27Al NMR STUDY ON MULTIDENTATE COMPLEXATION BEHAVIOR OF CYCLO-TRI-μ-IMIDO TRIPHOSPHATE ANIONS

HIDESHI MAKI, TOHRU MIYAJIMA, SHIN-ICHI ISHIGURO, HIROYUKI NARAI, ITARU MOTOOKA, MAKOTO SAKURAI, and MAKOTO WATANABE

DEPARTMENT OF CHEMICAL SCIENCE AND ENGINEERING, FACULTY OF ENGINEERING, KOBE UNIVERSITY, ROKKODAI-CHO, NADA-KU, KOBE, JAPAN

INTRODUCTION

Cyclo-tri imido-μ-triphosphate (cP3(NH)3) anions composed of three P-NH-P linkages contain oxygen atoms and nitrogen atoms, which may participate in coordination with metal ions. Much attention has been drawn for the multideterminate complexation property of the cyclic ligand molecule, because most of inorganic polyphosphate anions have only phosphate oxygen atoms as coordination atoms. The present authors have observed a preferential binding of divalent transition metal ions, such as Cu2+ and Cd2+...
ions to cP$_3$(NH)$_3$ anions.$^1$ Also, by comparison with the complexation behavior of anions of cyclo triphosphate, cyclo-mono-µ-imido triphosphate, and cyclo-di-µ-imido triphosphate anions, participation of nitrogen atoms in the coordination of cP$_3$(NH)$_3$ anions has been indicated.$^2$ It has been claimed by the present authors that metal NMR technique is one of the promising approaches to investigate the microscopic structures of the complexes with the ligands composed of different coordinating atoms.$^3$ In the present study, $^{27}$Al NMR spectra of mixture solutions of Al$^{3+}$ and cP$_3$(NH)$_3$ anions have been obtained and are analyzed by peak deconvolution.

**EXPERIMENTAL**

Sodium salt of cP$_3$(NH)$_3$ has been prepared and purified according to the literature.$^4$ All reagents used in this work were of analytical grade. $^{27}$Al NMR spectra were obtained at 22 ± 1°C with a JEOL-GX 400 NMR spectrometer, operating at 104.2 MHz for $^{27}$Al nucleus (Reference: 0.1 mol dm$^{-3}$ Al(NO$_3$)$_3$). The solution of 1.0 mol dm$^{-3}$ cP$_3$(NH)$_3$ was added stepwisely to 3.00 cm$^3$ portions of Al(NO$_3$)$_3$ solution contained in a NMR sample tube (φ = 10 mm) by use of a micro-syringe. The pH value of the sample solutions was kept between 4.2 and 4.7, which ensures all phosphate groups of cP$_3$(NH)$_3$ anions are almost completely dissociated. The spectra were deconvoluted in Lorentzian curves.

**RESULTS AND DISCUSSION**

A representative $^{27}$Al NMR spectra of Al$^{3+}$-cP$_3$(NH)$_3$ mixture solution is shown in Figure 1. The peaks appearing at -4, -8, and -12 ppm are attributed to mono-, di-, and tridentate complexes, respectively. This peak assignment is based on the fact that

![Figure 1](image-url)
Al NMR chemical shift changes stepwisely by successive complexation. Also, it is obvious that the spectra can be deconvoluted by the three Lorentzian peaks as indicated in the same figure. Peak position, peak area, together with the width at half height ($W_{1/2}$) of respective peak have been determined. By taking the ratio of the peak area of tridentate complex ($S_3$) to that of didentate complex ($S_2$), it is obvious that $S_3/S_2$ remains constant irrespective of the total concentrations of $\text{Al}^{3+}$ ions, $C_\text{Al}$, and the ligand, $C_L$, as shown in Figure 2. This indicates formation of tridentate complex from didentate complex is intramolecular reaction.

Comparison of the $W_{1/2}$ value of didentate complex peak with those of mono- and tridentate complexes tells us that the didentate complex peak is composed of three peaks due to two coordinating atoms, i.e., non-bridging oxygen and/or nitrogen. In order to express these multidentate coordination states of $\text{Al}^{3+}$ ions, the didentate complexes are expressed as, $\text{Al}^{3+}$-(O, O), $\text{Al}^{3+}$-(O, N), and $\text{Al}^{3+}$-(N, N). Also, the peak corresponding to monodentate complexes can be expressed as the sum of the peaks due to $\text{Al}^{3+}$-(O) and $\text{Al}^{3+}$-(N) complexes. In order to get much deeper insights into the microscopic information on the coordination states, the spectra are further deconvoluted into six Lorentzian curves, i.e., $\text{Al}^{3+}$-(O), -(N), -(O, O), -(O, N), -(N, N) and $\text{Al}^{3+}$-tridentate complexes. The resolved peaks together with the spectra are shown in Figure 3; the spectrum is well-reproduced by this peak deconvolution.

It is believed that the $^{27}\text{Al}$ NMR chemicals shift changes in additive to the number of atoms coordinating with $\text{Al}^{3+}$ ions as,

$$\delta_{\text{Al}} = i \delta(P-O^-) + j \delta(P-N) \quad (1)$$

Figure 3 $^{27}\text{Al}$ NMR spectrum deconvoluted by six Lorentzian curves (The original spectrum is shown in Fig.1).

1; $\text{Al}^{3+}$-(O), 2; $\text{Al}^{3+}$-(N), 3; $\text{Al}^{3+}$-(O,O), 4; $\text{Al}^{3+}$-(O,N), 5; $\text{Al}^{3+}$-(N,N), 6; $\text{Al}^{3+}$-tridentate complex.
where $i$ and $j$ indicate the number of coordinating oxygen and nitrogen atoms, respectively. $\delta(P-O^-)$ and $\delta(P-N)$ are the eigen-shift-values of respective coordination. The $\delta_{Al}$ values determined by the peak deconvolution are plotted in Figure 4 against $i$ and $j$. Two different straight lines have been drawn; the upper solid line corresponds to coordination with nitrogen atoms and the lower dotted line to coordination with oxygen atoms. The $\delta(P-O^-)$ and $\delta(P-N)$ values thus determined are $-3.2$, and $-3.9$ ppm respectively; the $\delta(P-O^-)$ value is consistent with the value obtained in $Al^{3+}$-cyclo-polypophosphate anions. It should be pointed out that the $\delta_{Al}$ value for $Al^{3+}$-(O, N) complexes, $-7.4$ ppm is consistent with the value calculated by use of the eigen values ($-7.1$ ppm). All these results obtained by the peak resolution strongly indicate the multidentate property of cP$_3$(NH)$_3$ anions.

Finally, it is notable that the $\delta_{Al}$ value of the $Al^{3+}$-tridentate complex lies quite close to the upper solid line shown in Figure 4, indicating the direct coordination of three nitrogen atoms to $Al^{3+}$ ion. Since it has already been revealed that the coordination is due to intramolecular reaction, three-nitrogen atoms belonging to the same ligand molecule participate in the complexation.

REFERENCES


