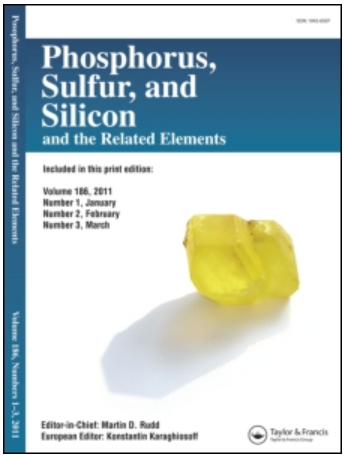

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Inconsistency in the Stability Constants of Inorganic Polyphosphate Anions Determined by Potentiometry and Spectroscopy

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INCONSISTENCY IN THE STABILITY CONSTANTS OF INORGANIC POLYPHOSPHATE ANIONS DETERMINED BY POTENTIOMETRY AND SPECTROSCOPY

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Compared with cyclo-*triphosphate anions,* cyclo-*tri-μ-imidotriphosphate anions (Figure 1), $cP_3(NH)_3^{3-}$, form stable complexes with transition metal ions. Two experimental procedures, potentiometry and spectroscopy, have been applied to determine the stability constants of the complexes with Co^{2+}, Ni^{2+}, and Cu^{2+} ions at 25°C and at $I = 0.10$ ($NaClO_4$). One-to-one (ML) complex formation has been assumed for the analyses. In the presence of sufficiently high concentration of metal ions, the log β_1 values determined by both methods are consistent with each other, whereas the log β_1 value determined by spectroscopy decreases with the decrease in metal ion concentration. This peculiar phenomenon cannot be explained by the presence of additional complexes, that is, ML_2 or M_2L. One possible reasoning is agglomeration formation of ligand molecules mediated by countercations in aqueous solution.*

Keywords: Aggregation; hydrophobic interaction; imido phosphate; potentiometry; spectroscopy; stability constants

Cyclo-μ-imidotriphosphate anions which composed of P—O—P and/or P—NH—P linkages are shown in Figure 1. The complexation behavior of these *cyclo*-μ-imidotriphosphate anions is expected to be much different from that of *cyclo*-triphosphate anions, cP_3. The high basicity of the

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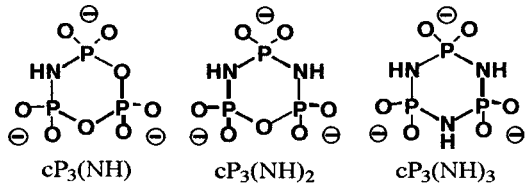

FIGURE 1 Structural formulas of $cP_3(NH)_n$ ($n = 1$–3) anions.

phosphorus atoms comes from the imino groups.[1] For example, the protonation and the complex formation constants increase linearly with an increase in the number of imino groups. In addition, these *cyclo*-μ-imidotriphosphate ligands have not only nonbridging oxygen atoms but also bridging nitrogen atoms as donor atoms. Moreover, it is considered that the hydrophobicity is high for the central region of the molecular ring in which the imino nitrogen atoms exist, so some hydrophobic interactions may affect the complexation behavior. In order to elucidate the dissolution condition of *cyclo*-μ-imidotriphosphate anions in aqueous solution, potentiometry and spectroscopy were applied in this study.

EXPERIMENTAL PROCEDURE

Potentiometry was applied "indirectly" as potentiometric titration, which is made to compete in the protonation and complexation. A glass electrode and a single-junction electrode in a titration cell were connected to an ion meter. For the determination of the complex formation constants, a 20-ml portion of the solution of 0.01 mol dm^{-3} $cP_3(NH)_n$ ($n = 0$–3) + 0.01 mol dm^{-3} $M(NO_3)_2$ (M; Co^{2+}, Ni^{2+}, Cu^{2+}) + 0.10 mol dm^{-3} $NaNO_3$ was titrated by the solution of 0.01 mol dm^{-3} HNO_3 + 0.10 mol dm^{-3} $NaNO_3$. All titrations were carried out at 25°C under nitrogen atmosphere. Spectroscopy was employed by adding stepwise a portion of a solution of 0.10 mol dm^{-3} $cP_3(NH)_3$ + 0.10 mol dm^{-3} $NaClO_4$ by microsyringe to a 2.5-ml of a solution of 0.005, 0.007, 0.01, 0.03, and 0.05 mol dm^{-3} $M(ClO_4)_2$ (M; Co^{2+}, Ni^{2+}, Cu^{2+}) + 0.10 mol dm^{-3} $NaClO_4$ in a quartz cell. The temperature in these measurements were kept at 25°C by water circulation.

RESULTS AND DISCUSSION

The protonation and the complex formation reactions compete in a mixture solutions for the potentiometric titration.

$$H + L \overset{K_H}{\rightleftharpoons} HL \qquad M + L \overset{K_M}{\rightleftharpoons} ML$$

TABLE I Logarithmic Complex Formation Constants of $cP_3(NH)_n^{3-}$ ($n = 0$–3) Anions Determined by Potentiometry [298.15 K, $I = 0.1$ ($NaNO_3$)]

	cP_3^{3-}	$cP_3(NH)^{3-}$	$cP_3(NH)_2^{3-}$	$cP_3(NH)_3^{3-}$
Co^{2+}	1.89 ± 0.01	2.07 ± 0.01	2.39 ± 0.01	2.80 ± 0.02
Ni^{2+}	1.84 ± 0.01	2.14 ± 0.00	2.23 ± 0.02	2.64 ± 0.00
Cu^{2+}	2.26 ± 0.03	2.37 ± 0.02	2.75 ± 0.03	3.50 ± 0.03

The average number of binding protons, $\bar{n}_H$, can be written as

$$\bar{n}_H = \frac{C_H - [H]}{C_L} = \frac{A(A+1) + A\sqrt{(A+1)(A+4K_MC_L+1)}}{2C_L(K_M + K_MA)} \qquad (A = K_H \cdot [H])$$

where C_L and C_H are the total concentration of the ligands and the added acid, respectively. It is possible to obtain the $\bar{n}_H$ value from the experimental data by use of the second term of this equation, and the protonation constant, K_H, is already known. So the complex formation constants, K_M, can be determined by the nonlinear least squares method. The determined log K_M values are listed in Table I. The log K_M values increase almost linearly with an increase in the number of imino groups. This shows that the basicity of the phosphate groups in the cyclic trimers increases with replacement by P—N—P linkages of the ligand. Moreover, it is apparent that the order of the formation constants for each ligands is almost in accordance with the Irving–Williams order. This result indicates that imino nitrogen atoms in *cyclo*-μ-imidotriphosphate anions are not involved in the coordination as donor atoms. This tendency has been confirmed from a spectroscopy—that is, the absorption wavelengths with the respective complex formation show a slight shift.

The obtained UV-VIS spectra have been analyzed by the nonlinear least squares method,[2] and the log K_M values determined are listed in Table II. In the presence of sufficiently high concentration of metal ions, the formation constants of $cP_3(NH)_3^{3-}$ determined by potentiometry

TABLE II Logarithmic Complex Formation Constants of $cP_3(NH)_3^{3-}$ Anions Determined by Spectroscopy [298.15 K, $I = 0.1$ ($NaNO_3$)]

C_M^0 (mol dm^{-3})	0.005	0.007	0.01	0.03	0.05
Co^{2+}	—	—	1.71 ± 0.01	2.26 ± 0.01	2.88 ± 0.01
Ni^{2+}	—	—	2.22 ± 0.01	2.32 ± 0.01	2.53 ± 0.01
Cu^{2+}	2.33 ± 0.01	2.32 ± 0.01	2.49 ± 0.01	2.94 ± 0.01	3.37 ± 0.01

and spectroscopy are consistent with each other, whereas the formation constants determined by spectroscopy decrease with the decrease in metal ion concentration. This phenomenon cannot be explained by the presence of other complexes as ML_2 or M_2L. In the case of $cP_3(NH)_3{}^{3-}$, the molecular structure is ligid, so the water molecule is difficult to go into the central of the ring in aqueous solution. In addition, the imino nitrogen atoms does not have a charge. Thus, the ring central region may be hydrophobic, and the hydrophobic interaction seems to cause an agglomeration formation. The countercation may be also be concerned in the agglomeration.

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