair inversion of the nitrogen atom [1]; (3) equilibrium between associated and dissociated states of a coordinated acetate [2]. When the Δ, Λ conversion or nitrogen inversion process is rapid, one could observe the change of NMR lineshape of the acetate methylenic protons, e.g. the broadening of spectral lines or even coalescence among them. The information on the structure of complexes, the rate of intramolecular acetate rearrangement and the activation parameters of the migration processes should be obtained by investigating the change in lineshape [3–9]. The third process would lead to the change in chemical shift when temperature, pH and solvent etc. are varied. The information on the population possibility of associated or dissociated state of an acetate, which is related to the strength of the acetate coordinated bond, is included in the change in chemical shift. In general, this equilibrium process is difficult to be studied by NMR because of the perturbation of the fast Δ, Λ conversion process unless the complexes have the special rigid structure such as 1,2-PDTA, CyDTA for which the conversion between Δ and Λ configuration is very difficult [10–14].

In this work we selected CyDTA metal complexes because the rigid cyclohexane ring of the ligand of the CyDTA metal complexes prevents the Δ, Λ conversion and so the study of the equilibrium between associated and dissociated states by NMR becomes possible when the nitrogen inversion process is slow on the NMR time scale. Moreover, as the effect of pH has been an important aspect of investigation for aqueous solution system [15–18], we studied the pH dependence of the acetate coordination and nitrogen inversion for CyDTA metal complexes.

EXPERIMENTAL

Chemicals of analytical-reagent grade were used without further purification. Complexes were pre-

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pared by dissolving a 1 : 1 mole ratio of CyDTA to metal nitrate in an appropriate amount of dilute KOH solution and adjusting the pH to the value at which no sediment existed, then concentrating the solution by heating and at last drying the concentrated product. The NMR sample of *ca* 0.2 M D_2O solution was prepared and placed in a 5 mm sample tube. DCl and NaOD were used to adjust the pH of the solution.

^{1}H NMR spectra were recorded on Varian FT-80A spectrometer. The resonance frequency of proton is 79.542 MHz. DSS was used as the internal standard.

RESULTS AND DISCUSSION

Zn-,Cd- *and* Hg-CyDTA *complexes*

When the nitrogen inversion is a slow process on the NMR time scale, the ^{1}H NMR spectrum of the acetate methylenic protons of the CyDTA complex consists of two AB quartets, one of which arises from the out-of-plane acetate methylenic protons and the other from the in-plane ones. With an increase in the rate of the nitrogen inversion the two AB quartets will coalesce into one AB pattern [13].

The resonance of the acetate methylenic protons in the ^{1}H NMR spectra of Zn-Cd- and Hg-CyDTA at room temperature consists of two AB quartets, as shown in Fig. 1. The one with larger chemical shift differences between two acetate methylenic protons is assigned to the out-of-plane acetate methylenic protons and the other with smaller chemical shift difference to the in-plane acetate methylenic protons, similarly to the assignment of Co-CyDTA and Co-PDTA, which has been proved by the isotopic exchange experiment of the protons [19].

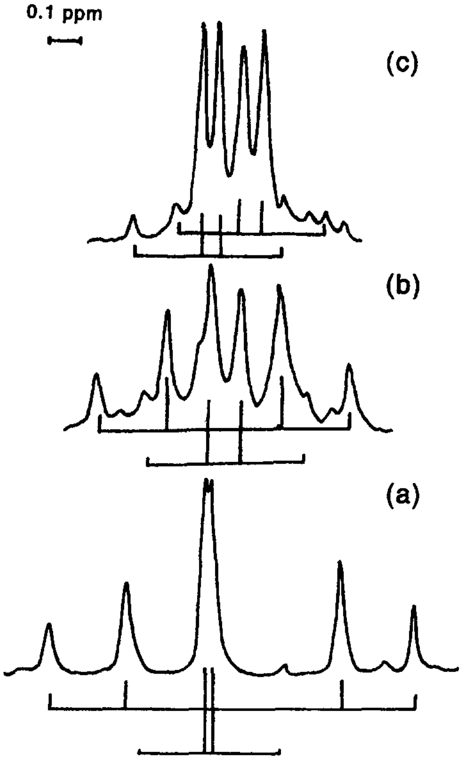

Fig. 1. The ^{1}H NMR subspectra and their assignment of the acetate methylenic protons for (a) Zn-CyDTA, pH = 6.0, (b) Cd-CyDTA, pH = 8.5 and (c) Hg-CyDTA, pH = 6.0 at room temperature.

Figure 2 exhibits the pH dependence of the chemical shifts of the acetate methylenic protons for Zn-, Cd- and Hg-CyDTA complexes at room temperature. For the Zn-CyDTA complexes [see Fig. 2(a)], it is found that the chemical shifts of the in-plane and out-of-plane acetate methylenic protons, represented by δ_i and δ_o respectively, shift downfield with decreasing pH value in the acidic rage of pH and δ_o shifts downfield faster than δ_i. This is a typical protonating process of the carboxyl oxygen and as a result it decreases shielding on the acetate methylenic protons with increasing H^+ concentration. The out-of-plane carboxyl oxygens are easier to be protonated than the in-plane carbonyl oxygens. Thus, it could be inferred that the out-of-plane carboxyl oxygens have the more electron density than the in-plane ones and the conclusion that the metal–oxygen bond is longer in the out-of-plane coordinated ring than in the in-plane ring might be drawn.

For Cd-CyDTA complexes, no distinct difference between δ_o and δ_i was observed, as shown in Fig. 2(b). Under the acidic condition the protonating behavior also occurs, but the rate of protonating is almost the same for the out-of-plane and in-plane carboxyl oxygens. This means that there is no distinct difference in the electron density between the out-of-plane and in-plane carboxyl oxygens and thus suggests that the metal–oxygen bond is almost as long in the out-of-plane ring as in the in-plane ring.

From Fig. 2(c) one can see that the pH dependence of δ_o and δ_i for Hg-CyDTA is similar to that for the Zn-CyDTA complex in the acidic range of pH, i.e. the chemical shifts move downfield with decreasing pH and δ_o shifts more rapidly than δ_i. This also indicates that both out-of-plane and in-plane carboxyl oxygens are protonated in the acidic range of pH and the out-of-plane carboxyl oxygens are with the stronger ability of protonating than the in-plane ones. Therefore, one could conclude that for Hg-CyDTA complex, the out-of-plane carboxyl oxygens possess more electron density and the metal–oxygen bond is longer in the out-of-plane ring than in the in-plane ring.

When the pH of Hg-CyDTA solution was increased to the alkaline range, the chemical shifts move surprisingly downfield with increasing pH. The change in chemical shift of the acetate methylenic proton of the Hg-CyDTA complex with pH is similar to CyDTA ligands in the acidic range, i.e. the chemical shifts of the acetate methylenic protons move downfield with decreasing pH due to the protonation, but different under the alkaline condition. In the alkaline range of pH, the acetate methylenic proton quartet shifts upfield for CyDTA, however, downfield for the

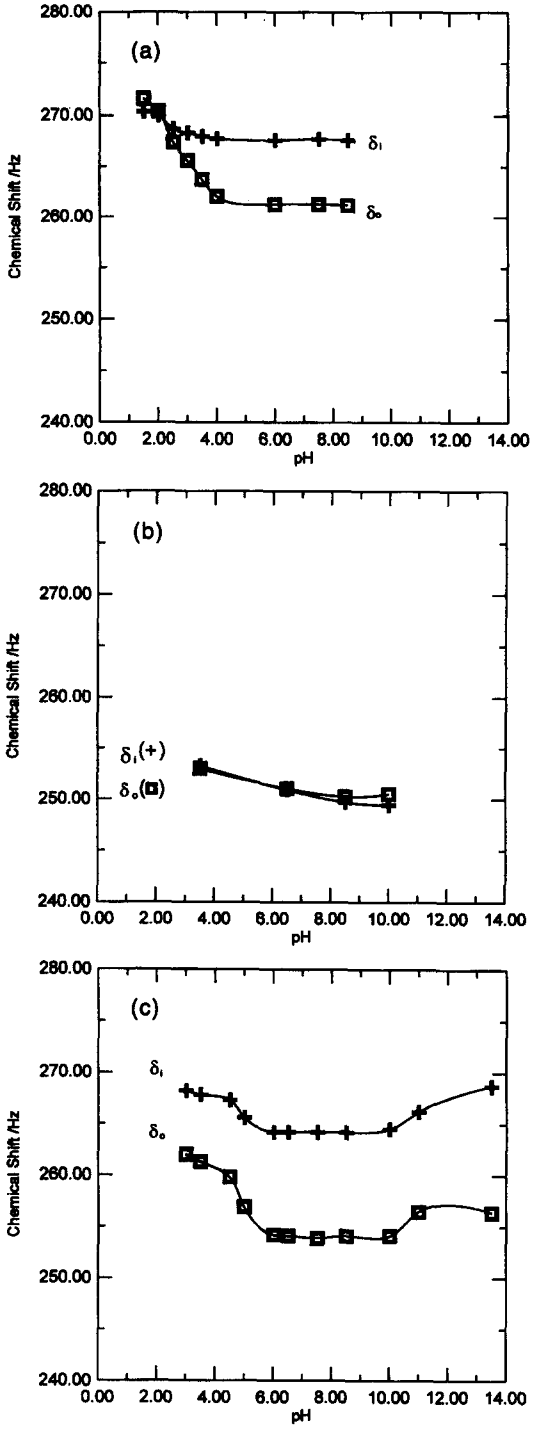

Fig. 2. The pH dependence of the chemical shift of the acetate protons out of plane δ_o and in plane δ_i for (a) Zn-CyDTA, (b) Cd-CyDTA and (c) Hg-CyDTA.

complex. For the former, the increase in the negative charge of the carboxyl increases the shielding of the acetate methylenic protons. Whereas for the latter, this shielding effect is counteracted by the deshielding effect resulting from the increase in the effective positive charge of the metal ion (see the following discussion).

In solution, the coordination of the carboxyl oxygen to the metal ion is in equilibrium between association and dissociation. When the carboxyl oxygen is bound completely to the metal ion, the AB subspectrum arising from the two acetate methylenic protons would give the largest chemical shift difference. In contrast, the chemical shift difference is the smallest when the carboxyl oxygen is dissociated completely from the metal ion, as the rotation of the carboxyl around C—N bond averages the environment of two acetate methylenic protons. In fact, the observed chemical shift difference $\Delta\delta$ is a weighted average of the chemical shift difference in these two extreme circumstances. $\Delta\delta$ depends on the population possibility of carboxyl oxygen in the dissociated state or the associated state. The larger the possibility in the dissociated state, the smaller will be $\Delta\delta$. Therefore, the change in $\Delta\delta$ with pH reflects the change in the strength of the metal–oxygen bond.

The effect of pH on $\Delta\delta$ is shown in Fig. 3. For Zn-CyDTA, $\Delta\delta_o$ decreases with decreasing pH under the acidic condition as shown in Fig. 3(a). It can be inferred that the dissociated possibility of the out-of-plane carboxyl oxygen increases with increasing H^+ concentration and the strength of the metal–oxygen bond decreases correspondingly. $\Delta\delta_i$ is too small for the resolution of our instrument to measure accurately and not given in the Fig. 3(a). No distinct change in $\Delta\delta_o$ and $\Delta\delta_i$ with pH was observed for Cd-CyDTA. For Hg-CyDTA, $\Delta\delta_o$ decreases slightly with decreasing pH in the acidic range of pH, indicating a slight increase in the dissociated possibility of the out-of-plane carboxyl oxygen. $\Delta\delta_i$ seems not to change distinctly with pH in the acidic range. However, under the alkaline condition, $\Delta\delta_o$ increases and $\Delta\delta_i$ decreases obviously with increasing pH. Thus, it can be suggested that OH^- facilitates the dissociation of the in-plane carboxyl oxygen. One of the reasons would be that the lower electron density of the carboxyl oxygen in the in-plane coordinated ring allows OH^- to obtain access to the metal ion more easily in the in-plane direction to help the association of the in-plane metal–oxygen bond. The increase in the possibility of the dissociated state of the in-plane carboxyl with increasing OH^- concentration results in the increase in the effective positive charge on the metal ion and as a result the increase in the possibility of the association state of the out-of-plane carboxyl oxygen.

By comparison, it was found that $\Delta\delta$ of Zn- and Hg-CyDTA change obviously with pH, but $\Delta\delta$ of Cd-CyDTA almost does not change with pH. The difference among them would be determined by their radii (*r*) and ratios (*Z*/*r*) of charge (*Z*) to radius. The rigid structure of CyDTA limits the volume of the octahedral complex. Too large or too small a radius of the ion would have the volume of the complex too large or too small and increase the strain of the

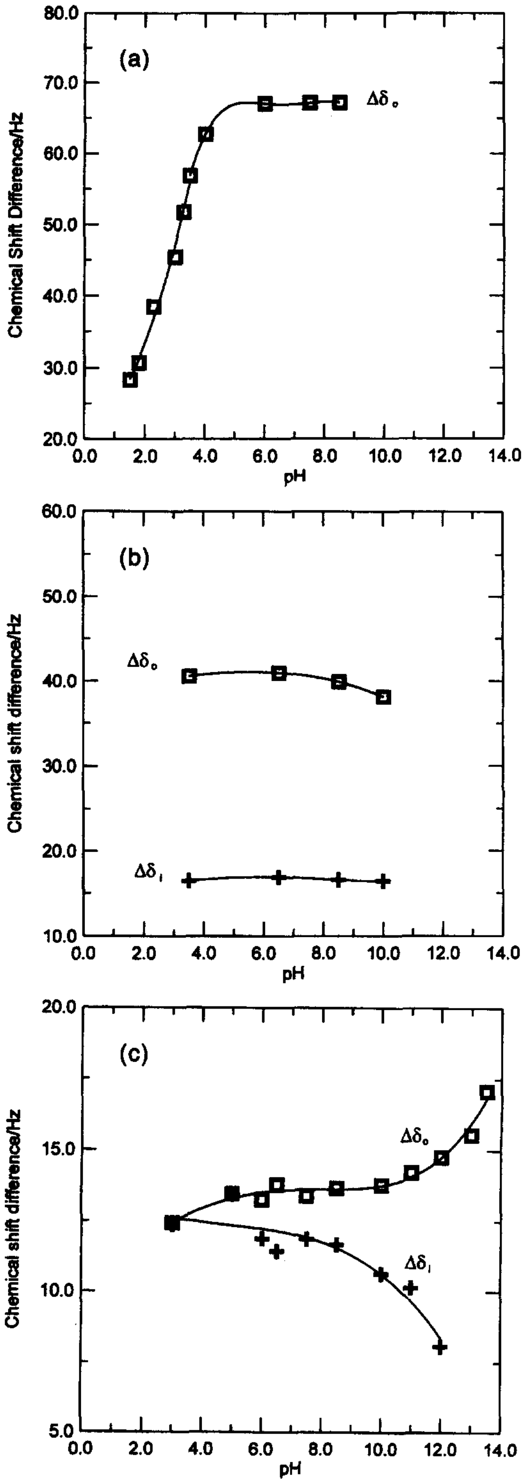

Fig. 3. The pH dependence of the chemical shift difference of the acetate protons out of plane $\Delta\delta_0$ and in plane $\Delta\delta_i$ for (a) Zn-CyDTA, (b) Cd-CyDTA and (c) Hg-CyDTA.

coordinated acetate ring and thus decrease the strength of the metal–oxygen bond. The larger the ratio *Z*/*r*, the stronger the M—O bond. The radii of Zn^{2+}, Cd^{2+} and Hg^{2+} are 0.74, 0.97 and 1.10 Å, respectively. Although the Zn^{2+} ion has the largest *Z*/*r* ratio among the three ions, its radius would be too small to match the ligand well. This would lead to the larger strain on acetate rings of the Zn-CyDTA complex and make the coordinated bond labile. The radii of Cd^{2+} and Hg^{2+} are larger and both would match the ligand better. However, Hg^{2+} has the smaller *Z*/*r* than Cd^{2+} and thus the strength of the coordinated bond of Hg-CyDTA would be smaller than that of Cd-CyDTA. Therefore, whether *r* or *Z*/*r* is considered, Cd-CyDTA complex would be the stablest among the three complexes. This is perhaps the reason why $\Delta\delta$ of Cd-CyDTA has no significant change with pH.

Ca-, Sr- *and* Ba-CyDTA *complexes*

For these complexes, we observed the effect of pH on the intramolecular rearrangement process. The ^1H NMR spectra of the acetate methylenic protons of these complexes also consist of two AB patterns. That with the larger chemical shift difference is assigned to the out-of-plane acetate methylenic protons and the other with a smaller chemical shift difference to the in-plane acetate methylenic protons, as for the assignment of Zn-, Cd- and Hg-CyDTA complexes. However, the coalescence of AB quartets was observed for the three complexes under 100°C. This indicated that the nitrogen inversion of these complexes is a process with intermediate rate on the NMR time scale.

When the temperature dependence of ^1H NMR spectra of the acetate methylenic protons was measured under different pH, it was found that the coalescence temperature (the temperature at which the coalescence of AB quartet occurs) is lower for Ca-CyDTA and Ba-CyDTA with the change of pH from 7.0 to 4.6 and from 9.3 to 13.6, respectively, but it has no distinct change for Sr-CyDTA from pH of 8.0 to 5.6. The change in the coalescence temperature reflects the change in the activation energy of the nitrogen inversion process. Table 1 lists the data of activation energy of the nitrogen inversion for Ca-, Sr- and Ba-CyDTA complexes with the various pH values. These data are in agreement with the coalescence temperature. It is suggested that either the increase in H^+ or OH^- concentration favors the breaking of the metal–nitrogen bond and thus decreases the activation energy of intramolecular rearrangement, as was observed in Ca- and Ba-CyDTA. It is supposed that a plateau would present on the curve of the activation energy *vs* pH. The range of pH for Sr-CyDTA might fall in the plateau as the change of the activation energy with pH is small. In the acidic solution, the decrease of the activation energy is relative to the protonation of carboxyl oxygen and nitrogen atoms. In the alkaline solution, it might be attributed to the increasing possibility of OH^- attacking the metal ion

Table 1. The activation energy parameters of nitrogen inversion for Ca-, Sr- and Ba-CyDTA complexes at various pH values

Complexes	Ca-CyDTA		Sr-CyDTA		Ba-CyDTA	
pH	5.0	7.0	6.0	8.0	14.0	9.3
E_a (kJ mol^{-1})	62.7±0.2	114.1[a]	60.4±0.7	66.5[a]	45±1	57.3[a]

[a] The data quoted from [13].

that leads to the weakness of the coordinated bond between metal and nitrogen.

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