Notes

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Complex Formation of Amino Polyphosphonates. 2. Stability and Structure of Nitrilotris(methylenephosphonato) Complexes of the Divalent Transition-Metal Ions in Aqueous Solution

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The amino polyphosphonates are well-known as crystal growth inhibitors[1-3] and have been widely used as scale inhibitors in industry. Nevertheless, their solution chemistry[4] is not so well understood as that of the amino polycarboxylates.[5] As stated by Martell et al.,[6,7] even the complex formation constants are not always reliable. In a previous paper,[8] we reported the complex formation equilibria and NMR behavior of a series of alkaline-earth-metal complexes of nitrilotris(methylenephosphonic acid) (NTMP, H_6L). These studies indicated that the first protonation of the metal complex occurs on the nitrogen atom of the ligand.

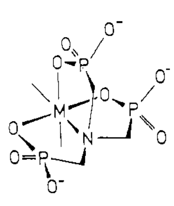
In the present paper, the formation and protonation of the NTMP complexes of divalent transition metals were investigated by potentiometry and NMR spectroscopy at 25.0 °C and at an ionic strength of 0.1 M (KNO_3). These results suggest that all protonations of the transition-metal–NTMP complexes (except that of nickel) occur on the free O^- of the phosphonate groups.

Results

Formation Constants. The mean number of protons bound to the ligand was obtained from the potentiometric data. The values of the formation constant of each metal complex, $K_{ML} = [ML]/[M][L]$, and of successive protonation constants of the complex, $K_{MH_mL} = [MH_mL]/[H][MH_{m-1}L]$, that would result in a minimum error for the mean number of proton were evaluated in the region of pH <7 with the aid of a computer. The results are listed in Table I, where the constants of copper(II) complexes obtained by the copper ion selective electrode measurements are also listed. Under the present experimental conditions, no formation of hydroxo complex M(OH)L or of a higher complex such as ML_2 or ML_3 was observed.

Although the equilibrium constants of the formation and protonation of the NTMP complexes have been reported for several transition metals,[9-12] these values show appreciable discrepancies from our results; the formation constant of a Zn^{2+} complex is 2 units away from our results.

The logarithmic protonation constants are plotted as a function of the logarithmic formation constant of the complex in Figure 1. In the case of the alkaline-earth-metal complexes,[8] the first protonation constant is very large ($\log K_{MHL} > 8.8$) and decreases with the increase in stability of the metal–NTMP complex, K_{ML}. These results indicate tht the first protonation of these complexes occurs on the nitrogen atom of NTMP (structure II), rupturing the M–N bond of the ML complex (structure I). But in the case of transition-metal complexes (Fe(II), Co(II), Zn(II), and Cu(II)), the constants of the first protonation, K_{MHL}, are almost the same irrespective of the metal ions, in spite of a large difference in their formation constants, K_{ML}. Furthermore, these values are smaller than the second protonation constant of ligand NTMP ($\log K_2 = 7.15$), which corresponds to the first protonation on the phosphonate group. Hence, the first protonation of the transition-metal complexes seems to occur on a free O^- of the phosphonate group (structure III). The fact that the difference of the logarithmic constants between the second protonation and third one, $\log K_{MH_2L} - \log K_{MH_3L}$, is almost the same as the difference $\log K_{MHL} - \log K_{MH_2L}$ indicates that the second and third protonations also occur on phosphonate.



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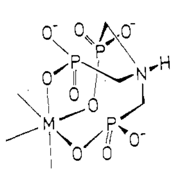

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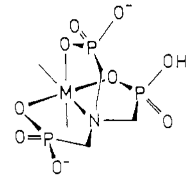

III

It is generally accepted[13] that the bond nature of the alkaline-earth-metal complexes is predominantly ionic and that the M–N bond is thus weak. Consequently, the M–N bond of the complexes is easily ruptured by the protonation on the nitrogen atom having a high basicity ($\log K_1 = 12.7$). On the other hand, the M–N bond of the transition-metal complexes is so strong that the protonations of the complexes occur on the phosphonate O^- of the NTMP. The equilibrium constants of the nickel complexes are quite different from those of the other transition-metal complexes. Therefore, different structures are anticipated for the nickel complexes.

Phosphorus-31 NMR Spectroscopy. ^{31}P NMR spectra of Zn(II)- and Cd(II)–NTMP 1:1 solutions were measured at various pH values. The signal of ^{31}P decoupled with ^1H shows only one singlet peak. The chemical shifts δ_m of each complex MH_mL were evaluated from the observed chemical shift by using the equilibrium constants of the complexes. The chemical shifts δ_m thus obtained are plotted in Figure 2 as a function of the number of protons, m, bound to the complex MH_mL, where the results of the NTMP ligand and strontium complex are also shown for comparison.

The ^{31}P NMR chemical shifts of the unprotonated complexes, δ_{ML}, of zinc(II) and cadmium(nII) are almost identical with those of the unprotonated species of ligand, $\delta_{L^{6-}}$, and alkaline-earth-metal complexes, δ_{ML}. The protonated species of the ligand and these complexes show a drastic upfield shift of ^{31}P signal when the protonation occurs on the nitrogen atom of NTMP.[8,14] In the case of Zn(II) and Cd(II) complexes, however, the upfield shift

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Table I. Logarithmic Equilibrium Constants[a] of Transition-Metal-NTMP Complexes at I = 0.1 M (KNO$_3$)

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}		Zn^{2+}	Cd^{2+}
log K_{ML}	10.9	13.5	14.0	11.7	17.2	16.9[b]	14.6	12.0
log K_{MHL}	7.37	6.49	6.18	8.11	6.33	6.50[b]	6.34	7.14
log K_{MH_2L}	5.93	5.41	5.09	5.56	4.53	4.69[b]	5.12	5.76
log K_{MH_3L}	4.7	4.2	3.6	3.5	3.5	3.6[b]	3.9	4.0

[a] K_{ML} = [ML]/[M][L], K_{MH_mL} = [MH$_m$L]/[H][MH$_{m-1}$L]. Uncertainties of the constants are ±0.1 for log K_{ML} (±0.2 for log K_{CuL} with pH titration), ±0.02 for log K_{MHL}, ±0.04 for K_{MH_2L}, and ±0.1 for K_{MH_3L}. [b] With pCu electrode.

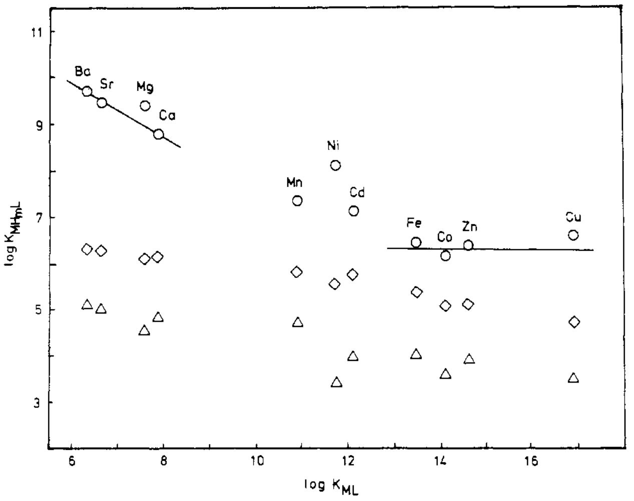

Figure 1. Plot of logarithmic protonation constants, log K_{MH_mL}, as a function of logarithmic formation constants of NTMP complexes, log K_{ML}: ○, K_{MHL}; ◇, K_{MH_2L}; △, K_{MH_3L}.

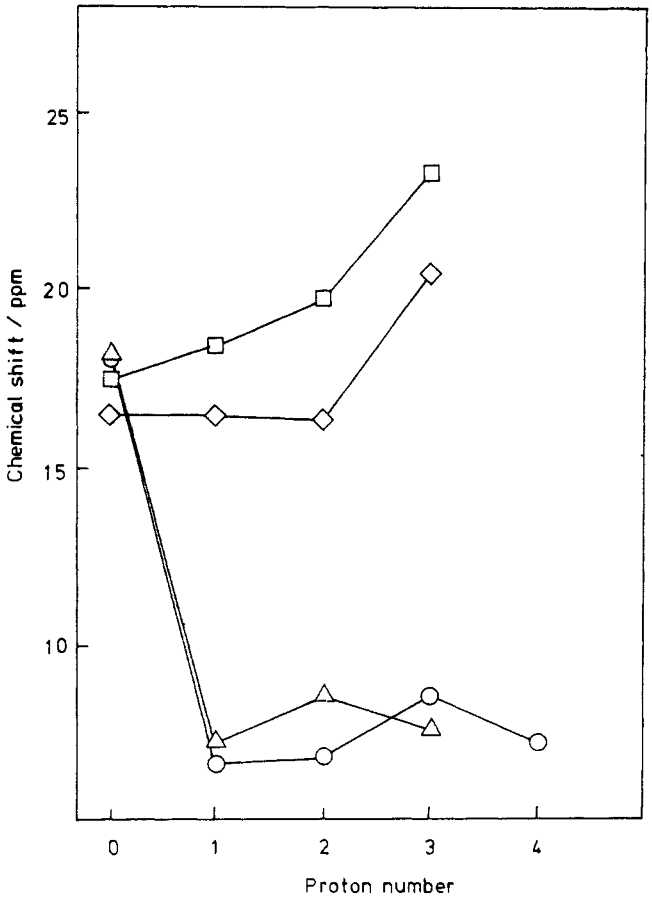

Figure 2. ^{31}P chemical shifts of NTMP (○) and Zn (□), Cd (◇), and Sr complexes (△) as a function of the number of protons bound to the ligand (H$_n$L), n, or metal complex (MH$_m$L), m.

of the signal is not observed at any step of protonation. These results support the conclusion that the protonation of the transition-metal complexes occurs on the phosphonate groups (structure III) throughout the protonation, from the first to the third step.

Experimental Section

The purity of nitrilotris(methylenephosphonic acid) (NTMP, H$_6$L) (Dojin) purified by a method described elsewhere[8] was more than 99.8%. The pH titration and ^{31}P NMR measurements were carried out as reported in the previous paper.[8] The copper ion selective electrode was calibrated with copper(II) standard solutions. The chemical shifts of ^{31}P NMR spectra are reported as the values relative to the aqueous 85% H$_3$PO$_4$ reference. The downfield shift is denoted by the positive sign of the chemical shift.

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Volume of Activation for the Axial Substitution Reaction of Monoligated Chloro(5,10,15,20-tetraphenylporphinato)chromium(III) via a Limiting Dissociative Mechanism

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Much attention has been drawn to the mechanisms of the axial ligand substitution reactions of metalloporphyrins of various metal ions.[3-17] In order to study the mechanism on the basis of the pressure effect, anation reactions of some water-soluble metalloporphyrins in aqueous solution have been followed at high pressure.[4c,18,19] The purpose of our present work is to investigate

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