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Structure and NMR Behavior of Cobalt(III) Polyamine Complexes of α,ω-Alkylenediamine-*N*,*N*,*N*′,*N*′-tetramethylenetetraphosphonate in Aqueous Solution

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The complex formation of α,ω-diaminopolyphosphonates (ethylenediamine- [H_8edtmp], trimethylenediamine- [H_8tdtmp] and hexamethylenediamine-*N*,*N*,*N*′,*N*′-tetramethylenetetraphosphonate [H_8hdtmp]) with cobalt(III) polyamine complexes has been investigated by means of ^{31}P NMR spectroscopy. The formation and protonation constants of the complexes and the ^{31}P NMR chemical shifts of each protonated species were determined from the pH dependence of the ^{31}P NMR signals. In any complexes, the nitrogen atom of the ligand is not coordinated to Co^{III}. The complex *cis*-$[CoCl(en)_2(NH_3)]^{2+}$ forms a mononuclear O-monodentate complex and two types of binuclear bis(O-monodentate) complexes by a reaction with edtmp and tdtmp, and forms a mononuclear O-monodentate complex and a dinuclear bis(O-monodentate) complex with hdtmp. The complex *cis*-$[CoCl_2(en)_2]^+$ forms a mononuclear O-monodentate complex and a mononuclear O,O-bidentate complex having an eight-membered chelate ring with edtmp and tdtmp, and forms a mononuclear O,O-bidentate complex and dinuclear bis(O-monodentate) complexes with hdtmp. In the case of the edtmp complexes, two iminodiphosphonate groups interact with each other: 1) an interaction between the nitrogen atoms of two imino fragments by a hydrogen bond ($NH^+\cdots N$) in a monoprotonated species and 2) an intramolecular interaction between the protonated nitrogen atom and phosphonate O^- of another imino group ($NH^+\cdots {}^-OP$) in triprotonated and tetraprotonated species.

The aminopolyphosphonates (APP), in which the carboxyl groups of aminopolycarboxylates are substituted by phosphonate groups, have been widely used for industrial purposes, such as a scale inhibitor for oil drilling and a geothermal power plant.[1—4] Many kinds of these compounds have been synthesized[5—8] and their complex formation has been studied.[6—21] The number of negative charges of aminopolyphosphonate is much higher than that of the corresponding aminopolycarboxylate, e.g., the charge of ethylenediamine-*N*,*N*,*N*′,*N*′-tetramethyleneteraphosphonate is minus eight (edtmp^{8-}), while that of ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate is minus four (edta^{4-}). Thus, the metal complexes of aminopolyphosphonates readily form protonated species. The thermodynamic properties and the structures of these complexes of labile metals have been studied by means of potentiometry,[13—18] ^{31}P NMR spectroscopy[19,20] and calorimetry.[21] *N*-Methyliminodimethylenediphosphonate (midmp^{4-}) and nitrilotrimethylenetriphosphonate (ntmp^{6-}) form O,O-bidentate eight-membered chelate-ring complexes with some metal ions.

Appleton et al. studied the complex formation of APP with the platinum^{II} complex, in which the number of sites available for the coordination of APP is restricted to two, and reported that N,O-coordinated complexes are the dominant species.[22,23] On the other hand, in the case of an inert Co^{III} (polyamine) complex, such as *cis*-$[CoCl_2(en)_2]^+$, APP does not form nitrogen-coordinated complexes.[24] By the complex formation of *cis*-$[CoCl_2(en)_2]^+$ with midmp and ntmp, O,O-bidentate complexes having an eight-membered chelate ring and O-monodentate complexes were obtained and separated by HPLC. The protonation equilibria and the structures of these complexes in solution were studied by means of ^{31}P NMR and UV-vis spectroscopies. In the case of the ligands, midmp and ntmp and their complexes, the ^{31}P NMR signals show a large upfield shift ($\Delta\delta\approx 10$ ppm) due to protonation of the imino nitrogen, and scarcely change by the protonation of phosphonate O^-.[19—21] However, the complex formation and protonation of diaminopolyphosphonates are rather complicated.[18,21,25] Particularly, the edtmp shows a peculiar ^{31}P NMR signal change due to protonation; these results indicate the presence of intramolecular interactions between two iminodiphosphonate groups.

In the present paper, in order to clarify such intramolecular interactions, the complex formation of α,ω-alkylenediaminetetramethylenetetraphosphonates having various lengths of alkylene chains with cobalt^{III} (polyamine) complexes was investigated by means of ^{31} NMR spectroscopy. The number of sites on the cobalt(polyamine) complex available for the coordination of diaminopolyphosphonate is restricted to one for *cis*-$[CoCl_2(en)_2(NH_3)]^{2+}$ or two for *cis*-$[CoCl_2(en)_2]^+$. The structures and intramolecular interactions of the complexes are discussed.

Experimental

Reagents. Co^{III}–polyamine complexes, *cis*-$[CoCl_2(en)_2]Cl$ and *cis*-$[CoCl(en)_2(NH_3)]Cl_2$, were synthesized according to literature procedures.[26] Aminopolyphosphonates, ethylenediamine-*N,N,N′,N′*-tetramethylenetetraphosphonic acid (H_8edtmp) (Dojin Chemicals) and hexamethylenediamine-*N,N,N′,N′*-tetramethylenetetraphosphonic acid (H_8hdtmp) (Monsanto) were purified by a recrystallization. Trimethylenediamine-*N,N,N′,N′*-tetramethylenetetraphosphonic acid (H_8tdtmp) was synthesized by a method described elsewhere.[25] The purities of edtmp, tdtmp and hdtmp were determined by ^{31}P NMR and potentiometry and were more than 99%. Other chemicals were of reagent grade (Wako Pure Chemicals).

Sample Preparation. The Co$^{\mathrm{III}}$ polyamine complex was reacted with edtmp, tdtmp or hdtmp at 50 °C at various mole ratios, reaction times and pH. The reaction was quenched by cooling the solution to 0 °C. In order to prevent any further reaction, all of the measurements of pH titration and ^{31}P NMR were performed at 0 °C.

Complex Separation. A mixture of the Co$^{\mathrm{III}}$ polyamine complex and hdtmp was separated by HPLC (Tosoh CCPD dual pump, Shimazu SPD-M6A UV-visible Detector) on a column (ϕ 20 mm×400 mm) packed with Toyopearl HW-40F (Tosoh). The loaded sample (3 cm^3) was eluted by H_2O at a flow rate of 3 cm^3 min^{-1}. The fractions of the eluent were freeze-dried just after collection. A chromatogram of the reaction mixture showed two peaks corresponding to the Co(en)$_2$–hdtmp complex and the Co$^{\mathrm{III}}$ reactant. Owing to poor separation, the complexes formed in the reaction with edtmp ant tdtmp were not separated.

Potentiometry. All pH measurements were carried out with a Corning M-130 pH meter. The glass electrode was calibrated by titration with nitric acid and potassium hydroxide at 0 °C ($I = 0.1$ mol dm^{-3} KNO_3, p$K_w = 14.98$). The pH, i.e., the logarithm of the reciprocal of the hydrogen-ion concentration, was evaluated from the electromotive force using the calibration curve. Ligand

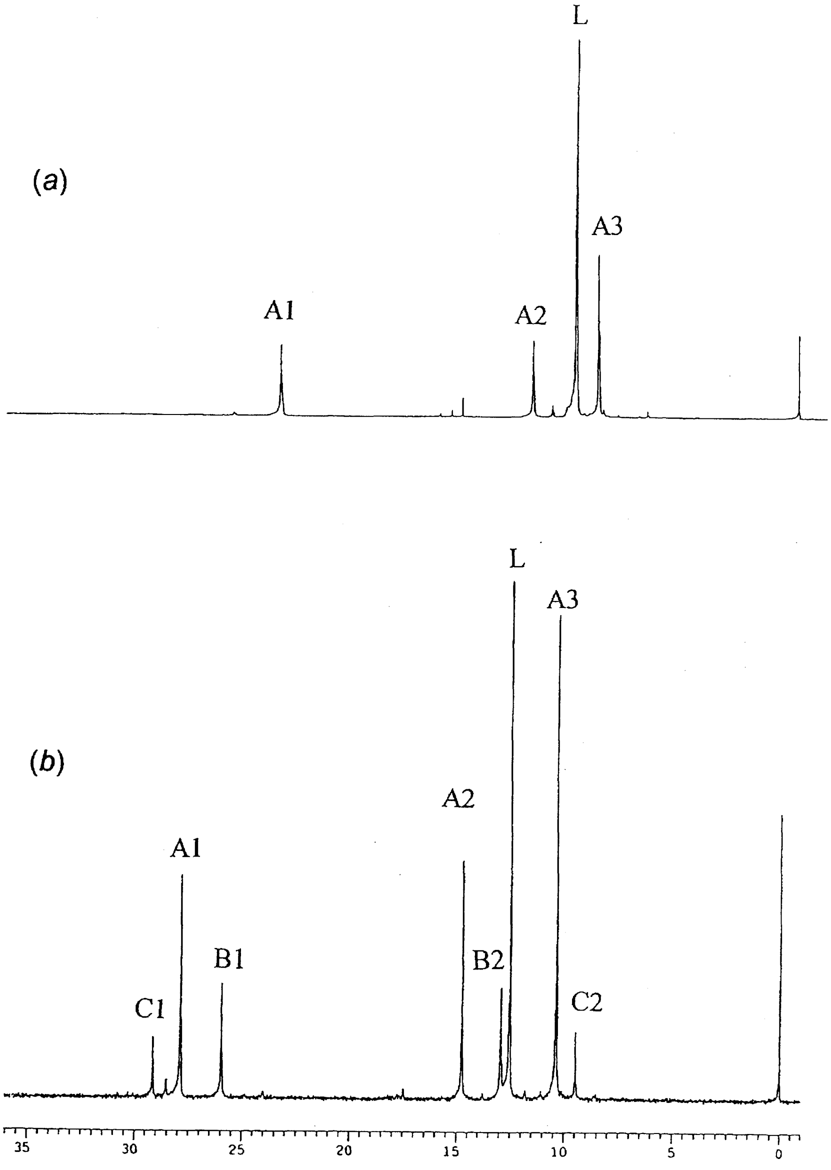


Fig. 1. The ^{31}P{^{1}H} NMR spectra of (a) a mixture of $[CoCl(en)_2(NH_3)]^{2+}$–edtmp (M : L = 1 : 1) at 0 °C at pH 8, (b) a mixture of large excess of $[CoCl(en)_2(NH_3)]^{2+}$ (M : L = 4 : 1) at 0 °C at pH 10.5, which had been allowed to react for 48 h at 50 °C and pH 4.

solutions (0.002 mol dm^{-3}) were titrated by potassium hydroxide (0.1 mol dm^{-3}) at 0 °C, $I = 0.1$ mol dm^{-3} KNO_3.

NMR Measurement. After adjusting the pH at 0 °C, the ^{31}P NMR spectra of reaction mixtures or of separated complexes were measured at 0 °C with a Varian Unity-500 FT NMR spectrometer (202.35 MHz for ^{31}P) with sample tube of 10 mm diameter. The NMR spectrometer was locked by the signal of D_2O, which served as an external standard of 0.5% H_3PO_4 in D_2O.

Result

Protonation Constants and the ^{31}P NMR Chemical Shifts of edtmp, tdtmp, and hdtmp. The protonation constants ($\log K_n$) of diaminopolyphosphonates were determined at 0 °C by means of potentiometry and ^{31}P NMR spectrometry (Table 1 (a)). The protonation constants and the chemical shifts of individual protonated species (δ_n) were obtained by an analysis of the pH dependence of the ^{31}P NMR signal[18,21] (Table 1). The values of $\log K_1$ (all system) and $\log K_2$ (hdtmp), determined by ^{31}P NMR, are more reliable than those by pH titration. The values of the protonation constants and chemical shifts at 0 °C are essentially the same as those at 25 °C, although small differences are observed for the protonation constants between two temperatures because of a change in the autoprotolysis constant, $\log K_w = 14.95$.

$Co(en)_2(NH_3)$–edtmp System. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at pH 8 at 0 °C is shown in Fig. 1 (a), where $[CoCl(en)_2(NH_3)]^{2+}$ was reacted with edtmp at a molar ratio 1 : 1, at pH 4 and 50 °C for 48 h. The spectrum consists of three main peaks (labeled A1, A2, and A3) besides the signal of the unreacted edtmp (L). The peak area ratio of the signals A1, A2, and A3 is 1 : 1 : 2 at any reaction time. The complex formation in neutral and alkaline solutions is quite slow.

Table 1. Logarithmic Protonation Constants and ^{31}P NMR Chemical Shifts of the Diaminotetramethylenetetraphosphates at 0 °C[a)]

a) Protonation constant

	$\log K_n$		
	edtmp	tdtmp	hdtmp
$\log K_1$	13.5[b)]	13.5[b)]	13.6[b)]
$\log K_2$	10.20	11.72	12.8[b)]
$\log K_3$	8.08	7.06	6.77
$\log K_4$	6.41	6.05	6.04
$\log K_5$	5.08	5.19	5.24
$\log K_6$	2.71	4.40	4.52
$\log K_7$	< 1	< 1	< 1

b) Chemical shift

	δ/ppm		
	edtmp	tdtmp	hdtmp
L	17.3	16.9	16.2
HL	11.7	11.5	10.1
H_2L	10.4	6.3	6.7
H_3L	10.9	6.6	7.2
H_4L	12.4	7.5	6.8
H_5L	12.9	7.1	8.6
H_6L	9.1	7.0	8.7

a) $K_n = [H_nL]/[H^+][H_{n-1}L]$, $I = 0.1$ mol dm^{-3} (KNO_3). b) Evaluated by ^{31}P NMR spectroscopy.

The pH dependence of the signals at 0 °C is shown in Fig. 2. The fact that these signals do not split at any pH indicates fast protonation equilibria. Consequently, the observed chemical shift for each signal (δ_{obs}) is a weighted average of the chemical shift of each protonated species of the $Co(en)_2(NH_3)$–edtmp complexes. Thus, the calculated chemical shift is given by

$$\delta_{calc} = \sum \delta_{M(NH_3)(H_nL)} X_{M(NH_3)(H_nL)},$$

where $\delta_{M(NH_3)(H_nL)}$ is the chemical shift of the protonated ($n \geq 1$) or unprotonated species ($n = 0$) of the complex $[M(NH_3)(H_nL)]^{n-5}$ ($M = Co(en)_2$). $X_{M(NH_3)(H_nL)}$ is the proportion of each species, and is calculated from the solution pH by using the protonation constant,

$$K_n = [M(NH_3)(H_nL)]/[H^+][M(NH_3)(H_{n-1}L)].$$

Henceforth, the changes of the chemical species are omitted for simplicity. The values of $\delta_{M(NH_3)(H_nL)}$ and K_n giv-

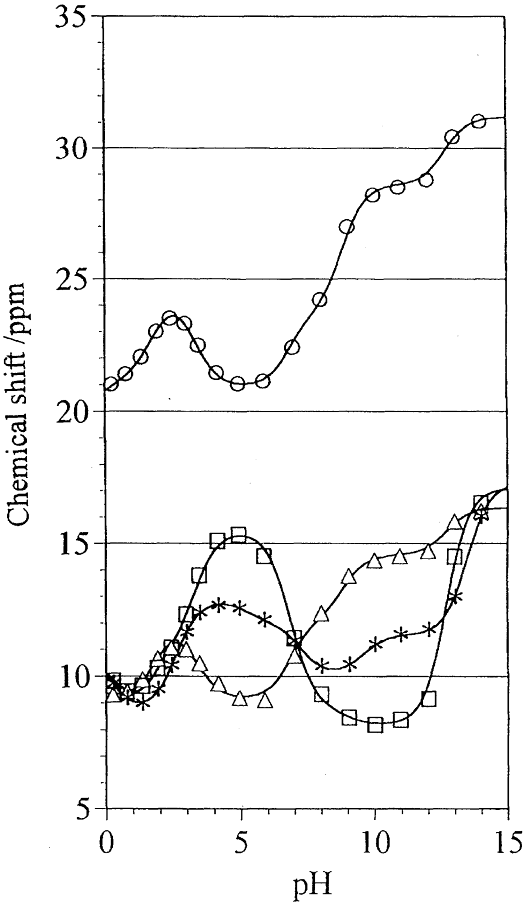


Fig. 2. ^{31}P NMR chemical shifts of mononuclear $Co(en)_2(NH_3)$–edtmp complex as a function of pH at 0 °C. O-monodentate edtmp complex: ○, coordinated phosphonate (A1); △, uncoordinated phosphonate (A2) of coordinated imino group, and □, phosphonates (A3) of uncoordinated imino group. *, unreacted edtmp. Solid lines are calculated curves, see text.

ing the minimum error square sum of the chemical shifts, $\Sigma(\delta_{\mathrm{calc}}-\delta_{\mathrm{obs}})^2$, were evaluated by a non-linear least-square calculation[24] (Table 2 (a)). The protonation constants obtained from signals A1, A2, and A3 agreed with each other. The solid lines in Fig. 2 are calculated curves obtained by using the values listed in Table 3 (a), and show good agreement with the experimental results. These facts support the idea that these signals were assigned to the same complex having three unequivalent phosphonate groups.

All signals of ^{31}P NMR show a large upfield shift upon first protonation. This fact indicates protonation on the nitrogen atom,[19—21,25] i.e., the nitrogen atoms of the edtmp of the complex are not coordinated to Co$^{\mathrm{III}}$. The signal of ^{31}P NMR shifts downfield due to the coordination of the phospho-

Table 2. Chemical Shifts (δ/ppm) and Logarithmic Protonation Constants ($\log K_n$) of *cis*-Co(en)$_2$(NH$_3$) and *cis*-Co(en)$_2$–edtmp Complexes at 0 °C [M≡Co(en)$_2$]

cis-Co(en)$_2$(NH$_3$) system.

(a) Mononuclear O-monodentate.					(b) Binuclear bis(O-monodentate) (N,N').				(c) Binuclear bis(O-monodentate) (N,N).		
	δ(A1)	δ(A2)	δ(A3)	$\log K_n$[a)]		δ(B1)	δ(B2)	$\log K_n$[b)]	δ(C1)	δ(C2)	$\log K_n$[b)]
$[M(NH_3)(L)]$	31.2	16.3	17.1		$[\{M(NH_3)\}_2(L)]$	31.7	17.3		31.5	16.5	
				12.7				10.8			11.8
$[M(NH_3)(HL)]$	28.6	14.6	8.2		$[\{M(NH_3)\}_2(HL)]$	26.0	12.9		29.5	9.3	
				8.9				8.0			7.7
$[M(NH_3)(H_2L)]$	23.7	12.2	8.9		$[\{M(NH_3)\}_2(H_2L)]$	24.6	12.7		23.8	12.5	
				6.9							6.4
$[M(NH_3)(H_3L)]$	20.9	9.2	15.5		$[\{M(NH_3)\}_2(H_3L)]$				21.5	17.5	
				3.3							
$[M(NH_3)(H_4L)]$	24.5	12.0	11.3								
				1.8							
$[M(NH_3)(H_5L)]$	21.4	9.1	8.9								
				0.3							
$[M(NH_3)(H_6L)]$	20.5	9.5	10.7								

cis-Co(en)$_2$ system.

(d) Mononuclear O-monodentate.					(e) Mononuclear O,O-bidentate.			
	δ(D1)	δ(D2)	δ(D3)	$\log K_n$		δ(E1)	δ(E2)	$\log K_n$[f)]
$[M(OH)(L)]$	30.1	15.3	16.7		$[M(L)]$	29.0	15.3	
				13.8[c)]				14.0
$[M(OH)(HL)]$	30.2	13.2	15.8		$[M(HL)]$	25.4	11.9	
				10.8[c)]				9.1
$[M(OH)(H_2L)]$	26.8	10.7	7.6		$[M(H_2L)]$	21.5	9.6	
				7.7[d)]				5.6
$[M(OH_2)(H_2L)]$	21.8	10.0	12.2		$[M(H_3L)]$	21.9	10.4	
				6.4[e)]				
$[M(OH_2)(H_3L)]$	21.4	9.0	16.1					

a) $K_n=[M(NH_3)(H_nL)]/[M(NH_3)(H_{n-1}L)][H^+]$, b) $K_n=[\{M(NH_3)\}_2(H_nL)]/[\{M(NH_3)\}_2(H_{n-1}L)][H^+]$, c) $K_n=[M(OH)(H_nL)]/[M(OH)(H_{n-1}L)][H^+]$, d) $K_n=[M(OH_2)(H_2L)]/[M(OH)(H_2L)][H^+]$, e) $K_n=[M(OH_2)(H_3L)]/[M(OH_2)(H_2L)][H^+]$, f) $K_n=[M(H_nL)]/[M(H_{n-1}L)][H^+]$.

Table 3. Chemical Shifts (δ/ppm) and Logarithmic Protonation Constants ($\log K_n$[a)]) of *cis*-Co(en)$_2$(NH$_3$) and *cis*-Co(en)$_2$–tdtmp Complexes at 0 °C [M≡CO(en)$_2$]

cis-Co(en)$_2$(NH$_3$) system.

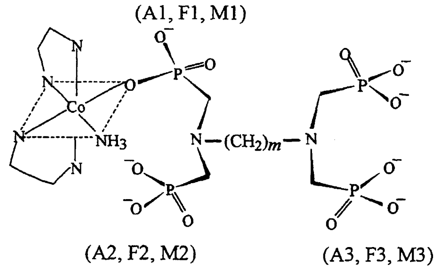
(a) Mononuclear O-monodentate.					(b) Binuclear bis(O-monodentate), (N,N').				(c) Binuclear bis(O-monodentate), (N,N).		
	δ(F1)	δ(F2)	δ(F3)	$\log K_n$[a)]		δ(G1)	δ(G2)	$\log K_n$	δ(H1)	δ(H2)	$\log K_n$
$[M(NH_3)(L)]$	30.9	16.7	17.0		$[\{M(NH_3)\}_2(L)]$	30.3	16.4		30.5	16.6	
				13.1				11.3			13.1
$[M(NH_3)(HL)]$	29.8	15.8	6.7		$[\{M(NH_3)\}_2(HL)]$	24.5	11.4		30.3	7.0	
				9.7				9.2			8.9
$[M(NH_3)(H_2L)]$	18.9	6.9	6.4		$[\{M(NH_3)\}_2(H_2L)]$	19.3	7.1		19.9	6.3	

cis-Co(en)$_2$ system.

(d) Mononuclear O-monodentate.					(e) Mononuclear O,O-bidentate.			
	δ(I1)	δ(I2)	δ(I3)	$\log K_n$		δ(J1)	δ(J2)	$\log K_n$
$[M(OH)(L)]$	29.6	16.9	16.6		$[M(L)]$	26.6	16.2	
				13.8				13.1
$[M(OH)(HL)]$	26.7	12.7	12.8		$[M(HL)]$	25.9	6.6	
				12.1				9.5
$[M(OH)(H_2L)]$	26.7	11.2	6.5		$[M(H_2L)]$	17.1	6.2	
				8.0				
$[M(OH_2)(H_2L)]$	19.6	7.22	5.9					

a) Definitions of protonation constants: see Table 2.

nate group to an inert metal ion.[22,24,27,28] Thus, signal A1 is assigned to ^{31}P of coordinated phosphonate group. Since the number of sites of the complex $[CoCl(en)_2(NH_3)]^{2+}$ available for substitution is restricted to one, the complex formed by the reaction with edtmp is concluded to be an O-monodentate complex (Chart 1). From the peak area ratio (1 : 2), signals A2 and A3 were assigned to an uncoordinated phosphonate of the coordinated imino group and uncoordinated iminodiphosphonates, respectively.



$[M(NH_3)(L)]^{5-}$

$m = 2, 3, 6$

1

Chart 1.

Under the reaction conditions of the molar ratio of $[CoCl(en)_2(NH_3)]^{2+}$: edtmp=4 : 1, at pH 4 and 50 °C for 48 h, the growth of new signals was observed, as shown in Fig. 1 (b). The peak ratios of signals B1 to B2 and C1 to C2 were 1 : 1 at any reaction time. The chemical shifts and protonation constants of the complexes corresponding to signals B and C obtained by an analysis of the pH dependence of the chemical shift are listed in Table 2 (b) and (c). Since the protonation constants obtained from signals B1 and B2 agreed with each other, it has been confirmed that these signals are assigned to the same species. The fact that the peak areas of these signals are the same as each other indicates that the complex has two equivalent coordinated and uncoordinated phosphonates. Thus, the complex is assigned to be a dinuclear complex. In the same manner, signals C1 and C2 are also assigned to a dinuclear complex. The first protonation constant of the complex corresponding to signals C (complex C) is larger than that of complex B. This means that complex C has an uncoordinated iminodiphosphonate group, i.e., signals C are assigned to a complex given by Chart 3. Another dinuclear complex (B) is given in Chart 2.

$Co(en)_2$–edtmp System. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at pH 13 at 0 °C is shown in Fig. 3, where $[CoCl_2(en)_2]^+$ was reacted with edtmp at a molar ratio of 1 : 1, at pH 4 and 50 °C for 3 h. The spectra of this

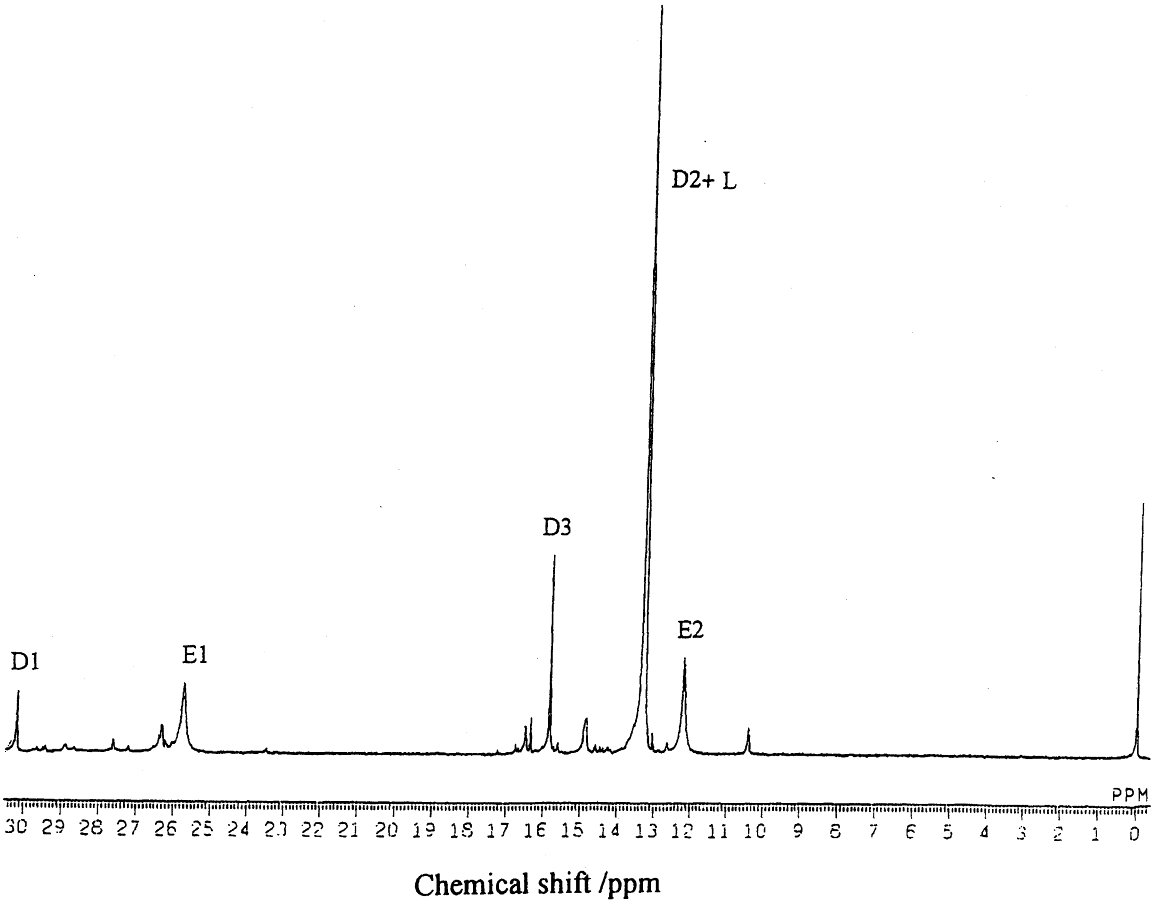
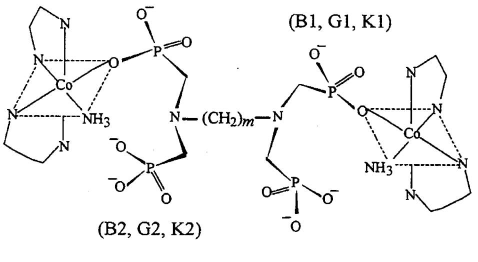


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of a mixture of $[CoCl_2(en)_2]^+$–edtmp at 0 °C at pH 13, which had been allowed to react for 3 h at 50 °C and pH 4.

system are rather complicated and consist of five main peaks labeled D1, D2, D3, E1, and E2. Although D2 signal is overlapped with the signal of unreacted ligand L at this pH, it is separated at other pH. The signals labeled D1, D2, and D3 grow with a peak ratio 1 : 1 : 2 at an early reaction time followed by the growth of peaks E1 and E2 with a peak ratio of 1 : 1, which came to be the dominant signals after a prolonged reaction time. The chemical shifts of these signals are plotted as a function of the pH in Fig. 4. The chemical shifts and protonation constants of each species were calculated (Table 2 (d) and (e)).

By the same analysis of the signals as that of signals A1, A2, and A3, signals D1, D2, and D3 are assigned to a mononuclear O-monodentate complex (Chart 1), where a water molecule is coordinated to Co^{III} instead of NH_3.[24] The peak area ratio of E1 to E2 (1 : 1) indicates that two phosphonates (E1) are coordinated to Co^{III} and the other two (E2) are uncoordinated. The high value of the first protonation constant ($\log K_1 = 14.0$, Table 2 (e)) suggests that this complex has an uncoordinated iminodiphosphonate group (E2). The value of the second protonation constant ($\log K_2 = 9.1$, Table 2 (e)) is larger than that of the complex in which one iminodiphosphonate group is coordinated to two Co^{III} (Chart 3) ($\log K_2 = 7.7$, Table 2 (c)). Consequently, this complex is not a dinuclear complex. Consequently, signals E are assigned to a mononuclear O,O-bidentate complex (Chart 4) in which one iminodiphosphonate group forms an eight-membered chelate ring in the same manner as the $Co(en)_2$–midmp complex.[24] Signals other than signals D and E in Fig. 3 might be assigned to decomposition products of edtmp, their com-

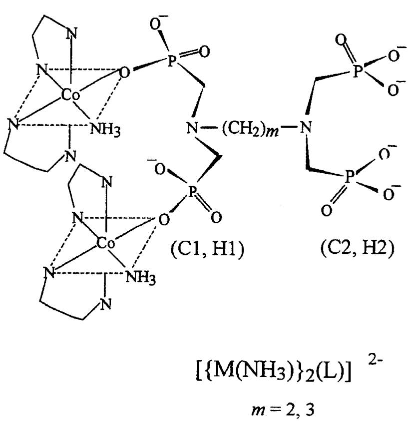


$[\{M(NH_3)\}_2(L)]^{2-}$

$m = 2, 3, 6$

2

Chart 2.



$[\{M(NH_3)\}_2(L)]^{2-}$

$m = 2, 3$

3

Chart 3.

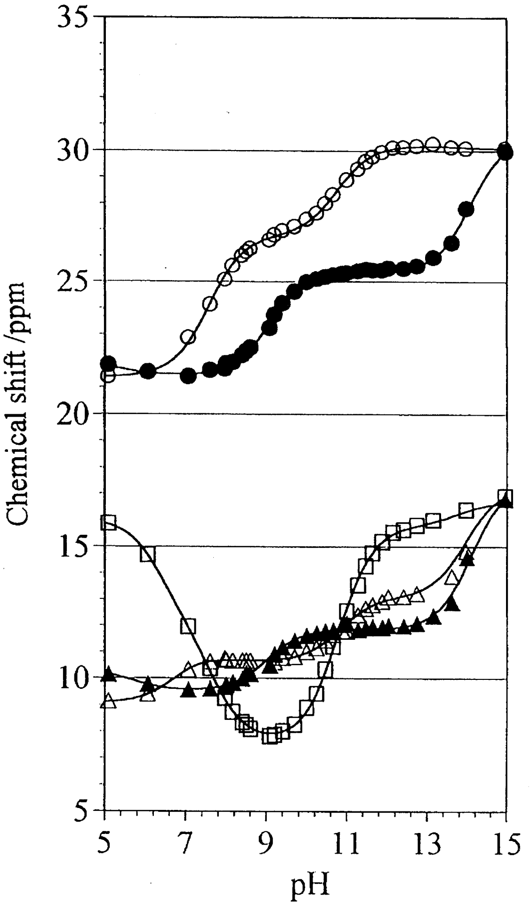
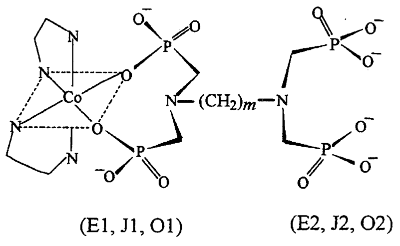


Fig. 4. ^{31}P NMR chemical shifts of mononuclear $Co(en)_2$–edtmp complexes as a function of pH at 0 °C. O-monodentate complex: ○, coordinated phosphonate (D1); △, uncoordinated phosphonate (D2) of coordinated imino group, and □, phosphonates (D3) of uncoordinated imino group. O,O-bidentate complex: ●, coordinated phosphonates (E1) and ▲, uncoordinated phosphonates (E2).



$[M(L)]^{6-}$

$m = 2, 3, 6$

4

Chart 4.

plexes, and dinuclear complexes, but the spectra were too complicated to analyze.

Co(en)$_2$(NH$_3$)–tdtmp System. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture of *cis*-$[CoCl(en)_2(NH_3)]^{2+}$ and tdtmp at pH 11 reacted at pH 4 and 50 °C for 48 h is shown in Fig. 5 (a). The ^{31}P NMR spectra and pH dependence of the Co(en)$_2$(NH$_3$)-tdtmp system are quite similar to those of the Co(en)$_2$(NH$_3$)-edtmp system. Signals F, G, and H correspond to signals A, B, and C of the Co(en)$_2$(NH$_3$)-edtmp system, respectively. Thus, signals F are assigned to a mononuclear O-monodentate complex (Chart 1) and signals G and H are dinuclear complexes, Charts 2 and 3, respectively. The protonation constants and chemical shifts of the complexes are listed in Table 3 (a)—(c).

Co(en)$_2$–tdtmp System. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture at pH 11.5 is shown in Fig. 5 (b), where $[CoCl_2(en)_2]^+$ was reacted with tdtmp at a molar ratio of 1 : 1, at pH 4 and 50 °C for 3 h. The spectra of this system are similar to those of the Co(en)$_2$–edtmp system. That is, signals I are assigned to a mononuclear O-monodentate complex (Chart 1) and signals J are assigned to a mononuclear O,O-bidentate complex (Chart 4).

Co(en)$_2$(NH$_3$)–hdtmp System. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture at pH 13 at 0 °C is shown in Fig. 6 (a), where *cis*-$[CoCl(en)_2(NH_3)]^{2+}$ was reacted with hdtmp at a molar ratio of 1 : 1, pH 4 and 50 °C for 48 h. In the same manner as the edtmp and tdtmp systems, signals K1 and K2 are assigned to the O-monodentate dinuclear

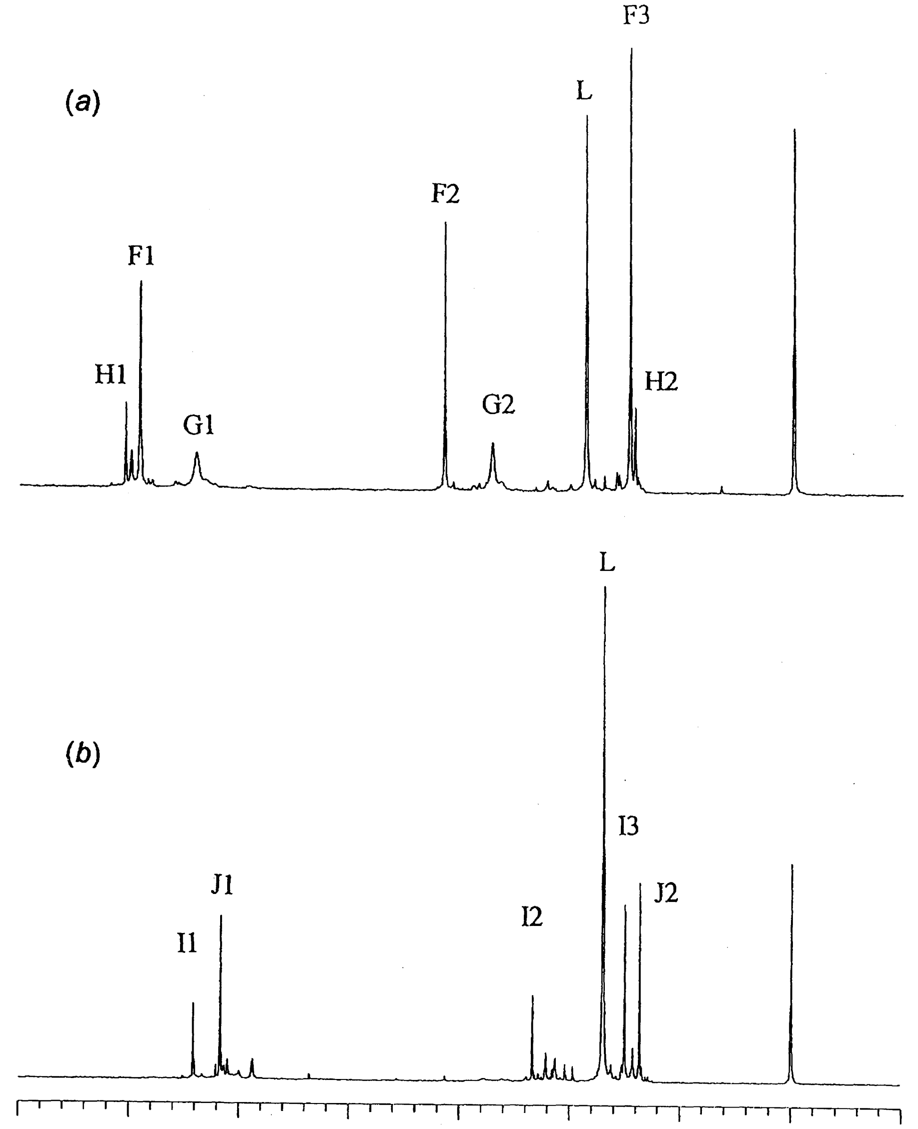


Fig. 5. The ^{31}P{^{1}H} NMR spectra of (a) a mixture of $[CoCl(en)_2(NH_3)]^{2+}$–tdtmp at 0 °C at pH 11 which had been allowed to react for 48 h at 50 °C and pH 4 and (b) a mixture of $[CoCl_2(en)_2]^+$–tdtmp at 0 °C at pH 11.5, which had been allowed to react for 3 h at 50 °C and pH 4.

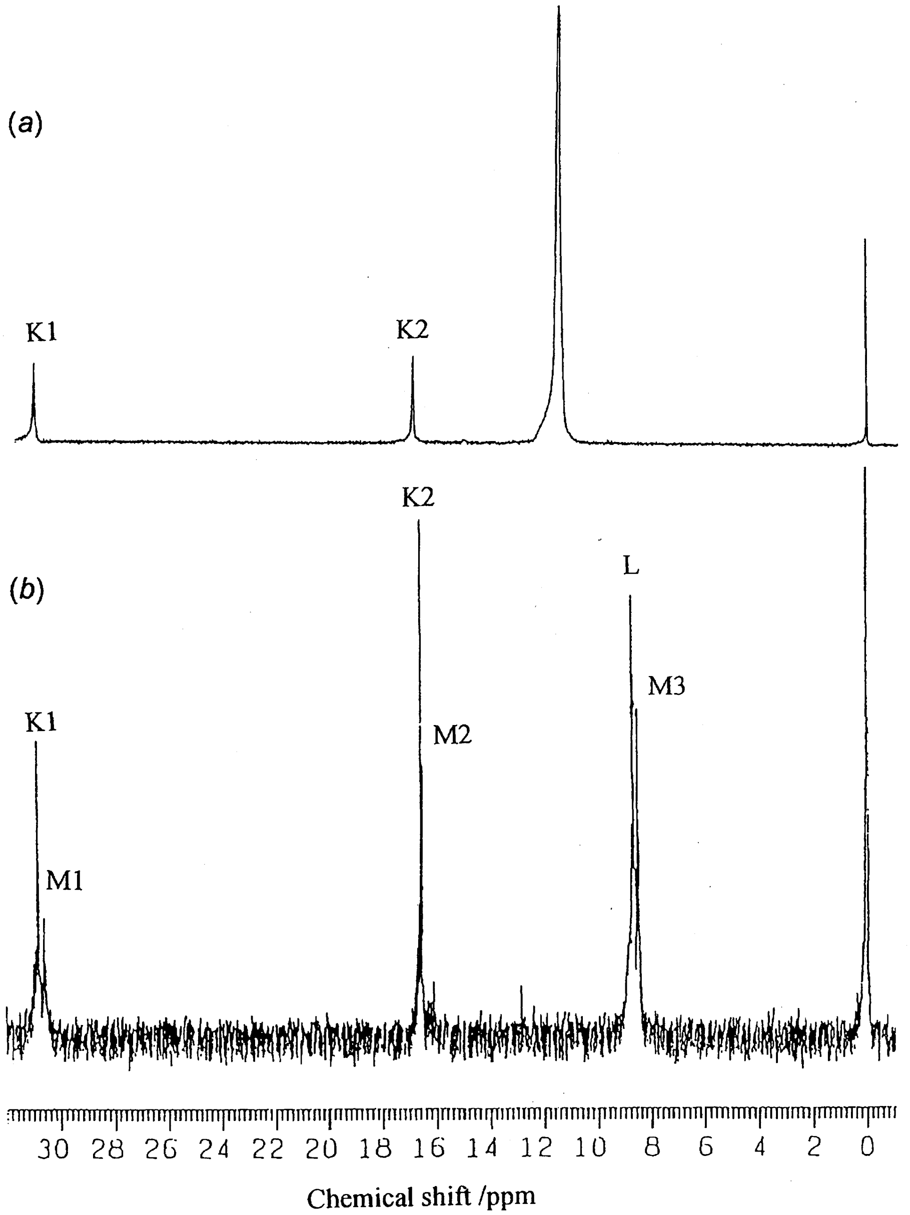


Fig. 6. $^{31}P\{^1H\}$ NMR spectra of (a) a mixture of $[CoCl(en)_2(NH_3)]^{2+}$–hdtmp at 0 °C at pH 13 which had been allowed to react for 48 h at 50 °C and pH 4 and (b) a fraction at pH 12.5 separated from main product.

complex in which each phosphonate of both imino groups is coordinated to Co^{III} (Chart 2). The reaction mixture of *cis*-$[CoCl(en)_2(NH_3)]^{2+}$ and hdtmp was separated by HPLC. The NMR spectrum of the fraction separated from the dominant product (signals K) is shown in Fig. 6 (b). The chemical shifts of the newly observed signals (M1, M2, and M3) are quite close to signals K1, K2, and L at any pH, respectively. This result and the peak height ratio (M1 : M2 : M3=1 : 1 : 2) suggest the formation of the O-monodentate mononuclear complex (Chart 1).

The fact that the chemical shifts of the monocoordinated (M1, M2) and uncoordinated iminodiphosphonate (M3) fragments of the O-monodentate mononuclear complex are almost the same as those of dinuclear O-monodentate (K1, K2) and ligand hdtmp (L), respectively, suggests that the protonation of one imino group scarcely affects that of another group. This result is quite reasonable, because two imino groups are separated by a long alkylene chain ($-C_6H_{12}-$). Consequently, the protonation constants of two fragments of the dinuclear bis(O-monodentate) complex (signals K) can be assumed to be very close to each other ($\log K_1 \approx \log K_2$, $\log K_3 \approx \log K_4$, and $\log K_5 \approx \log K_6$). The thus-obtained values of K_n and δ_n are listed in Table 4 (a), where the protonation constants are considered to be the mean values of two step protonations (e.g. K_1 and K_2). The protonation constants and the chemical shifts of the O-monodentate mononuclear complex were evaluated (Table 4 (b)).

Co(en)$_2$–hdtmp System. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at pH 12.9 at 0 °C is shown in Fig. 7 (a), where *cis*-$[CoCl_2(en)_2]^+$ was reacted with hdtmp at a molar ratio of 1 : 1, pH 4 and 50 °C for 1 h. Signals N1 and N2 show the same NMR behaviors as do signals K_1

Table 4. Chemical Shifts (δ/ppm) and Logarithmic Protonation Constants ($\log K_n$) of *cis*-$Co(en)_2(NH_3)$ and *cis*-$Co(en)_2$–hdtmp Complexes at 0 °C [$M\equiv CO(en)_2$]

cis-$Co(en)_2(NH_3)$ system.

(b) Binuclear bis(O-monodentate), (*N*,*N*′).				(b) Mononuclear O-monodentate.[b]				
	δ(K1)	δ(K2)	$\log K_n$[a]		δ(M1)	δ(M2)	δ(M3)	$\log K_n$[c]
$[\{M(NH_3)\}_2(L)]$	30.6	16.6		$[M(NH_3)(L)]$	30.6	16.6	16.2	
			11.0					13.6
$[\{M(NH_3)\}_2(H_2L)]$	18.9	6.8		$[M(NH_3)(HL)]$	30.6	16.6	6.7	
			4.8					11.0
$[\{M(NH_3)\}_2(H_4L)]$	18.9	7.6		$[M(NH_3)(H_2L)]$	18.9	6.8	6.7	
			2.4					6.8
$[\{M(NH_3)\}_2(H_6L)]$	20.2	7.6		$[M(NH_3)(H_3L)]$	18.9	6.8	6.8	
								4.8
				$[M(NH_3)(H_4L)]$	18.9	7.6	6.8	

cis-$Co(en)_2$ system.

(c) Binuclear bis(O-monodentate) (*N*,*N*′).				(d) Mononuclear O,O-bidentate.			
	δ(N1)	δ(N2)	$\log K_n$[a]		δ(O1)	δ(O2)	$\log K_n$[d]
$[\{M(OH)\}_2(L)]$	29.2	16.5		$[M(L)]$	26.7	16.2	
			12.9				13.2
$[\{M(OH)\}_2(H_2L)]$	23.1	9.0		$[M(HL)]$	26.7	6.7	
			8.0				10.8
$[\{M(OH_2)\}_2(H_2L)]$	19.6	6.7		$[M(H_2L)]$	17.7	6.7	
			4.9				6.8
$[\{M(OH_2)\}_2(H_4L)]$	20.2	7.6		$[M(H_3L)]$	17.7	6.8	
			2.9				4.9
$[\{M(OH_2)\}_2(H_6L)]$	20.6	7.6		$[M(H_4L)]$	17.7	7.6	

a) Mean value of two step protonations. b) Estimated from the values of protonations of binuclear complex and ligand.
c) $K_n=[M(NH_3)(H_nL)]/[M(NH_3)(H_{n-1}L)][H^+]$, d) $K_n=[M(H_nL)]/[M(H_{n-1}L)][H^+]$.

and K_2 of dinuclear bis(O-monodentate) complex of the $Co(en)_2(NH_3)$–hdtmp system; thus, these signals are assigned to a complex of Chart 2. By analyzing the pH dependence of signals O1 and O2, these signals have been assigned to a mononuclear O,O-bidentate complex (Chart 4). The K_n and δ_n values of these complexes are listed in Table 4 (c) and (d).

The reaction mixture which reacted at a molar ratio, Co^{III} : hdtmp, of 5 : 1 was separated by HPLC. The $^{31}P\{^1H\}$ NMR spectrum (pH 13) of fractions separated from the main product is shown in Fig. 7 (b). Since new signal (Q) has no pairing signal, all phosphonates are equivalent and are coordinated to Co^{III}. The pH dependence of the signal indicates that signal Q can be assigned to an dinuclear O,O-bidentate complex. Signals P1 and P2 are assigned to phosphonates of the O-monodentate imino fragment. Thus, these signals and a signal overlapped to Q are a dinuclear O-monodentate O, O-bidentate complex.

Discussion

Structures of $Co(en)_2(NH_3)$ Mononuclear O-Monodentate Complexes. The changes in the chemical shifts of the $Co(en)_2(NH_3)$ mononuclear O-monodentate complexes (Chart 1) are plotted as a function of the number of protons bound to be complex in Fig. 8. The first protonation of the complex causes a large upfield shift of the signal of the phosphonates of an uncoordinated imino fragment (□). The changes in the chemical shifts of both phosphonates (coordinated; ○, uncoordinated; △) of a coordinated imino fragment are very small although they increase due to a decrease in the number of alkylene chains (*m*). These results indicate that the first protonation occurs on the imino nitrogen atom of an uncoordinated fragment. The large values of the first protonation constants ($\log K_1=12.7$, 13.1, and 13.2 for edtmp, tdtmp, and hdtmp) support this argument.

The change in the chamical shift of the uncoordinated iminodiphosphonates (□) due to the second protonation is quite small, while the phosphonates of coordinated imino fragment (○, △) of the tdtmp and hdtmp systems show a large upfield shift. Consequently, the second protonation occurs on the imino nitrogen of a coordinated imino fragment. The fact that the values of the protonation constant and chemical shifts of the O-monodentate iminodiphosphonate fragments of the tdtmp and hdtmp complexes are very close to that of the O-monodentate complex of midmp[24] supports the idea that the interaction between two imino fragments is negligible. On the other hand, in the case of the edtmp complex, the second protonation constant is smaller than those of other systems. This result indicates that the imino nitrogen atoms of the monoprotonated species $[M(NH_3)(Hedtmp)]^{4-}$ interact with each other by a $NH^+\cdots N$ hydrogen bond (Scheme 1). The second protonation occurs mainly on the phosphonate oxygen atom (Scheme 1), $[M(NH_3)(H_2L)]^{3-}$).

In the triprotonated species, $[M(NH_3)(H_3L)]^{2-}$, both of the imino nitrogen atoms and one phosphonate are protonated in any ligand systems. The changes in the chamical shifts of the hdtmp complex due to the higher protonation are very small (Fig. 8 (c), $n\geq3$), i.e., protonation on the phosphonate O^-. However, those of the edtmp complex show

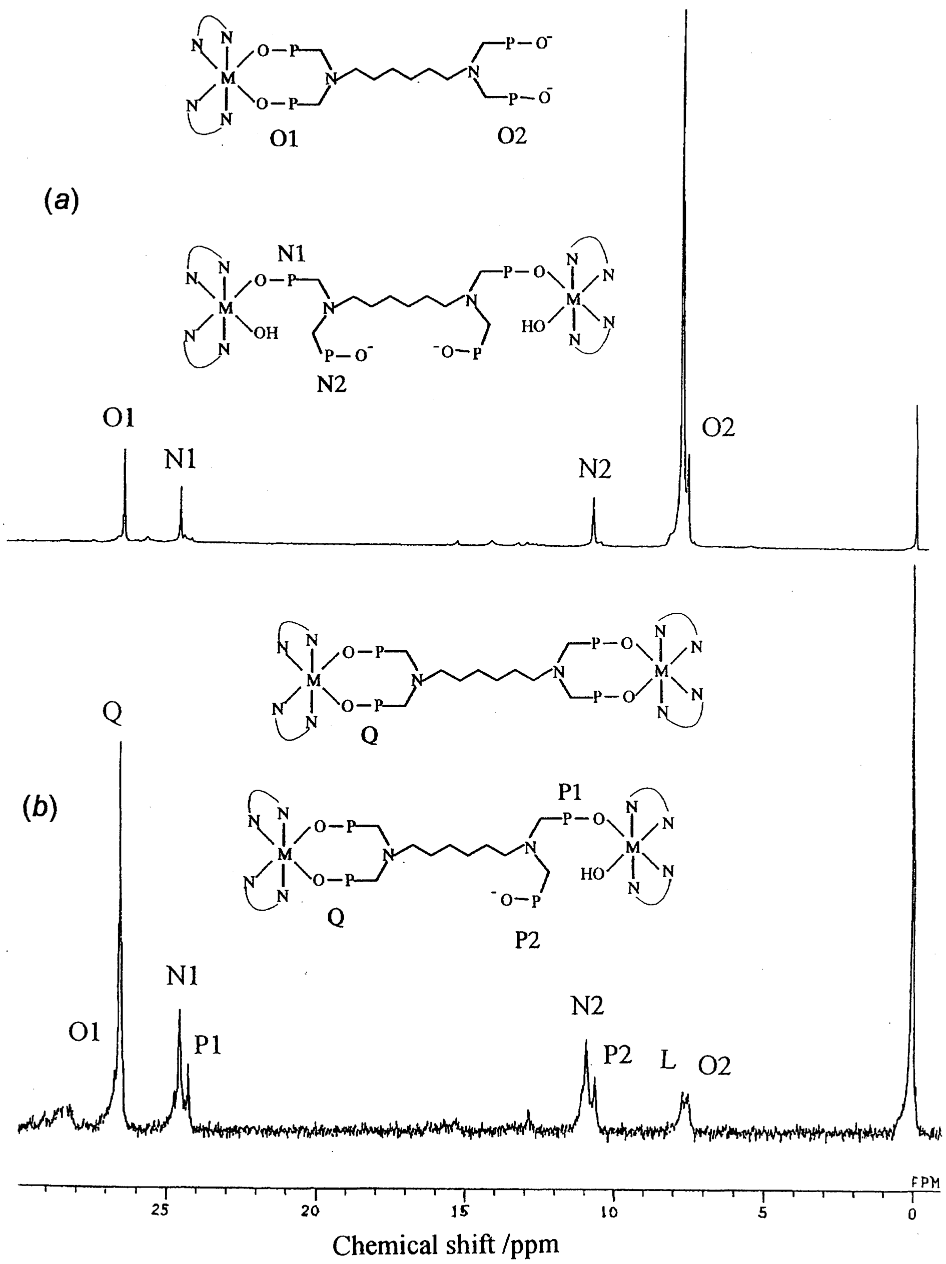


Fig. 7. $^{31}P\{^{1}H\}$ NMR spectra of (a) a mixture of $[CoCl_2(en)_2]^+$–hdtmp at 0 °C at pH 12.9 which had been allowed to react for 1 h at 50 °C and pH 4, and (b) a fraction at pH 13 separated from main product.

peculiar behaviors, i.e., the signals shift downfield by the further protonation (Fig. 8 (a)). This result is explained by an intramolecular interaction between the iminodiphosphonate fragments in the protonated edtmp complexes in the same manner as the ligand edtmp.[25] The protonated imino nitrogen forms hydrogen bonds with the phosphonate O^- of the other imino fragment ($NH^+\cdots{}^-OP$). ($[M(NH_3)(H_3edtmp)]^{2-}$ and $[M(NH_3)(H_4edtmp)]^-$ in Scheme 1) The pentaprotonated species $[M(NH_3)(H_5edtmp)]$ shows normal values of chemical shifts. Since all of the uncoordinated phosphonate groups are protonated in this complex, the intramolecular interaction is ruptured. When the alkylene chain is long (m=3 (tdtmp) and m=6 (hdtmp)), these interactions do not operate in these complexes.

Structures of $Co(en)_2$ Mononuclear O,O-Bidentate Complexes. The changes in the chemical shifts of the $Co(en)_2$ mononuclear O,O-bidentate complexes are plotted as a function of the number of protons bound to the complexes in Fig. 9. The pattern of the chemical shift change caused by the protonation of the complex is quite similar to that of the corresponding $Co(en)_2(NH_3)$ monodentate complex (Fig. 8). Furthermore, the protonation constants of the complexes are also almost the same between them. Consequently, the order of the protonation of the $Co(en)_2$ mononuclear O,O-bidentate complexes is the same as that of the $Co(en)_2(NH_3)$ monodentate complexes. Although the chemical shifts of the higher protonated species were not obtained for the edtmp complex because of the line broadening of the signals, the fact that $[Co(en)_2(H_3edtmp)]^{2-}$ shows a small downfield shift compared with $[Co(en)_2(H_2edtmp)]^{3-}$ sug-

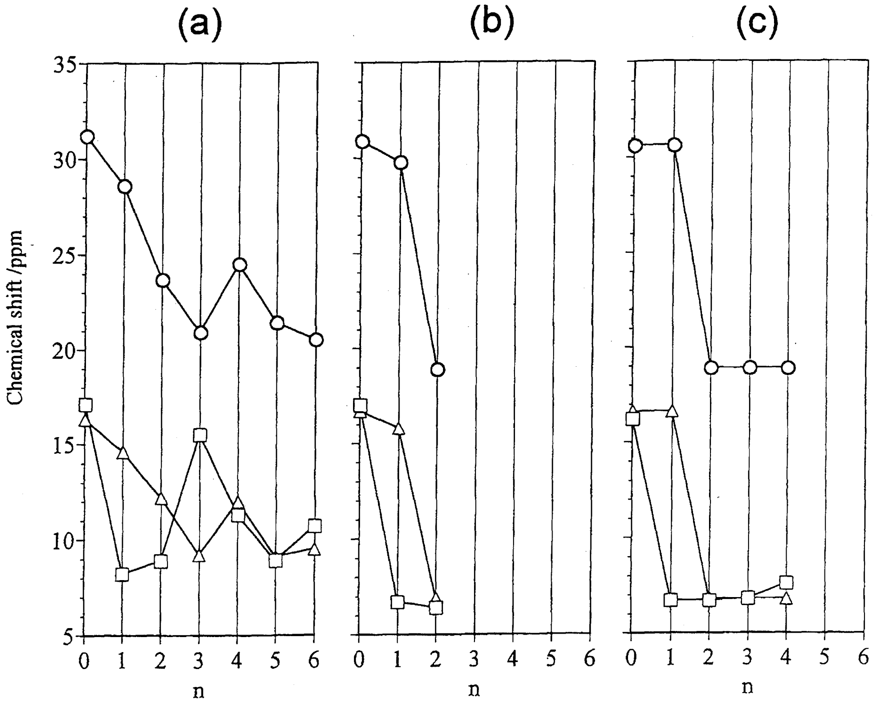
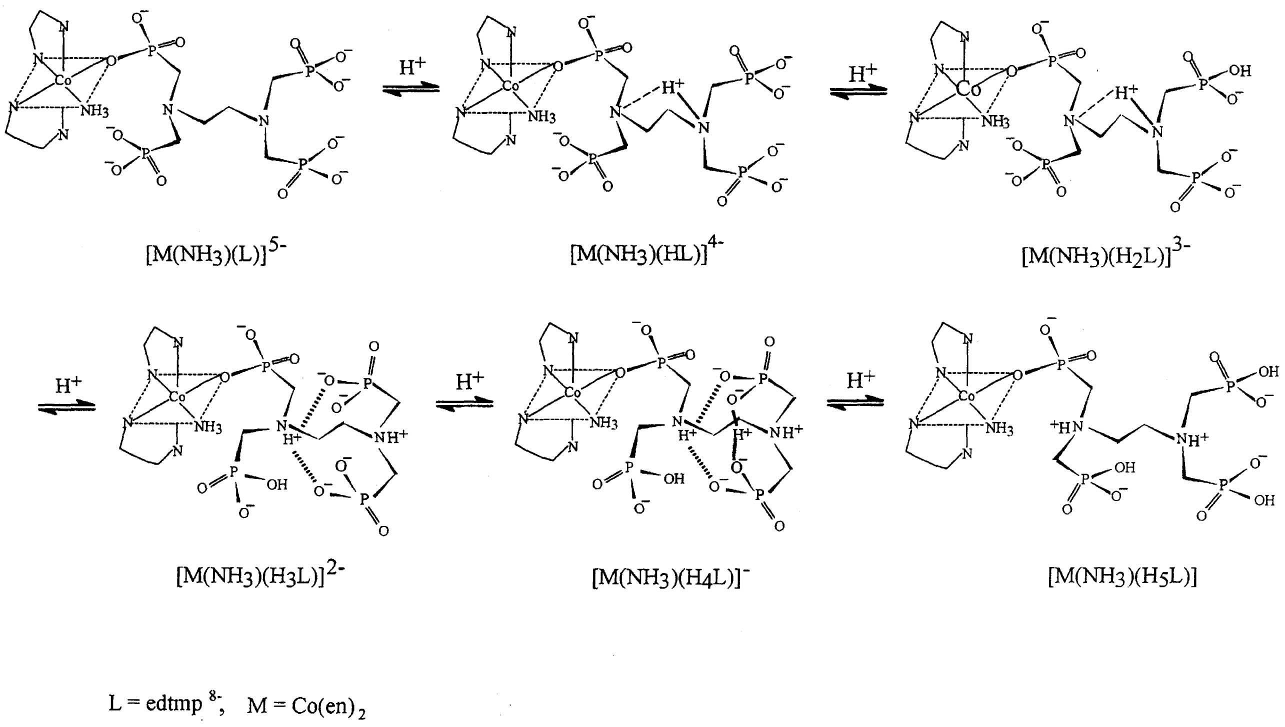


Fig. 8. Plot of chemical shifts of (a) mononuclear O-monodentate $Co(en)_2(NH_3)$–edtmp, (b) –tdtmp, and (c) –hdtmp complexes as a function of a number of proton bound to complex. ○, coordinated phosphonate; △, uncoordinated phosphonate of coordinated imino group, and □, phosphonates of uncoordinated imino group.



Scheme 1.

gests that the triprotonated species also has an intramolecular interaction, as shown in Scheme 1.

Structures of $Co(en)_2$ Mononuclear O-Monodentate Complexes. The chemical shifts of the $Co(en)_2$ mononuclear O-monodentate complexes are plotted as a function of the number of protons bound to the complex in Fig. 10. The changes in the chemical shifts caused by the protonation are rather complicated compared with that of other complexes. In those complexes, one site of Co^{III} is coordinated by phosphonate O^- of the iminodiphosphonate, and another site is coordinated by a water molecule.[31] As has been shown for the midmp complexes,[24] this water molecule is deproton-

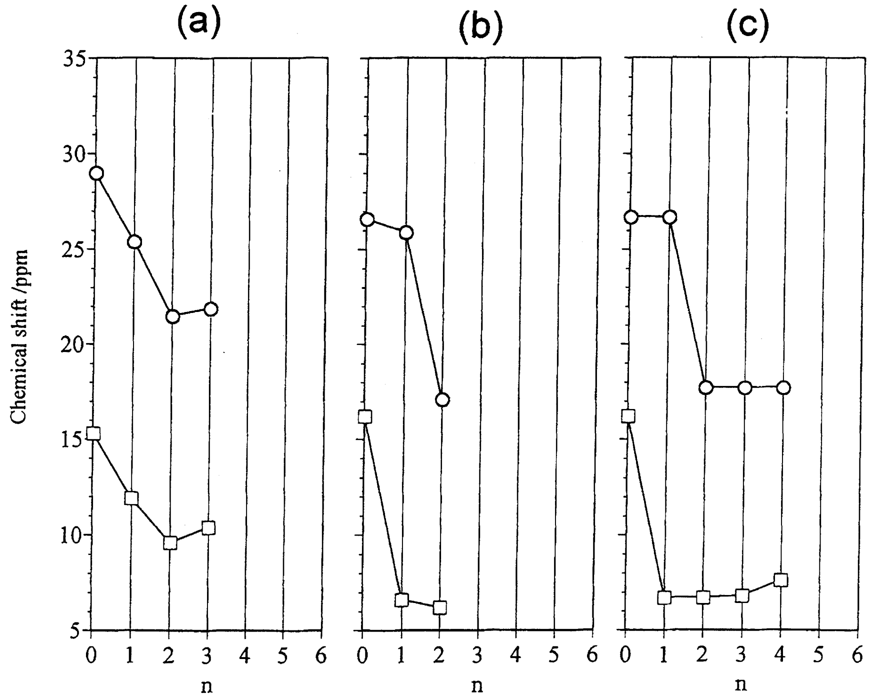
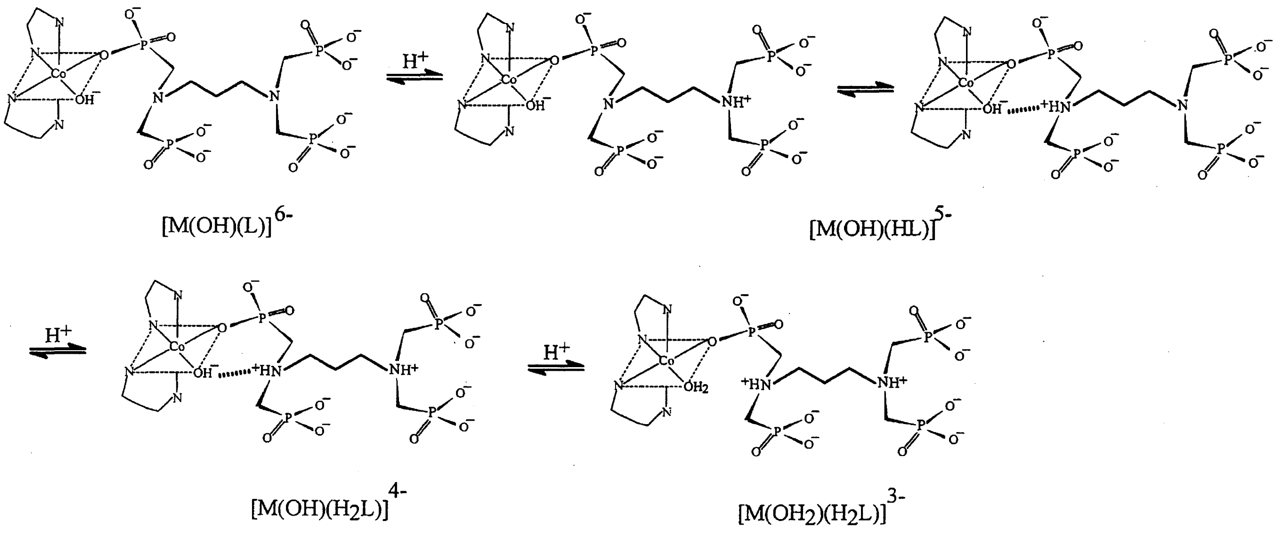


Fig. 9. Plot of chemical shifts of (a) mononuclear O,O-bidentate $Co(en)_2$–edtmp, (b) –tdtmp, and (c) –hdtmp complexes as a function of a number of protons bound to complex. ○, coordinated phosphonates and □, uncoordinated phosphonates.



$L = tdtmp^{8-}$, $M = Co(en)_2^{3+}$

Scheme 2.

ated, i.e., a hydroxide ion is coordinated to Co^{III} at high pH (Scheme 2, $[M(OH)(L)]^{6-}$).

In the case of the tdtmp complex, the first protonation constant of $[M(OH)L]^{6-}$ ($\log K_1 = 13.8$) is larger than that of $[M(NH_3)(L)]^{5-}$ ($\log K_1 = 13.1$). This result suggests that the first protonation occurs mainly on the imino nitrogen atom of a coordinated fragment (Scheme 2, $[M(OH)(HL)]^{5-}$), which is stabilized by a hydrogen bond between the coordinated hydroxide ion and the protonated nitrogen atom ($OH^- \cdots {}^+HN$).[24] Since the basicity of the uncoordinated imino nitrogen atom does not differ so much from that of the hydrogen bonded imino nitrogen, the monoprotonated species might be in equilibrium between two types of N-protonated species (Scheme 2, $[M(OH)(HL)]^{5-}$). The small upfield shift of the phosphonates of an uncoordinated imino fragment by the first protonation (Fig. 10 (b)) supports these structures. The relatively high value of the second protonation constant ($\log K_2 = 12.1$) indicates that both nitrogen

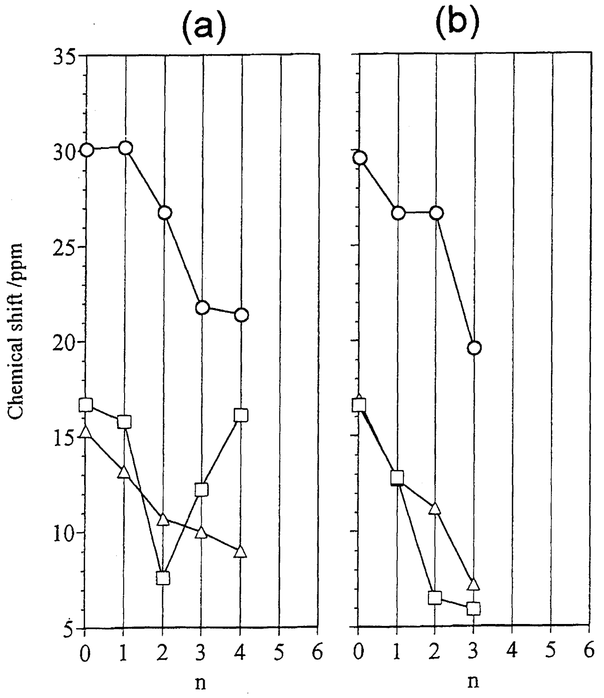


Fig. 10. Plot of chemical shifts of (a) mononuclear O-monodentate $Co(OH)(en)_2$–edtmp and (b) –tdtmp complexes as a function of a number of protons bound to complex. ○, coordinated phosphonates; △, uncoordinated phosphonates of coordinated imino group, and □, phosphonates of uncoordinated imino group.

atoms are protonated in the diprotonated species. The fact that the third protonation constant ($\log K_3=8.0$) is close to the second protonation constant of $[Co(en)_2(OH)(Hmidmp)]^-$ ($\log K_2=8.0$)[24] supports protonation on the hydroxide ion coordinated to Co^{III}.[29,31]

The first protonation constant of the edtmp complex is comparable to that of the tdtmp complex. The smaller value of the second protonation constant of the edtmp complex ($\log K_2=10.8$) compared with that of the tdtmp complex ($\log K_2=12.1$) suggests a hydrogen bond between the imino nitrogen atoms ($NH^+\cdots N$) in the mono protonated species of the edtmp complex. The downfield shift of higher protonated species suggests that the intramolecular interaction between the imino fragments operates in the tri- and tetraprotonated complexes.

Dinuclear Complexes. A detailed discussion concerning the results of dinuclear complexes is omitted here. The results concerning the protonation constants and chemical shifts of the dinuclear hdtmp and midmp complexes are reasonably explained by taking into consideration that the two iminodiphosphonate groups are independent of each other upon protonation.

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