involved from the Epstein–Kustin[7] mechanism of the chlorite–iodide reaction does not impair the agreement between the calculated and found periodic character of the reaction in CSTR, but even improves it, indicate that $IClO_2$ does not play a significant role. Both the autocatalytic character of the reaction and the formation of chlorine dioxide can be quantitatively described by considering the formation and reactions of Cl_2O_2, a firmly established intermediate of redox reactions involving oxyanions of chlorine.[8]

Chlorine and hypochlorous acid formed in reactions 6, 8, and 9 react with chlorite ion:

$$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O \qquad (10)$$

$$ClO_2^- + Cl_2 \rightarrow Cl_2O_2 + Cl^- \qquad (11)$$

An approximation on the rate constants of (10) and (11) can be made from a kinetic study by Emmenegger and Gordon.[9] Under the given experimental conditions the most likely source of ClO_2 is the reaction of Cl_2O_2 with chlorite ion:

$$Cl_2O_2 + ClO_2^- \rightarrow 2ClO_2 + Cl^- \qquad (12)$$

The autocatalysis observed in the decrease of iodine concentration can be accounted for by the plausible reaction between Cl_2O_2 and iodine:

$$Cl_2O_2 + I_2 + 2H_2O \rightarrow 2HOCl + 2HOI \qquad (13)$$

Table III summarizes the reactions and the corresponding rate constants used in the calculation of the kinetic curves by the Gear algorithm. Most of the numerical values for the rate constants are hypothetical, but all of them are chemically reasonable. No distinction was made in the calculations between IO_2^- and HIO_2, as well as between ClO_2^- and $HClO_2$. In Figures 1–7 the calculated curves are shown as dashed lines. The agreement of the measured and calculated kinetic curves obtained for fairly broad ranges of reactant concentrations clearly indicates that the suggested mechanism is a likely one. We do believe that the formation and redox reactions of Cl_2O_2 play a crucial role in general in the unusual kinetics of reactions involving chlorite ion.

Registry No. I_2, 7553-56-2; ClO_2^-, 14998-27-7; HOCl, 7790-92-3.

---

(7) Epstein, I. R.; Kustin, K. *J. Phys. Chem.* **1985**, *89*, 2275.

(8) Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330.

(9) Emmenegger, F.; Gordon, G. *Inorg. Chem.* **1967**, *6*, 633.

Contribution from the Department of Chemistry,
Faculty of Science, Niigata University, Niigata 950-21, Japan

Complex Formation of Amino Polyphosphonates. 1. Potentiometric and Nuclear Magnetic Resonance Studies of Nitrilotris(methylenephosphonato) Complexes of the Alkaline-Earth-Metal Ions

Kiyoshi Sawada,* Tsutomu Araki, and Toshio Suzuki

Received June 4, 1986

The complex formation equilibria of nitrilotris(methylenephosphonic acid) (NTMP, H_6L) with the alkaline-earth-metal ions (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) have been studied potentiometrically at 25.0 °C and at an ionic strength of 0.1 M (KNO_3). The successive protonation constants of ligand NTMP, K_n, were determined as log K_1 = 12.7 ± 0.1, log K_2 = 7.15 ± 0.02, log K_3 = 5.88 ± 0.02, log K_4 = 4.62 ± 0.02, and log K_5 = 1.4 ± 0.1. The first protonation constant K_1 was confirmed by the ^{31}P NMR chemical shift of the ligand. The complex formation constants were obtained as log K_{ML} = 7.52, 7.86, 6.52, and 6.34 (±0.02) for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively. The first protonation constants of the complexes reveal quite large values and are in the reverse order of K_{ML} (log K_{MHL} = 9.42, 8.80, 9.41, and 9.72 (±0.02) for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively). The second and third protonation constants are nearly equal for the four metal ions (log K_{MH_2L} = 6.10–6.16, log K_{MH_3L} = 4.8–5.1). The ^{31}P NMR spectra of the complexes have been measured in aqueous solution under the same conditions as used in the potentiometric studies. The chemical shifts of each species of H_nL and MH_mL were evaluated on the basis of the formation constants obtained potentiometrically. The ^{1}H and ^{13}C NMR spectra are also reported. The results of potentiometric and nuclear magnetic resonance studies suggest strongly that the first protonation of a metal complex occurs on the nitrogen atom of the ligand, with the M–N bond ruptured.

Introduction

The properties of amino polyphosphonates (APP) were first reported as early as 1949 by Schwarzenbach[1] concurrently with those of amino polycarboxylates (APC). The protonation and complex formation of alkaline-earth and transition metals with ethylenediaminetetrakis(methylenephosphonic acid) (EDTMP) and nitrilotris(methylenephosphonic acid) (NTMP) have been studied by Martell et al.[2–4] Rizkalla and Zaki[5–7] have reported the results for EDTMP and Irani et al.[8,9] and Nikitina et al.[10] for NTMP. These results show very large discrepancies. Martell[3,4] has noted that the results reported before 1976 contain a considerable degree of inaccuracy because the reagents were not pure. Other properties of NTMP and EDTMP complexes have been studied mainly by Dyatlova et al.[10,11] and other Russian investigators.[12]

---

(1) Schwarzenbach, G.; Ackermann, H.; Ruckstull, P. *Helv. Chim. Acta* **1949**, *32*, 1175.

(2) Westerback, S.; Rajan, K. S.; Martell, A. E. *J. Am. Chem. Soc.* **1965**, *87*, 2567.

(3) Motekaitis, R. J.; Murase, I.; Martell, A. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1103.

(4) Motekaitis, R. J.; Murase, I.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 2303.

(5) Zaki, M. T. M.; Rizkalla, E. N. *Talanta* **1980**, *27*, 423.

(6) Rizkalla, E. N.; Zaki, M. T. M. *Talanta* **1979**, *26*, 507.

(7) Rizkalla, E. N.; Zaki, M. T. M. *Talanta* **1980**, *27*, 769.

(8) Moedrizer, K.; Irani, R. R. *J. Org. Chem.* **1966**, *31*, 1603.

(9) Carter, R. P.; Carroll, R. L.; Irani, R. R. *Inorg. Chem.* **1967**, *6*, 939.

(10) Nikitina, L. V.; Grigor'ev, A. I.; Dyatlova, N. M. *Zh. Obshch. Khim.* **1974**, *44*, 1598, 1669.

(11) (a) Kabachnik, M. I.; Medved, T. Ya.; Dyatlova, N. M.; Rudomino, M. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1974**, *43*, 733. (b) Dyatlova, M. N.; Medyntsev, V. V.; Medved, T. Ya.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1968**, *38*, 1065. (c) Grigorev, A. I.; Nikitina, L. V.; Dyatlova, N. M. *Zh. Neorg. Khim.* **1974**, *19*, 1970. (d) Marov, I. N.; Ruzaikina, L. V.; Ryabykhin, V. A.; Korovaikov, P. A.; Dyatlova, N. M. *Koord. Khim.* **1977**, *3*, 1333. (e) Goeva, L. V.; Dyatlova, N. M.; Kuznetsov, N. T.; Torsynova, N. I.; Frangulyan, D. G.; Tsapkin, V. V. *Radiokhimiya* **1982**, *24*, 591. (f) Popov, K. I.; Larchenko, V. E.; Chuvaev, V. F.; Dyatlova, N. M. *Zh. Neorg. Khim.* **1982**, *27*, 2756. (g) Larchenko, V. E.; Popov, K. I.; Grigorev, A. I.; Dyatlova, N. M. *Koord. Khim.* **1984**, *10*, 1187. (h) Samakaev, R. Kh.; Dyatlova, N. M.; Dytyuk, L. T. *Zh. Neorg. Khim.* **1984**, *29*, 3179.

0020-1669/87/1326-1199$01.50/0 © 1987 American Chemical Society

Besides EDTMP and NTMP, many kinds of (alkylamino)methylenephosphonates,[8,9] (carboxyamino)methylenephosphonates[2,13,14] and their methylenephosphinates[15] have been synthesized. The properties of methylenediphosphonate derivatives (e.g. 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)) have also been studied as a chelating agent by a variety of methods.[11e,16]

The NMR spectroscopy has been widely applied to the amino polycarboxylate complexes,[17] polyphosphates, and nucleotides.[18,19] The qualitative studies using this method have been carried out for EDTMP,[11d,20,21] NTMP,[8,9,11f,11g,12b] and others.[22] The NMR spectra of the nitrilomethylenephosphonates and their diammineplatinum(II) complexes have been reported.[23]

In the present study, the protonation and complex formation of nitrilotris(methylenephosphonic acid), which is one of the simplest APP compounds, with the alkaline-earth-metal ions have been investigated by means of potentiometry and NMR spectroscopy. The ^{31}P, ^{1}H, and ^{13}C NMR chemical shifts of the NTMP complexes of alkaline-earth metals were evaluated on the basis of the results of potentiometry, and the structures of the complexes have been estimated.

Experimental Section

Reagents. Commerically obtained trisodium salt of nitrilotris(methylenephosphonic acid) (NTMP) (Dojin Pure Chemicals) was recrystallized from ethanolic aqueous solution as the acid form (H_6L). After the remaining sodium ion was completely removed by the cationic exchange resin, the ligand was crystallized. The purity of the ligand was checked by a pH titration, Cu titration with a copper ion electrode, and ^{31}P NMR spectroscopy. All the metal nitrates used were of analytical grade (Wako Pure Chemicals), and concentrations of the stock solutions were determined by the chelatometric titration.

Potentiometric Measurements. The pH titration was carried out with a Corning Model 130 pH meter. The glass electrode was calibrated by titration with nitric acid or potassium hydroxide (I = 0.1 M KNO_3). The pH, the logarithm of the reciprocal of the hydrogen concentration, was evaluated from the electromotive force by using the calibration curve. In most cases, 10^{-2} M NTMP solution (M ≡ mol dm^{-3}) or the solution containing the equimolar alkaline-earth-metal ion was titrated in a water-jacketed cell (25.0 °C) with 0.1 M KOH at an ionic strength of 0.1 M (KNO_3).

Table I. Protonation Constants of NTMP at I = 0.1 (KNO_3)

log K_1	12.8 ± 0.2	12.7 ± 0.1[a]
log K_2	7.15 ± 0.02	
log K_3	5.88 ± 0.02	
log K_4	4.62 ± 0.02	
log K_5	1.4 ± 0.1	

[a] Evaluated from the ^{31}P NMR chemical shift.

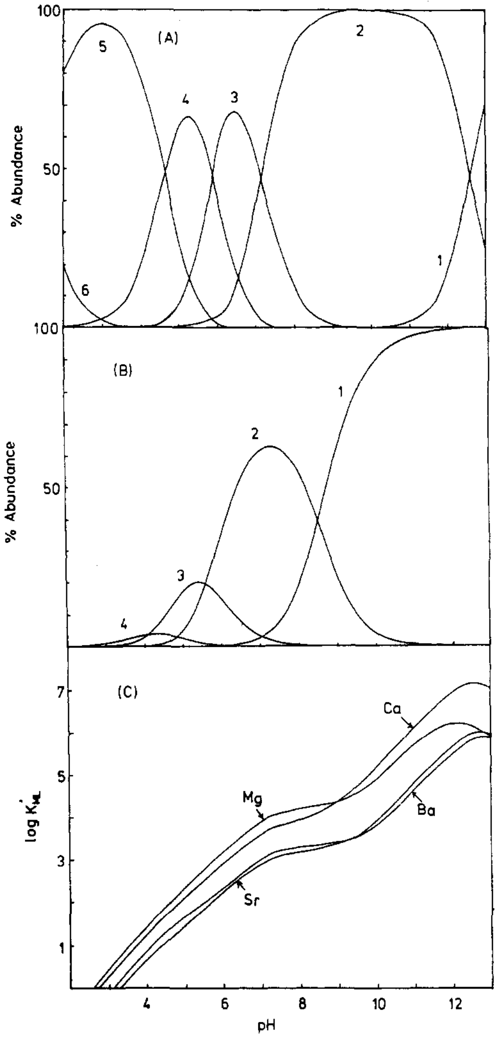


Figure 1. (A) Distribution diagram of the ligand as a function of pH: 1, $ntmp^{6-}$; 2, $Hntmp^{5-}$; 3, H_2ntmp^{4-}; 4, H_3ntmp^{3-}; 5, H_4ntmp^{2-}; 6, H_5ntmp^{-}. (B) Distribution diagram of calcium complexes as a function of pH: 1, $Ca(ntmp)^{4-}$; 2, $Ca(Hntmp)^{3-}$; 3, $Ca(H_2ntmp)^{2-}$; 4, $Ca(H_3ntmp)^{-}$. $C_{Ca} = C_{ntmp} = 5 \times 10^{-3}$ M. (C) Logarithmic conditional formation constant, K_{ML}', of alkaline-earth-metal–NTMP complexes as a function of pH.

NMR Measurements. ^{31}P, ^{1}H, and ^{13}C NMR measurements were carried out in aqueous solution on a JEOL-FT 90Q NMR spectrometer (89.95 MHz for ^{1}H) with a 10-mm-diameter sample tube at 25 °C. The NMR spectrometer was locked by the signal of D_2O, which served as external standard in a 5-mm-diameter concentric tube. The downfield shift is denoted by positive sign of the chemical shift. ^{31}P NMR was measured under the same conditions as in the potentiometric measurements. The ^{31}P NMR shifts were recorded against an external standard of 0.5% H_3PO_4 in D_2O and are reported as the values converted to the aqueous 85% H_3PO_4 reference.

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 10^{-1} M ligand and ligand–metal ion aqueous solutions were recorded by using (trimethylsilyl)propionate-d_4 in D_2O as an external standard in a 5-mm-diameter concentric tube. The signals of methyl protons and methyl carbons are referred to 0 ppm. In order to obtain information of NTMP complexes in the aqueous solution, the ^{1}H NMR spectra were measured by the inversion recovery method. As the proton relaxation of solvent water is very slow, the 180°–τ–90° double-pulse method (τ = 1.6 s) makes it possible to largely reduce the ^{1}H signal of solvent water.

---

(12) (a) Ruzaikina, L. B.; Ryabukhin, V. A.; Ermakov, A. N.; Marov, I. N.; Dabydova, L. S.; Krutko, E. B. *Zh. Neorg. Khim.* **1980**, *25*, 3254. (b) Marov, I. N.; Ruzaikina, L. B.; Ryabukhin, B. A.; Korovaikov, P. A.; Sokolov, A. B. *Koord. Khim.* **1980**, *6*, 375. (c) Tananaev, I. V.; Tereshin, G. S.; Kuznetsova, O. B.; Beresnev, E. N.; Goeva, L. B. *Zh. Neorg. Khim.* **1981**, *26*, 276. (d) Tananaev, I. V.; Beresnev, E. N.; Tereshin, G. S.; Kuznetsova, O. B.; Goeva, L. B. *Zh. Neorg. Khim.* **1981**, *26*, 278. (e) Ratina, M. A.; Dolmanova, I. F.; Fridman, A. Ya. *Koord. Khim.* **1982**, *8*, 613. (f) Myasoedov, B. F.; Karalova, Z. K.; Fedorov, L. A.; Rodionova, L. M.; Grebenshchikov, N. I. *Zh. Neorg. Khim.* **1983**, *28*, 697.

(13) Ockerbloom, N.; Martell, A. E. *J. Am. Chem. Soc.* **1958**, *80*, 2351.

(14) Rajan, K. S.; Murase, I.; Martell, A. E. *J. Am. Chem. Soc.* **1969**, *91*, 4408.

(15) Motikaitis, R. J.; Murase, I.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3353.

(16) (a) Přibil, R.; Veselý, V. *Talanta* **1967**, *14*, 591. (b) Irani, R. R.; Moedritzer, K. *J. Phys. Chem.* **1962**, *66*, 1349. (c) Carroll, R. L.; Irani, R. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2971. (d) Wada, H.; Fernando, Q. *Anal. Chem.* **1971**, *43*, 751. (e) Mioduski, T. *Talanta* **1980**, *27*, 299. (f) Stover, F. S.; Wagenknecht, J. H. *Anal. Chim. Acta* **1982**, *135*, 347. (g) Fonong, T.; Burton, D. J.; Pietrzyk, D. J. *Anal. Chem.* **1983**, *55*, 1089.

(17) (a) Nakamoto, K.; McCarthy, P. J. *Spectroscopy and Structure of Metal Chelate Compounds*; Wiley: New York, 1968. (b) Ueno, K. *Chelate Chemistry*; Nankodo: Tokyo, 1976.

(18) Gorenstein, D. G. *Phosphorus-31 NMR*; Academic: New York, 1984.

(19) Corbridge, D. E. C. *Phosphorus*, 2nd ed.; Elsevier: Amsterdam, 1985.

(20) Oakes, J.; Smith, E. G. *J. Chem. Soc., Dalton Trans.* **1983**, 601.

(21) Rizkalla, E. N.; Choppin, G. R. *Inorg. Chem.* **1983**, *22*, 1478.

(22) Oakes, J. *J. Chem. Soc., Dalton Trans.* **1984**, 1133.

(23) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 720, 726.

Table II. Formation Constants and Protonation Constants[a] of Alkaline-Earth-Metal–NTMP Complexes at $I = 0.1$ (KNO_3)

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log K_{ML}$	7.52	7.86	6.52	6.34
$\log K_{MHL}$	9.42	8.80	9.41	9.72
$\log K_{MH_2L}$	6.10	6.11	6.15	6.16
$\log K_{MH_3L}$	4.8	4.9	5.0	5.1

[a] Errors of the logarithmic constants were estimated as ±0.02 for log K_{ML} and log K_{MHL}, ±0.04 for log K_{MH_2L}, and ±0.1 for log K_{MH_3L}.

Results

Formation Constants. The stepwise protonation constant of NTMP, K_n, is defined as

$$K_n = [H_nL^{n-6}]/[H^+][H_{n-1}L^{n-7}] \qquad (1)$$

The mean number of protons bound to ligand, $\bar{n}$, is written as

$$\bar{n}_{calcd} = \sum n[H_nL]/C_L \qquad (2)$$

Since the ligand is prepared as the acid form, H_6L, the mean proton number is obtained from the electromotive force by using

$$\bar{n}_{obsd} = (6C_L - C_{OH} - [H^+] + [OH^-])/C_L \qquad (3)$$

where C_L and C_{OH} refer to the total concentrations of ligand and potassium hydroxide added, respectively.

By nonlinear regression with the aid of a computer, the protonation constants of the ligand minimizing the sum of square of deviations, ESS ($=\sum(\bar{n}_{obsd} - \bar{n}_{calcd})^2$), were evaluated. The logarithmic protonation constants thus obtained are listed in Table I. The distribution diagram of protonated species of the ligand NTMP is depicted in Figure 1A as a function of pH.

The formation constant of a metal complex and its successive protonation constant are defined by

$$K_{ML} = [ML]/[M][L] \qquad (4)$$

$$K_{MH_mL} = [MH_mL]/[H][MH_{m-1}L] \qquad (5)$$

Henceforth, the charges of chemical species are omitted for simplicity. With the use of these constants, the mean number of protons bound to a ligand and its complex is written as

$$\bar{n} = (\sum n[H_nL] + \sum m[MH_mL])/C_L \qquad (6)$$

By taking into consideration the formation of the hydroxo complex $M(OH)$[24] of the metal ion, the values of K_{ML} and K_{MH_mL} giving the minimum ESS were evaluated and are listed in Table II. The errors given to the constants were estimated from 30 to 40 data points. Under these conditions the hydrolysis of the complex ML, i.e., the formation of hydroxocomplex M(OH)L, was not observed.

Distribution diagrams of the calcium complexes calculated by using the constants listed in Table II are depicted in Figure 1B as an example of the metal complexes. The logarithmic conditional formation constant of the complex, $K_{ML}' = [ML']/[M'][L'] = K_{ML}\alpha_{ML(H)}\alpha_{L(H)}^{-1}\alpha_{M(OH)}^{-1}$, is plotted in Figure 1C as a function of pH, where the side reaction coefficients of the ligand and complex $\alpha_{L(H)}$ and $\alpha_{ML(H)}$, are defined as $[L'] = \sum_{n=0}^{6}[H_nL] = [L]\sum\beta_n[H]^n = [L]\alpha_{L(H)}$ and $[ML'] = \sum_{m=0}^{4}[MH_mL] = [ML]\sum\beta_m[H]^m = K_{ML}[M][L]\alpha_{ML(H)}$. $\beta_n = \Pi K_{H_nL}$ and $\beta_m = \Pi K_{MH_mL}$.

The value of ESS scarcely decreases even when the formation of additional species such as M_2L and ML_2 is taken into consideration besides the M:L = 1:1 complex, MH_mL. Thus, such species are not important under the present conditions.

Phosphorus-31 NMR. A typical ^{31}P NMR spectrum of NTMP is shown in spectrum 1 of Figure 2. The resonance line splits into a triplet peak with an intensity ratio 1:2:1 by coupling with the two protons of the adjacent methylene group. The spectra of NTMP at any pH have the same pattern as the spectrum 1. The resonance line becomes a singlet peak by complete decoupling with the proton as shown in spectra 2–11 of Figure 2. The chemical shift shows a drastic change in a pH range of 14–12 and there is no significant change in the neutral and acidic regions except for a small downfield shift at pH 4–3.

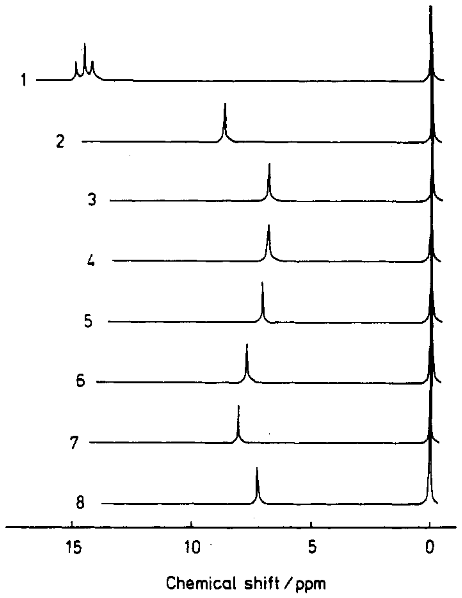


Figure 2. ^{31}P NMR spectra of NTMP at various pH: 1, 13.3; 2, 12.6; 3, 10.0; 4, 8.0; 5, 6.5; 6, 5.8; 7, 5.0; 8, 2.9. Spectrum 1 is nondecoupled; others are decoupled with ^1H.

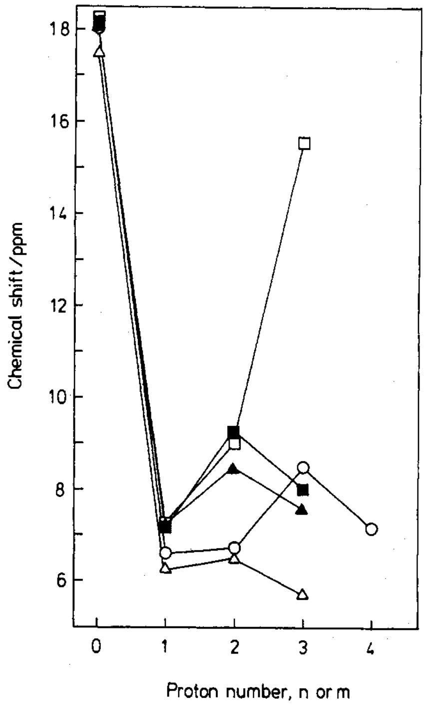


Figure 3. ^{31}P NMR chemical shifts of NTMP and alkaline-earth-metal–NTMP complexes as a function of the number of protons bound to ligand (H_nL), n, or metal complex (MH_mL), m: (○) alkaline-earth-metal free; (△) Mg; (□) Ca; (▲) Sr; (■) Ba. $C_{NTMP} = C_M = 5 \times 10^{-3}$ M.

In spite of the presence of many kinds of protonated species H_nL of NTMP, only one sharp singlet peak is observed in the $^{13}P\{^1H\}$ spectrum over a whole range of pH. This fact indicates that the proton exchange of NTMP is very fast. Thus, three phosphorus atoms of NTMP are averaged and the chemical shift is written by

$$\delta_P = \sum\delta_n X_{H_nL} \qquad (7)$$

where δ_n and X_{H_nL} are the chemical shift and the proportion of each protonated or unprotonated species, H_nL (n = 0–5), respectively. By the use of the protonation constants K_n, the in-

---

(24) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, 1964; p 1971.

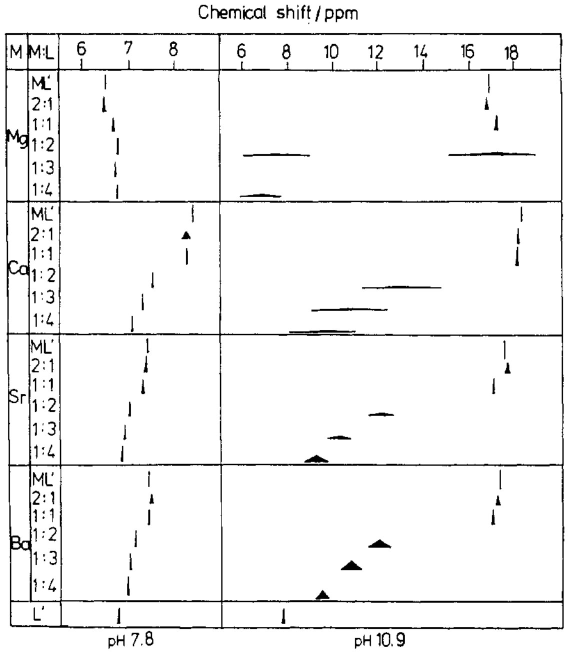


Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum pattern of alkaline-earth-metal–NTMP solutions at various metal to ligand ratios at pH 7.8 and 10.9. $C_L = 10^{-2}$ M.

dividual chemical shift δ_n, minimizing the sum of squares of deviations ESS from the chemical shifts observed (δ_{obsd}) was evaluated by nonlinear regression. δ_n values thus obtained are plotted as a function of the number of protons bound to ligand, n, in Figure 3.

The 1:1 alkaline-earth-metal ion–NTMP solution has the same ^{31}P NMR pattern and pH dependency of δ_P as those of the ligand. The pH region showing the steep change in δ_P moves to the acidic side by about 4 units compared with that of the ligand and corresponds to the pH region of the first protonation of the metal complex. The $^{31}P\{^{1}H\}$ peaks in these regions are quite broad (the half-height width is about 30 Hz). The chemical shift of the metal–ligand solution is written by a nonlinear combination of the chemical shifts of each species present in the solution as

$$\delta_P = \sum \delta_n X_{H_nL} + \sum \delta_m X_{MH_mL} \qquad (8)$$

where δ_m and X_{MH_mL} are the chemical shift and the ligand proportion of protonated or unprotonated complex, MH_mL, respectively. The chemical shift of each species of a complex, δ_m, minimizing the sum of squares of deviations ESS for the chemical shifts observed, was evaluated by linear regression. The chemical shifts of complexes, δ_m, thus obtained are plotted in Figure 3 as a function of the number of protons, m, bound to the complex MH_mL. The first protonation constants, K_1 and K_{MHL}, could also be evaluated from these NMR chemical shift data (Table I). The values of the constants K_{MHL} agree with the values obtained by potentiometry within experimental error.

The ^{31}P NMR at various ratios of C_M:C_L was measured at pH 7.8 and 10.9. The patterns of the $^{31}P\{^{1}H\}$ spectra are shown in Figure 4, where the width of the symbol of a triangle refers to the broadness of the peak. The chemical shift of the ligand, L', and the complex, ML', were evaluated by $\delta_{L'} = \sum \delta_n X_{H_nL}$ and $\delta_{ML'} = \sum \delta_m X_{MH_mL}$ at the given pH. Although the peaks of C_M:C_L = 2:1 solutions are relatively broad, all the spectra of the solutions at pH 7.8 have sharp single peaks. The chemical shift of the mixture approaches to that of free ligand, $\delta_{L'}$, with decrease in C_M:C_L ratio. In the case of alkaline solution (pH 10.9), the peaks of the solution containing an excess of ligand (C_M:C_L < 1) become quite broad. The peak width increases in the order of Ba < Sr < Ca. The signal of the Mg solution splits into two broad peaks corresponding to the ligand $\delta_{L'}$ and complex $\delta_{MgL'}$.

Carbon-13 and Hydrogen-1 NMR. The $^{13}C\{^{1}H\}$ signals of ligand show a double triplet resonance. The resonance of carbon splits into a doublet by coupling with an adjacent phosphorus and splits further into a triplet by three-bond coupling with two phosphorus ($^{1}J_{C-P}$ = 125.5 Hz and $^{3}J_{C-P}$ = 3.9 Hz at pH 10.0). The ligand and the ligand–metal solutions at any pH show the same pattern in the ^{13}C spectrum, a double triplet resonance. The ^{13}C signal shows an upfield shift after protonation of NTMP. The ^{1}H NMR spectrum of NTMP in aqueous solution obtained by the inversion recovery method shows a doublet resonance by coupling with an adjacent phosphorus atom (δ_H = 3.55 and $^{2}J_{H-P}$ = 10.8 Hz at pH 10.1) and shifts steeply downfield by the first protonation, followed by a gradual downfield shift with further protonation. The proton signals of the solvent water are not eliminated completely because of its very complexed hydrogen-bond networks, showing complicated peaks between 4.6 and 5.0 ppm. The ^{13}C and ^{1}H signals of ligand–metal solution show the same pattern of spectra and change in chemical shift of ligand with pH.

Discussion

Complex Formation Constants. The protonation constants of NTMP reported by Nikitina et al.[10] do not differ greatly from our results except for the first protonation constant. The pH titration at high pH causes often a very large error. On the other hand, the spectroscopic method is suitable for the analysis of such a system. As seen from Table I, both values of the constant K_1 obtained by potentiometry and NMR spectroscopy are in good agreement. The complex formation and protonation constants of NTMP with calcium and magnesium reported by Irani et al.[9] show relatively large discrepancies from present results. The discrepancies of these constants between the present results and those reported by Nikitina et al.[10] are within 0.5 unit. However, analysis of the results of the ^{31}P NMR shift change with pH by using the equilibrium constants reported by Nikitina et al. did not give a proper fitting between the observed and calculated values of chemical shifts.

The fact that K_1 is much larger than K_2 indicates that the first protonation of NTMP takes place on the nitrilo nitrogen in the same manner as that of amino polycarboxylates.[17b] The large first protonation constant of NTMP (log $K_{H_{ntmp}}$ = 12.7) compared with that of NTA (log $K_{H_{nta}}$ = 9.75[25]) is interpreted in terms of the increase in electron density on the nitrogen atom caused by the high negative charge of phosphonate groups (6–). The small differences between K_2 and K_3 and between K_3 and K_4 indicate a small effect of protonation of one phosphate on the further protonations. This is analogous to the situation observed for the protonation of NTA (log K_1 = 9.75, log K_2 = 2.43, log K_3 = 1.97).[25] The fact that the fifth protonation constant (K_5) is much smaller than the fourth one (K_4) indicates that further protonation on the phosphonate group already protonated (PO_3H^-) is very unfavorable compared with that on PO_3^{2-}.

The formation constant of magnesium chelate with amino polycarboxylates is usually smaller than that of calcium ion except for simple ligands such as glycine and iminodiacetic acid.[26] The complexes of NTMP and EDTMP[27] reveal also the same order as seen for APC. The hydration energy of Mg^{2+}, $-\Delta H$, is fairly large because its small ion size, and thus the enthalpy of formation of Mg^{2+} chelate is much smaller than those of other alkaline-earth-metal ions.[28] The complex formation of the Mg^{2+} ion with EDTA is driven by the increase in entropy, i.e., the increase in free water molecules released from the coordination sheath of the aqua Mg^{2+} ion on complex formation. The same complex formation mechanism was revealed for the NTMP complexes by the calorimetric studies.[29]

The basicity of the phosphonate O^- of NTMP is expected to decrease by the coordination of NTMP to the metal ion. Thus, if the first protonation of a complex occurs on the phosphonate O^- uncoordinated to the metal ion, the first protonation constant

---

(25) Collange, E.; Thomas, G. *Anal. Chim. Acta* **1973**, *65*, 87.

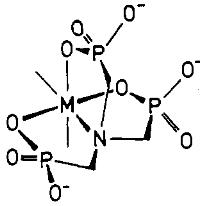
(26) Ringbom, A. *Complexation in Analytical Chemistry*; Wiley: New York, 1963.

(27) Sawada, K., unpublished data. Doi, K., private communication, Nagoya Institute of Technology.

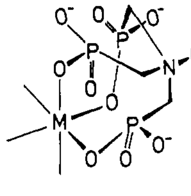
(28) Charles, R. C. *J. Am. Chem. Soc.* **1954**, *76*, 5854.

(29) Sawada, K., unpublished data.

of the complex ML (K_{MHL}) should be smaller than that of the phosphonate O^- of the free ligand, where the second protonation of NTMP (K_2) corresponds to the first protonation of phosphonate ion of the free ligand. Nevertheless, the first protonation constants of complexes ($\log K_{MHL} = 8.8–9.7$) are larger than the second one of the free ligand ($\log K_2 = 7.15$). This fact suggests that, in the first protonation process in ML, the proton attacks the nitrilo nitrogen of NTMP (structure II) rupturing the M–N bond of the complex $M(ntmp)^{4-}$ (structure I). The IR data reported by Nikitina et al.[10] also support these structures. The bonding manner of structure II is attributable to the very high basicity of the nitrogen atom of the amino polyphosphonate ($\log K_1 = 12.7$ for NTMP) compared with that of the amino polycarbonate ($\log K_1 = 9.75$ for NTA[25]). The fact that the formation constants of the Ca and Mg complexes of nitrilotris(methylenephosphoric acid) *N*-oxide,[30] in which the nitrogen has no ability to coordinate to the metal ion, do not differ largely from those of NTMP supports the idea that structure II is not so unstable. Reducted basicity of the nitrilo nitrogen in the ML complex compared with that of the free ligand ($\log K_1 = 12.7$) is attributable to the inductive effect of coordinating the oxygen atoms to the metal ion and to the bond rupturing of the M–N bond in ML.



I



II

In the case of EDTA complexes, the order of value of K_{MHL} ($K_{MgHL} > K_{CaHL} < K_{SrHL} < K_{BaHL}$) is in the reverse of that of K_{ML} ($K_{MgL} < K_{CaL} > K_{SrL} > K_{BaL}$).[31] That is, the protonation constant of the complex K_{MHL} decreases with an increase in the strength of the ML bond. These results are explained by the substitution of M in the M–O bond for the proton. The fact that the orders of the constants K_{ML} and K_{MHL} of the NTMP complexes are the same as those of NTA complexes corroborates substitution of M in the M–N bond for the proton, i.e. M–N bond rupture followed by protonation. This assumption is also supported by the fact that the difference between $\log K_{MHL}$ and $\log K_{MH_2L}$ is considerably larger than that between $\log K_{MH_2L}$ and $\log K_{MH_3L}$. On the other hand, the second and third protonation constants of NTMP complexes scarcely change with the metal ions, and the difference between the logarithmic constants of the second and third protonation of the complex ($\log K_{MH_2L} - \log K_{MH_3L} = 1.2$) is close to that of the ligand ($\log K_{H_2L} - \log K_{H_3L} = 1.27$). These facts indicate that the difference in the M–L bond strengths scarcely changes the protonation constant of the free O^- of the phosphonate group coordinating to the metal ion. That is, if the first protonation of a complex occurs on the phosphonate O^-, the value of K_{MHL} should not differ so much with different metal ions.

Although the proposed structure of a protonated complex MHL (structure II) has 8-membered rings, the molecular model of the complex indicates a strain-free configuration. The α,γ-triphosphate complex of bis(ethylenediamine)cobalt(III) $[(en)_2\overline{CoOPO_2HOPO_2OPO_2HO}]$, which also has a 8-membered ring, is a stable complex.[32] It is somewhat less stable than β,γ complex having a 6-membered ring.[33] In the case of the ethylenediamine platinum(II) the α,γ complex is, however, more stable than the β,γ complex.[34]

^{31}P Chemical Shift. Carter et al.[30] have reported qualitative data on ^1H and ^{31}P NMR chemical shifts of $N(C_2H_5)_{3-x}(CH_2PO_3^{2-})_x$ and have shown a steep downfield shift of the ^{31}P NMR signal at the equivalence point by the titration of the acid form compound with sodium hydroxide. Appleton et al.[23] have studied quantitatively the ^1H, ^{13}C, and ^{31}P NMR spectra of NTMP and related ligands. The results on NTMP show a reasonable agreement with the present data. The ^{31}P NMR chemical shift jump between L and HL, however, occurs at a relatively low pH compared with the present data ($\Delta(pH) = 1.3$ unit). This might be attributable to the difference in K_1 of NTMP caused by the difference in medium conditions (e.g., ionic strength and alkaline-earth-metal ion) and in the definition of pH (they used the activity of the hydrogen ion).

The ^{31}P NMR chemical shifts of unprotonated complexes, δ_{ML}, are almost identical with each other irrespective of the kinds of metal ions and are the same as that of free ligand, δ_L (Figure 3). The chemical shifts of the monoprotonated complexes, δ_{MHL}, are also the same as that of monoprotonated ligand, δ_{HL}; i.e., the first protonation causes a drastic upfield shift for the complex as well as for the ligand.

As can be seen from the molecular model of the MHL complex (structure II), the NH^+ is oriented outward from the central metal ion and is far away from the phosphonate O^-. Thus, the effect of the protonation of the N atom on the phosphate P through the hydrogen bond or some electrostatic interaction between O^- and ^+HN is hardly expected. Appleton et al. have studied the ^1H, ^{13}C, and ^{31}P NMR chemical shifts of $NH_2(CH_2)_xPO_3^{2-}$ and reported that the difference in ^{31}P chemical shift between the unprotonated and monoprotonated species became small with an increase in the numbers of methylene groups x.[35] These facts may indicate that the electronic states of the P atom are affected by the protonation of the N atom through the $P–(C–)_xN$ bonds. In the case of heavier nuclei such as phosphorus, the contribution of a temperature-independent paramagnetic term, σ_p, to the shielding is much larger than that of a diamagnetic term, σ_d.[36] Thus, the upfield shift of the ^{31}P signal is interpreted in terms of the change in the electronic configuration of phosphorus atom caused by the protonation on the nitrilo nitrogen rather than the decrease in electron density on it.[37]

The change in ^{31}P chemical shift on the protonation of phosphonate O^-, i.e., the difference in δ_P between protonated species, H_nL or MH_mL, is relatively small. This fact is consistent with the results for $^+NH_3(CH_2)_xPO_3^{2-}$.[35] That is, the δ_P change on the protonation of phosphonate O^- decreases with the decrease in the number of methylenes x, and the change in δ_P (2–3 ppm) by the protonation of O^- of $NH_3CH_2PO_3H_n$ is very small compared with that of the N atom (9.9 ppm). This might indicate that the effect of protonation of phosphonate on the P atom is diminished by the increase in the effect of the protonation of the N atom on P. Because the protonation equilibria on O^- is fast, the observed ^{31}P shift of H_nL ($n = 2, 3$) or MH_mL ($m = 2, 3$) is a weighted average of the three P atoms. Thus, it is very difficult to discuss the detailed mechanism of the change in the ^{31}P chemical shift by the protonation of the phosphonate ion.

The $^{31}P\{^1H\}$ signal of metal–ligand 1:1 mixture becomes quite broad in the region of the NMR shift jump (pH 8–10), where ML and MHL are predominant. The broadening is largest at $pH = \log K_{MHL}$ where $[ML] = [MHL]$. On the other hand, the ^{31}P NMR shift is sharp in the whole range of pH for solutions containing only the ligand NTMP. Thus, the broadening of the M:L = 1:1 solution in this pH region is interpreted in terms of

---

(30) Carter, R. P.; Crutchfield, M. M.; Irani, R. R. *Inorg. Chem.* **1967**, *6*, 943.

(31) (a) Schwarzenbach, G.; Ackerman, H. *Helv. Chim. Acta* **1947**, *30*, 1798. (b) Schwarzenbach, G.; Gut, R.; Anderegg, G. *Helv. Chim. Acta* **1954**, *37*, 937.

(32) (a) Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 6151. (b) Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 657.

(33) (a) Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D.; Cleland, W. W. *Biochemistry* **1978**, *17*, 3275. (b) Reibenspies, J.; Cornelius, R. D. *Inorg. Chem.* **1984**, *23*, 1563.

(34) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3336.

(35) Appleton, T. G.; Hall, J. R.; Harris, A. D.; Kimlin, H. A.; McMahon, I. J. *Aust. J. Chem.* **1984**, *37*, 1833.

(36) Lynden-Bell, R. M.; Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Thomas Nelson: Middlesex, England, 1969.

(37) Prado, F. R.; Geissner-Prettre, C.; Pullman, B.; Daudey, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 1737.

a slow protonation equilibrium of the metal complex, ML + H $\rightleftharpoons$ MHL, and will suggest the drastic structural change from structure I to II. Under these conditions (C_M:C_L = 1:1), some proportion of NTMP dissociates into free ligand. It was, however, confirmed by the studies of the solution containing an excess of the metal ion (C_M:C_L = 2:1) that the dissociation of complex, ML′ $\rightleftharpoons$ M + L′, had little effect on the broadening of the signal. On the other hand, the sharp signals at lower pH (pH 7.8) indicate the fast protonation equilibria, MHL + H $\rightleftharpoons$ MH_2L and MH_2L + H $\rightleftharpoons$ MH_3L; that is, the protonation of phosphonate ion is very fast.

The $^{31}P\{^1H\}$ NMR signal of the M–L solution at pH 7.8 shows a sharp single peak at any M:L ratio (Figure 4). As can be seen from the conditional formation constants (Figure 1B,C), 15–40% of the ligand in a C_M:C_L = 1:1 solution does not form any complex. Thus, the chemical shift approaches the position of the ML′ shift, $\delta_{ML'}$, on addition of excess of metal ion (C_M:C_L = 2:1). When the M:L ratio is less than 1, the solution is a mixture of the complex ML′ and the excess ligand L′. With decrease in the C_M:C_L ratio, the signal shifts to the position of the L′ shift, $\delta_{L'}$. The signal appears at the position corresponding to the [ML′]:[L′] ratio. At this pH the predominant species are HL and MHL, and thus the predominant ligand exchange reaction is

$$\mathrm{MHL} + \mathrm{HL}^* \rightleftharpoons \mathrm{MHL}^* + \mathrm{HL} \qquad (9)$$

The sharp $^{31}P\{^1H\}$ signal indicates the fast ligand exchange of eq 9.

On the other hand, very broad signals were obtained for the solutions at pH 10.9 containing an excess ligand (C_M:C_L < 1) and the signal of the Mg solution splits into two peaks. The signal of a Ba, Sr, or Ca solution appears at the position corresponding to the ratio of [ML′] and [L′]; i.e., the plots of observed δ_P as a function of C_M:C_L show straight lines in the range of C_M:C_L ≤ 1. This fact supports the formation of M:L = 1:1 complexes (MH_mL) under the conditions C_M:C_L ≤ 1. The peaks for a Mg solution appear at the positions of ML′ and L′ signals. As the predominant species at pH 10.9 are HL and ML, the ligand exchange is written

$$\mathrm{ML} + \mathrm{HL}^* \rightleftharpoons \mathrm{ML}^* + \mathrm{HL} \qquad (10)$$

The broadened signal indicates that this exchange reaction is relatively slow. The rate of exchange increases in the order Mg < Ca < Sr < Ba, which is the order of the ion size. Since in the case of the C_M:C_L = 1:1 solution more than 90% of the total ligand exists in a single chemical form, unprotonated complex ML, the solution shows a sharp signal for ML. The fact that the ^{31}P NMR shift is not constant at higher C_M:C_L ratios (C_M:C_L > 1) may indicate the formation of polynuclear complexes such as M_2L under these conditions.

Thus, the ^{31}P NMR data at various C_M:C_L ratios (Figure 4) indicate that the ligand exchange at pH 10.9 is much slower than at pH 7.8. As the difference of chemical shift between MHL and HL is much smaller than that between ML and HL and the contribution of the hydrogen ion concentration to the exchange rate was not studied, it is hard to discuss quantitatively the mechanism of ligand exchange. However, the results of line broadening suggest that the ligand exchange of the unprotonated species ML is slower than that of the protonated species MHL. This fact supports the structures proposed above; i.e., NTMP coordinates tightly to the alkaline-earth-metal ion as a tetradentate ligand in the ML complex (structure I) whereas it coordinates loosely by the ionic bond of three phosphonate ions in the MHL complex (structure II).

Acknowledgment. Financial support of this work from the Ministry of Education, Science, and Culture, Japan, is gratefully acknowledged. We thank Dr. K. Doi, Nagoya Institute of Technology, and Prof. T. Sotobayashi, Niigata University, for helpful discussions.

Contribution from the Chemistry Departments, University of Virginia, Charlottesville, Virginia 22901,
and Dickinson College, Carlisle, Pennsylvania 17013

Empirical Intensity Parameters for the 4f → 4f Absorption Spectra of Nine-Coordinate Erbium(III) Complexes in Aqueous Solution

Mark T. Devlin,[†] Eileen M. Stephens,[†] F. S. Richardson,*[†] Thomas C. Van Cott,[‡] and Scott A. Davis[‡]

Received July 17, 1986

The Judd–Ofelt parametrization scheme for lanthanide 4f → 4f transition intensities is used to analyze absorption intensity data obtained for a series of Er(III) complexes in aqueous solution. Oscillator strengths are reported for eight multiplet-to-multiplet transition regions of each complex, and values for the Judd–Ofelt intensity parameters, Ω_λ (λ = 2, 4, 6), are determined and reported for each of the systems. Variations in the values of these parameters from system to system are discussed in terms of structural differences between the complexes (with respect to ligand properties *and* coordination geometry).

Introduction

In a recent study[1] we reported absorption spectra, 4f → 4f oscillator strengths, and empirically determined 4f → 4f intensity parameters for a series of neodymium(III) and holmium(III) complexes in aqueous solution. The ligands included in that study were oxydiacetate (ODA), dipicolinate (DPA), iminodiacetate (IDA), (methylimino)diacetate (MIDA), and malate (MAL). The principal objectives were to characterize and compare the 4f → 4f absorption intensities observed for the various complexes, to obtain values for the Judd–Ofelt intensity parameters (Ω_λ) for each complex, and to relate variations in these parameters (among the different complexes) to differences in ligand structural properties.[2] In the present study, we report absorption spectra, 4f → 4f oscillator strengths, and Judd–Ofelt intensity parameters for a series of erbium(III) complexes in aqueous solution. The ligands included in this study are ODA, DPA, IDA, MIDA, and MAL, *as well as* chelidamate (CDA)[3] and chelidonate (CDO).[4] The objectives of this study are similar to those of our previously reported studies on neodymium(III) and holmium(III) complexes.[1,2]

[†] University of Virginia.

[‡] Dickinson College.

(1) Stephens, E. M.; Davis, S. A.; Reid, M. F.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 4607.

(2) Stephens, E. M.; Reid, M. F.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 4611.

(3) Chelidamate (CDA) refers here to the deprotonated form of chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) in aqueous solution under alkaline pH conditions.

(4) Chelidonate (CDO) refers here to the deprotonated form of chelidonic acid (4-hydroxypyran-2,6-dicarboxylic acid) in aqueous solution under alkaline pH conditions.