A ^9Be NMR STUDY ON THE COORDINATION STRUCTURES OF Be^{2+}
COMPLEXES WITH *CYCLO*- μ -IMIDOTRIPHOSPHATE ANIONS (II)

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Abstract Macroscopic and microscopic complexation behaviors of Be^{2+} ions with cyclic imidotriphosphate ligands, involving P-O-P and/or P-NH-P linkages, i.e., *cyclo*- μ -monoimidotriphosphate, $\text{cP}_3(\text{NH})$, *cyclo*- μ -diimidotriphosphate, $\text{cP}_3(\text{NH})_2$, and *cyclo*- μ -triimidotriphosphate, $\text{cP}_3(\text{NH})_3$, anions have been investigated by a ^9Be NMR technique. The stability constants of monodentate and bidentate complexes, as well as those of oxygen-coordination and nitrogen-coordination complexes have been determined by the peak area ratio calculation of the ^9Be NMR spectra. The stability constants of oxygen-coordination and nitrogen-coordination monodentate complexes increase in the order of $\text{cP}_3(\text{NH}) < \text{cP}_3(\text{NH})_2 < \text{cP}_3(\text{NH})_3$. However, the magnitude of the increase is much more pronounced in the case of the stability constants of nitrogen-coordination monodentate complexes, since the number of binding nitrogen atoms in the ligand molecules increases with the same order.

INTRODUCTION

Despite a large number of thermodynamic studies on inorganic polyphosphate complexation equilibria, quite a limited number of studies has been employed on the microscopic coordination behavior of the complexation equilibria in aqueous solution. This is due to the difficulty in the determination of microscopic complex stability constants by the use of conventional thermodynamic methods on these multidentate ligand molecules¹. A metal NMR technique is expected to give direct and quantitative

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information on the microscopic complexation equilibria. Due to the slow chemical exchange in aqueous solution, Be^{2+} ion complexation system is one of the most suitable systems for the microscopic complexation equilibrium analyses, i.e., separate signals for respective microscopic coordination structures of the complexes are expected to be observed in the ^9Be NMR spectra. This technique has been applied to the Be^{2+} complexation studies on the series of ligands, $\text{cP}_3(\text{NH})$, $\text{cP}_3(\text{NH})_2$, and $\text{cP}_3(\text{NH})_3^{2-}$; however, quite little has been disclosed by these studies, since the solution concentration examined was limited. In the present work, the complexation systems were reexamined by investigating the sample solutions of wide concentration range. In our previous study, it has been clarified that $\text{cP}_3(\text{NH})_3$ ligand forms monodentate complexes with oxygen-coordination and nitrogen-coordination, as well as bidentate complexes coordinated with two oxygen atoms. In this study, the microscopic complexation equilibria for the series of ligand molecules, $\text{cP}_3(\text{NH})_n$ ($n=1-3$) have been elucidated from the quantitative treatment of ^9Be NMR spectra of Be^{2+} -ligand mixture solutions. As shown in Figure 1, the ligand molecules carry the same charge of "-3", however the complexing abilities of nitrogen atoms as well as oxygen atoms must be different from each other and the comparison of the microscopic complex stability constants is expected to give deeper insights into these multicoordination complexation behaviors.

FIGURE 1 Structural formulas of $\text{cP}_3(\text{NH})_n$ ($n=1-3$) anions.

EXPERIMENTAL PROCEDURE

Trisodium salt of $\text{cP}_3(\text{NH})_n$ ($n=1-3$) have been prepared according to the literatures³⁻⁵. The purities of the samples were checked by ^{31}P NMR. All other reagents used in this work were of analytical grade. ^9Be NMR spectra were recorded on a Bruker DPX-250 (5.87T) NMR spectrometer operated at 35.147 MHz. An acquisition time was 0.4-0.8 sec, and the data points of free induction decay were 2K-4K; a relaxation delay between each scan of 0.1 sec was employed. The Lorentzian line-broadening factor of 1.0 Hz was applied to the total free induction decay prior to Fourier transformation. All spectra were recorded with a non-proton-decoupling mode. An NMR titration procedure has been employed by adding stepwisely by the use of a micro-syringe a portion of a

sodium salt solution of $\text{cP}_3(\text{NH})_3$ to a 3.00 cm^3 portion of BeCl_2 solution contained in an NMR sample tube. The initial concentration of $\text{cP}_3(\text{NH})_3$ was kept 0.2 mol dm^{-3} , while the initial BeCl_2 concentration of the titrants, C_{Be}^0 , were 0.005 , 0.01 , and 0.02 mol dm^{-3} , respectively for three different titration runs. The pH of the sample solutions was carefully kept between 2.3 and 2.7 with the addition of diluted hydrochloric acid in order to avoid hydrolysis of Be^{2+} ions. All of the ^9Be NMR spectra were obtained at 271.2 K for the better peak resolution, and the temperature was calibrated by using 1,2-ethanediol sample⁶. The accuracy is $\pm 1 \text{ K}$ or better, and the reproducibility is 0.2 K .

RESULTS AND DISCUSSION

A representative ^9Be NMR spectrum of $\text{Be}^{2+}\text{-cP}_3(\text{NH})_2^{3-}$ mixture solution is shown in Figure 2-A. The ^9Be NMR spectrum can be deconvoluted into three peaks by the non-linear least squares method by assuming the Lorentzian curves. Three peaks appearing at 0 , -0.6 , and -1.2 ppm are due to $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, monodentate, and bidentate complexes, respectively⁷. Since $\text{cP}_3(\text{NH})_n$ ($n=1\text{-}3$) ligands has oxygen atoms as well as nitrogen atoms as donor atoms, and it has been revealed that Be^{2+} ions can coordinate to both of them in the case of $\text{cP}_3(\text{NH})_3$ ligand⁸, the peak due to monodentate complex was deconvoluted into two peaks as shown in Figure 2-B. Also since the formation of bidentate complex has been revealed in an intermolecular mode for $\text{cP}_3(\text{NH})_3$ by our previous work⁸, the following two complexation schemes will be discussed hereafter.

FIGURE 2 Deconvoluted ^9Be NMR spectrum of $\text{Be}^{2+}\text{-cP}_3(\text{NH})_2^{3-}$ mixture solution.
 $C_{\text{Be}}=0.89 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{L}}=1.11 \times 10^{-2} \text{ mol dm}^{-3}$; pH 2.5; 271.2 K
 A peak 1; free Be^{2+} ion, peak 2; monodentate complex, peak 3; tridentate complex
 B peak 1; free Be^{2+} ion, peak 2; $\text{Be}^{2+}\text{-(N)}$, peak 3; $\text{Be}^{2+}\text{-(O)}$,
 peak 4; $\text{Be}^{2+}\text{-(O,O)}$ complex

1) 1:1 and 1:2 complexations,

where L indicates a ligand molecule, and K_1 and K_2 represent the stepwise stability constants of the complexes, respectively, and

2) microscopic complexations with oxygen and nitrogen coordination,

where $K_{1,\text{O}}$ and $K_{1,\text{N}}$ represent the microscopic stability constants of monodentate complexes with oxygen and nitrogen coordinations, respectively. The K_1 and K_2 values can be evaluated by the peak area of the complexes of monodentate (S_1), bidentate (S_2), and free Be^{2+} ions (S_0) as,

$$K_1 = \frac{[\text{BeL}^-]}{[\text{Be}^{2+}] \cdot [\text{L}^{3-}]} = \frac{S_1}{S_0} \cdot \frac{1}{[\text{L}^{3-}]}, \quad K_2 = \frac{[\text{BeL}_2^{4-}]}{[\text{BeL}^-] \cdot [\text{L}^{3-}]} = \frac{S_2}{S_1} \cdot \frac{1}{[\text{L}^{3-}]} \quad (3)$$

The concentration of free ligand, $[\text{L}^{3-}]$, can be calculated by the following equation,

$$[\text{L}^{3-}] = C_L - \sum_{i=0} \left(\frac{i \cdot S_i \cdot C_{\text{Be}^{2+}}}{\sum_{i=0} S_i} \right) \quad (4)$$

where C_L and $C_{\text{Be}^{2+}}$ are the total concentrations of the ligand, and Be^{2+} ion, respectively, and i is the coordination number of the complexes. The peak area ratio,

FIGURE 3 Plots of S_1/S_0 vs. $[\text{L}^{3-}]$ for the Be^{2+} - $\text{cP}_3(\text{NH})_n$ ($n=1-3$) system. ($\circ$); $C_{\text{Be}}^0=0.005 \text{ mol dm}^{-3}$, (Δ); $C_{\text{Be}}^0=0.01 \text{ mol dm}^{-3}$, ($\diamond$); $C_{\text{Be}}^0=0.02 \text{ mol dm}^{-3}$ open; $n=1$, closed; $n=2$, shaded; $n=3$

S_1/S_0 , and S_2/S_1 values are plotted in Figures 3 and 4 against the $[\text{L}^{3-}]$ values, respectively; the plots give straight lines, whose slopes are equal to K_1 , and K_2 , respectively. The microscopic complex stability constants of O-coordinating and N-coordinating monodentate complexes, $K_{1,\text{O}}$ and $K_{1,\text{N}}$ can respectively be expressed as follows.

$$K_{1,O} = \frac{[\text{Be}^{2+}-(\text{O})]}{[\text{Be}^{2+}]} \cdot \frac{1}{[\text{L}^{3-}]} = \frac{S_{1,O}}{S_0} \cdot \frac{1}{[\text{L}^{3-}]}, \quad K_{1,N} = \frac{[\text{Be}^{2+}-(\text{N})]}{[\text{Be}^{2+}]} \cdot \frac{1}{[\text{L}^{3-}]} = \frac{S_{1,N}}{S_0} \cdot \frac{1}{[\text{L}^{3-}]} \quad (5)$$

where $\text{Be}^{2+}-(\text{O})$, and $\text{Be}^{2+}-(\text{N})$ indicate oxygen-coordinating and nitrogen-coordinating monodentate complexes, respectively. $S_{1,O}$ and $S_{1,N}$ are the the peak areas due to respective monodentate complexes. The peak area ratios, $S_{1,O}/S_0$, and $S_{1,N}/S_0$ values are plotted in Figure 5 against $[\text{L}^{3-}]$, which give straight lines whose slopes are equal to $K_{1,O}$ and $K_{1,N}$, respectively.

FIGURE 4 Plots of S_2/S_1 vs. $[\text{L}^{3-}]$ for the Be^{2+} - $\text{cP}_3(\text{NH})_2$ system. open; Be^{2+} - $\text{cP}_3(\text{NH})_2^{3-}$ system closed; Be^{2+} - $\text{cP}_3(\text{NH})_3^{3-}$ system ($\circ$); $C_{\text{Be}}^0 = 0.005 \text{ mol dm}^{-3}$, (Δ); $C_{\text{Be}}^0 = 0.01 \text{ mol dm}^{-3}$

The logarithmic values of all these microscopic complex stability constants are listed in Table 1 together with the macroscopic constants. It is clarified that $K_{1,N}$ is lower than $K_{1,O}$ for the $\text{cP}_3(\text{NH})$ and $\text{cP}_3(\text{NH})_2$ systems, whereas it becomes greater than $K_{1,O}$ in the case of $\text{cP}_3(\text{NH})_3$ system. This trend observed specifically for $\text{cP}_3(\text{NH})_3$ seems somewhat surprising, since Be^{2+} ion is one of the hardest cations by an HSAB scale, and this Be^{2+} -N direct coordination structure does not seem to follow the HSAB rule. The present result shows that electron-crowded donor nitrogen atoms in the ring center of these ligands form a specific binding site, which enables hard Be^{2+} ions to coordinate directly to nitrogen atoms.

All the macroscopic and microscopic complex stability constants thus obtained are

FIGURE 5 Plots of $S_{1,O}/S_0$ vs. $[\text{L}^{3-}]$ or $S_{1,N}/S_0$ vs. $[\text{L}^{3-}]$ for the Be^{2+} - $\text{cP}_3(\text{NH})_n$ ($n=1-3$) systems. ($\circ$); $C_{\text{Be}}^0 = 0.005 \text{ mol dm}^{-3}$, (Δ); $C_{\text{Be}}^0 = 0.01 \text{ mol dm}^{-3}$, ($\diamond$); $C_{\text{Be}}^0 = 0.02 \text{ mol dm}^{-3}$ open; $n=1$, closed; $n=2$, shaded; $n=3$

Table 1 Logarithmic macroscopic and microscopic stability constants for the interaction of $\text{cP}_3(\text{NH})_n$ ($n=1-3$) anions with Be^{2+} ion.

	$\log K_1$	$\log K_2$	$\log K_{1,\text{O}}$	$\log K_{1,\text{N}}$
$\text{cP}_3(\text{NH})^{3-}$	2.79	—	2.71	1.97
$\text{cP}_3(\text{NH})_2^{3-}$	3.34	1.11	3.08	3.00
$\text{cP}_3(\text{NH})_3^{3-}$	3.92	1.18	3.11	3.85

plotted in Figure 6 against the number of imino groups in the $\text{cP}_3(\text{NH})_n$ ($n=1-3$) ligands. Since the basicity of non-bridging oxygen atoms increases to a small extent with a replacement of P-O-P linkage by P-NH-P linkage in the ligand, $K_{1,\text{O}}$ increases with the

" n " increase in $\text{cP}_3(\text{NH})_n$ molecule. On the other hand, the magnitude of the increase in $K_{1,\text{N}}$ is much more pronounced than that in $K_{1,\text{O}}$, since the number of nitrogen atoms which are coordination atoms in a ligand molecule increases with the " n " increase. It can be concluded that the increase in the macroscopic stability constants of monodentate complexes with $\text{cP}_3(\text{NH})_n$ ($n=1-3$) ligands with respect to " n " is mainly due to the contribution of Be^{2+} -nitrogen atom direct binding.

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FIGURE 6 The change in the complex formation constants with the number of imino groups. (●); $\log K_{1,\text{O}}$, (▲); $\log K_{1,\text{N}}$, (○); $\log K_1$, (□); $\log K_2$