ductance measurement was extended to 10^{-2} mho with an extension decade conductance box. The extension conductor was coupled with a General Radio Co. polystyrene decade capacitor (Type 1419-A) and a General Radio Co. variable air precision capacitor (Type 722-CB) for extended capacitance balance. An R-C oscillator (Type 1210-C) and an amplifier and null detector (Type 1231-B), both of General Radio manufacture, were used as the signal source and the detector, respectively. Power was supplied by a General Radio Co. power supply (Type 1203-B). The conductance was measured at 1 kc.

Two conductance cells consisting of two parallel, bright platinum electrodes sealed into a spherical glass bulb were used. Two glass outlets, one at the bottom and one at the top of the bulb, were used to facilitate flushing with nitrogen. The cell constants were 0.1671 and 0.1084, respectively. The cells were placed in a water thermostat maintained at $25.0 \pm 0.1°$.

The specific conductance of the water used was $K = 2.062 \times 10^{-6}$ mho cm.$^{-1}$. THF, Baker Analyzed reagent grade, was distilled over lithium aluminum hydride in a current of nitrogen. It had $K = 4.02 \times 10^{-10}$ mho cm.$^{-1}$. The value of K for the mixture of 80% water and 20% THF was 1.685×10^{-6} and that for the mixture of 20% water and 80% THF was 6.695×10^{-7} mho cm.$^{-1}$.

The THF solution of $NaCo(CO)_4$ (ca. 0.15 M) used in the conductance measurements was prepared as indicated above. The aqueous $NaCo(CO)_4$ solution (ca. 2 M) was prepared by the reaction of $Hg[Co(CO)_4]_2$ with 10% less than the required amount of $Na_2S \cdot 9H_2O$. The solution in the mixture of 80% THF and 20% water was prepared by mixing 4 volumes of the THF solution with 1 volume of water. It was subsequently diluted with the premixed diluent. The solutions in the mixture of 20% THF and 80% water were prepared likewise starting from the aqueous solution.

The concentrations of the $Co(CO)_4^-$ solutions were determined photometrically with the color developed with nitroso-R-salt and cationic cobalt. An aliquot was withdrawn from each conductance measurement solution. It was allowed to decompose in air. After evaporating the organic solvent, it was treated according to a standard procedure.[16] The volume of the sample solution was adjusted so that the cobalt content of the final 50 ml. of color-developed solution fell in the range of 0.03 to 0.15 mg. A calibration curve was constructed using Baker Analyzed reagent grade $CoCl_2 \cdot 6H_2O$. The absorbance was measured at 520 mμ with a Bausch and Lomb Spectronic 20 spectrophotometer.

(16) "ASTM Methods for Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, Pa., 1960, p. 185.

New Multidentate Ligands. III. Amino Acids Containing Methylenephosphonate Groups[1]

S. Westerback,[2] K. S. Rajan, and A. E. Martell

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Syntheses, properties, and metal chelate formation constants are reported for the new ligands nitriloaceticdi-(methylenephosphonic) acid (NADMP), nitriloacetic-β-propionicmethylenephosphonic acid (NAPMP), and N,N,-N',N'-ethylenediaminetetra(methylenephosphonic) acid (ENTMP). The stoichiometries of their acid–base and metal ion interactions are deduced from potentiometric data, and the probable structures of the metal chelates formed are inferred by comparison of their metal ion affinities with those of analogous ligands.

Since the report by Schwarzenbach and co-workers[2] of the high affinity of the anion of nitrilodiaceticmethylenephosphonic acid for the Ca(II) ion, it appeared that the phosphonate group might be as effective or even more effective than the carboxylate group in contributing to the chelating tendencies of polyfunctional amino acids.[3] It was the purpose of this research, therefore, to prepare additional analogs of the well-known chelating agents nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). The method of Schwarzenbach, et al.,[2] was employed for the synthesis of nitriloaceticdi(methylenephosphonic) acid (NADMP), nitriloacetic-β-propionicmethylenephosphonic acid (NAPMP), and N,N,N',N'-ethylenediaminetetra(methylenephosphonic) acid (ENTMP).[3] This paper describes the synthesis and properties of these new ligands and a potentiometric study of their proton and metal ion affinities in aqueous solution.

Experimental

Nitriloaceticdi(methylenephosphonic) Acid. A 0.10-mole sample of chloromethylphosphonyl chloride was added dropwise to 100 ml. of water, 0.40 mole of NaOH was added, and the solution was allowed to stand overnight. The sodium chloride was filtered off, an equivalent (0.10 mole) of glycine was then added, and the solution was heated on a steam bath at pH 10–11 for

(2) G. Schwarzenbach, H. Ackermann, and P. Ruchstuhl, Helv. Chim. Acta, 32, 1175 (1949).

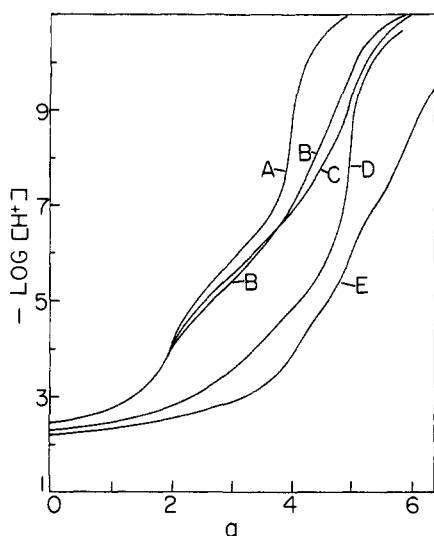(3) S. Westerback and A. E. Martell, Nature, 178, 321 (1956).

Figure 1. Potentiometric titrations of A, 2.0 × 10⁻³ M solution of nitriloaceticidi(methylenephosphonic) acid (NADMP); B, Mn(II)–NADMP chelate (1:1); C, Ca(II)–NADMP chelate (1:1); D, Cu(II)–NADMP chelate (1:1); E, Fe(III)–NADMP chelate (1:1); 25°, μ = 0.10 (KNO₃).

approximately 2 weeks. The reaction mixture was neutralized with nitric acid, and the insoluble lead salt of the product was isolated by the addition of excess lead nitrate. The lead salt was filtered from the solution at the boiling point, washed three times with boiling water and once with methanol, and dried in an oven at 110°. The yield of lead salt was 50% of the theoretical amount.

The free acid was prepared from the lead salt by treatment of an aqueous suspension of the salt with hydrogen sulfide, separation of the lead sulfide by filtration, and evaporation of the filtrate. The product, a colorless hygroscopic material, could not be recrystallized as such, but was purified by reconversion to the lead salt and regeneration of the acid with hydrogen sulfide. The product was found to be very soluble in water, slightly soluble in ethanol, and insoluble in ether.

Anal. Calcd. for $C_4H_{11}NO_8P_2$: C, 18.2; H, 4.2; N, 5.32. Found: C, 18.8; H, 4.7; N, 5.20.

Nitriloacetic-β-propionicmethylenephosphonic Acid. To a solution of 0.10 mole of chloromethylenephosphonic acid, prepared as described above, was added 0.10 mole of imino-β-propionicacetic acid. The reaction mixture was heated on a steam bath for 7 days at pH 10–11. The product was isolated as described above in the form of the lead salt at 53% yield. The free acid, obtained as described above by treatment of the lead salt with H₂S, was obtained in crystalline form and was recrystallized from water. It had no melting point but decomposed at about 230°.

Anal. Calcd. for $C_6H_{12}NO_7P$: C, 29.9; H, 5.02; N, 5.81. Found: C, 29.6; H, 5.13; N, 5.91.

N,N,N′,N′-Ethylenediaminetetra(methylenephospho-) nic Acid. Chloromethylenephosphonic acid (0.40 mole), prepared as described above, was treated with 0.10 mole of ethylenediamine (70% aqueous solution) in the same manner that was employed for the other ligands. The reaction mixture was heated on a steam bath for 4 days at pH 10–11. It was then filtered and brought to pH 6 with concentrated HCl. After the removal of inorganic

material by filtration, the solution was heated to the boiling point and the theoretical amount of lead acetate (to produce Pb₄L) was added. The lead salt was filtered and washed four times with boiling water and once with ethanol. The yield was 83% of the theoretical amount. The lead salt was converted to the free acid, as before, and the product was then treated with 4 equiv. of potassium hydroxide and evaporated to dryness. Although the tetrapotassium salt was first obtained as a colorless sirup, it was gradually converted to a colorless crystalline solid when allowed to stand in a vacuum desiccator. It was very soluble in water, slightly soluble in ethanol, and insoluble in ether. The over-all yield of the potassium salt was 40% of the theoretical amount.

Anal. Calcd. for $C_6H_{16}N_2O_{12}P_4K_4 \cdot 4H_2O$: C, 10.9; H, 3.64; N, 4.2. Found: C, 10.9; H, 3.81; N, 4.1.

Potentiometric Measurements. The potentiometric investigations of acid–base and metal-binding equilibria were carried out at 25° and an ionic strength of 0.10 controlled by the addition of KNO₃ to the solution. The measurements were made with a Beckman Model G pH meter fitted with extension glass and calomel electrodes. Calibration of the pH meter electrode system was carried out by the titration of standard HCl with standard NaOH and with acetic acid. The concentration constant of acetic acid in 0.10 M KNO₃ was considered to be the same as that given by Harned and Owen[4] for 0.10 M KCl. Other details of the experimental method are as given previously.[5] The concentrations of phosphonic acids in the experimental solutions were kept low (from 0.0015 to 0.004 M). All of the investigations in the presence of metal ions were carried out at a 1:1 molar ratio of metal ion to ligand.

Results

The procedure employed by Schwarzenbach, *et al.*,[2] for preparing other methylenephosphonic acids was found to be satisfactory for the formation of the three new ligands described in this investigation. Nitriloaceticdi(methylenephosphonic) acid and nitriloacetic-β-propionicmethylenephosphonic acid were obtained as colorless, crystalline, very hygroscopic solids. Ethylenediaminetetra(methylenephosphonic) acid was not obtained in crystalline form but was crystallized as the tetrapotassium salt. These compounds were best purified by precipitation of the lead salt.

Acid Dissociation Constants. Potentiometric titration curves of the ligands are shown in Figures 1–3. The forms of these curves indicate some interesting similarities and differences in these compounds. All three compounds have two strongly acidic functional groups. This fact, as well as subsequent acid–base reactions, become understandable if all of the free acids are assumed to consist of dipolar ions in aqueous solution (Ia, IIa, and IIIa). Thus the first dissociation step of 2 equiv. corresponds to dissociation of the most acidic groups present, which would be either a carboxyl group or the first proton to dissociate from a phosphonic acid group, in cases where two protons are still present. This first dissociation step therefore involves two acid groups (phosphonic or carboxylic) for the dissociation

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958.
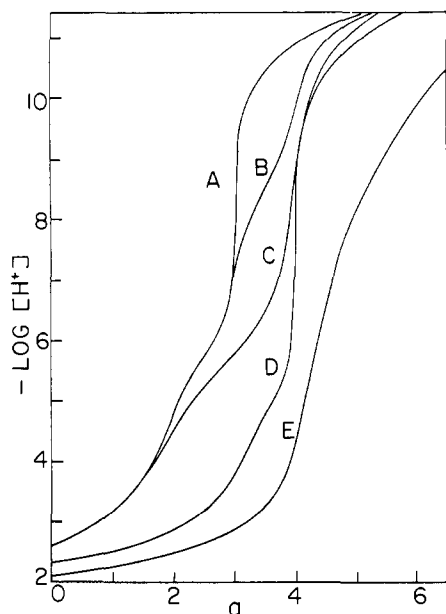(5) R. L. Gustafson, C. Richard, and A. E. Martell, *J. Am. Chem. Soc.*, 82, 1526 (1960).

Figure 2. Potentiometric titrations of A, 2.0 × 10⁻³ M solution of nitriloacetic-β-propionicmethylenephosphonic acid (NAPMP); B, Ca(II)–NAPMP chelate (1:1); C, Mn(II)–NAPMP chelate (1:1); D, Cu(II)–NAPMP chelate (1:1); E, Fe(III)–NAPMP chelate (1:1); 25°, μ = 0.10 (KNO₃).
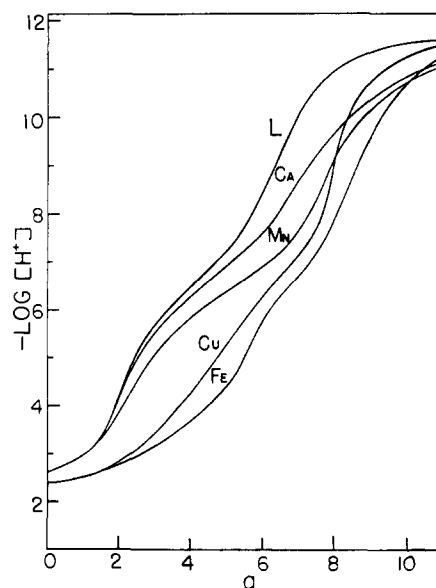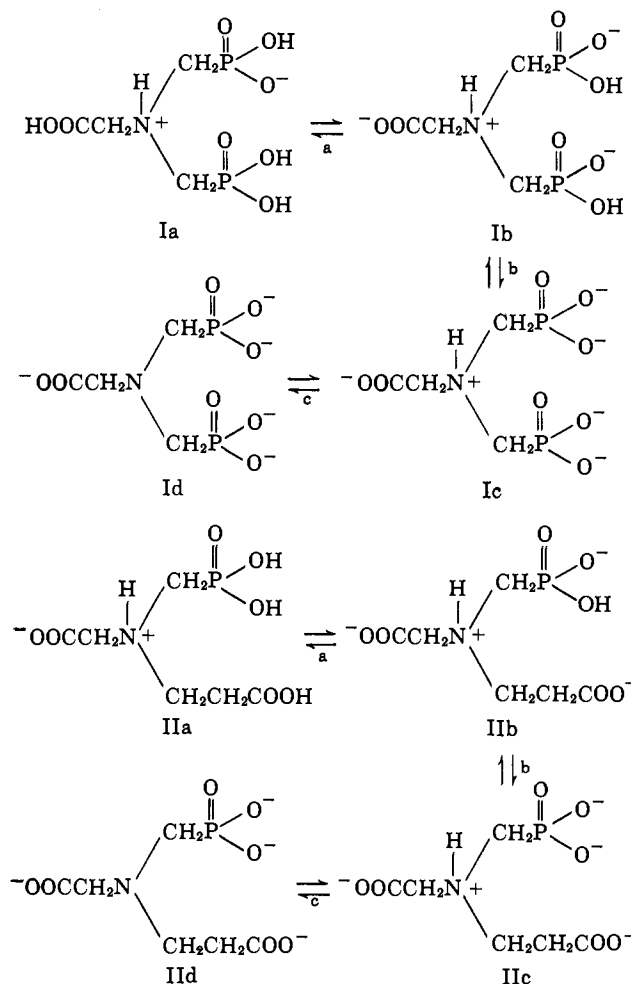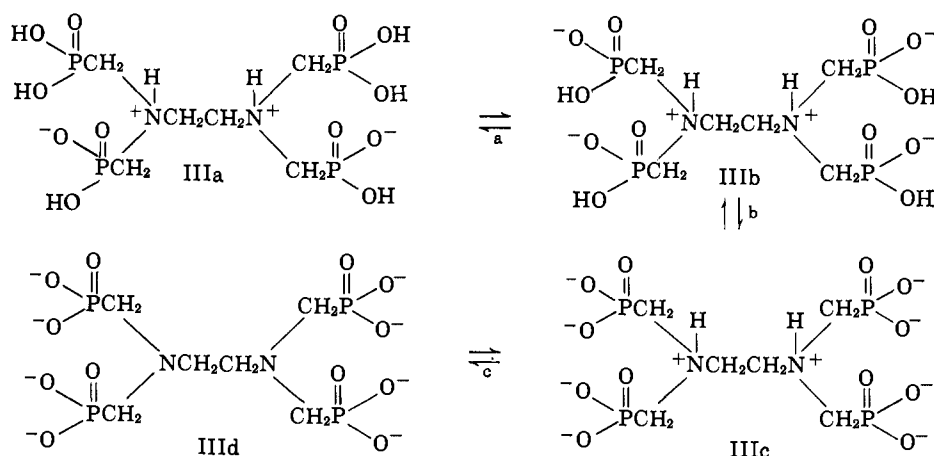

Figure 3. Potentiometric titrations of L, 2.0 × 10⁻³ M solution of N,N,N′,N′-ethylenediaminetetra(methylenephosphonic) acid (ENTMP); Ca, Ca(II)–ENTMP chelate (1:1); Mn, Mn(II)–ENTMP chelate (1:1); Cu, Cu(II)–ENTMP chelate (1:1); Fe, Fe(III)–ENTMP chelate (1:1); 25°, μ = 0.10 (KNO₃).

of all three species Ia, IIa, and IIIa. It is seen that all three species have alternative sites for the binding of the most acidic protons.

The compounds Ib, IIb, and IIIb may be considered in the light of the fact that the second dissociation step occurring in the pH range 4–8 required 2, 1, and 4 equiv. of base, respectively. It is apparent, therefore, that the second buffer region corresponds to the dissociation of the last, most strongly bound, proton from all of the phosphonic acid groups present in each ligand.

The high pH buffer region (step C) corresponding to the dissociation of Ic, IIc, and IIIc results from the dissociation of the most strongly held protons bound to the basic nitrogen atoms.

Calculation of acid dissociation constants were carried out on the basis of the dissociation reactions illustrated above for compounds Ia–Id, IIa–IId, and IIIa–IIId. Standard algebraic relationships were employed for the calculation of dissociation constants for buffer regions involving a single equivalent of base. For dissociation steps involving 2 or more equiv., the graphical method of Schwarzenbach, et al.,[6] was employed. In the case of ENTMP, the dissociation constants for the 4-equiv. buffer region were determined by a modification of the same method. In this case pK_3 and pK_6 were obtained readily from graphical plots involving pK_3 and pK_4, on one hand, and pK_5 and pK_6 on the other, respectively. The determination of pK_4 and pK_5 by this method was tested by recalculation of pK_4 and pK_5 from a similar graphical plot involving these two constants, with data adjusted for overlapping with the fourth and sixth dissociation steps, respectively. Repetition of the calculation gave reasonably constant values of the constants through the use of data adjusted for overlapping with adjacent dissociation steps, the adjust-

ment being made on the basis of the previous approximation.

The acid dissociation constants calculated in this way are listed in Table I.

(6) G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta,* 30, 1303 (1947).

HO O   O OH
  \ || || /
   PCH₂ CH₂P
  / H H \
HO   \ | | / OH
    ⁻O O ⁺NCH₂CH₂N⁺ O O⁻
      \ || /   \ || /
       PCH₂ IIIa CH₂P
      /   \
    HO⁻   OH

⇌ a

⁻O O   O O⁻
  \ || || /
   PCH₂ CH₂P
  / H H \
HO⁻ \ | | / OH
    ⁻O O ⁺NCH₂CH₂N⁺ O O⁻
      \ || /   \ || /
       PCH₂ IIIb CH₂P
      / ↑↓ b   \
    HO⁻   OH

⁻O O   O O⁻
  \ || || /
   PCH₂ CH₂P
  /   \
⁻O⁻ NCH₂CH₂N O⁻
    ⁻O O /   \ O O⁻
      \ || \ || /
       PCH₂ IIId CH₂P
      /   \
    ⁻O⁻   O⁻

⇌ c

⁻O O   O O⁻
  \ || || /
   PCH₂ CH₂P
  / H H \
⁻O⁻ \ | | / O⁻
    ⁻O O ⁺NCH₂CH₂N⁺ O O⁻
      \ || /   \ || /
       PCH₂ IIIc CH₂P
      /   \
    ⁻O⁻   O⁻

Metal Chelate Formation Constants. Evaluation of the chelating tendencies of these ligands, limited by the relatively small amounts of purified materials obtained, was carried out with four representative metal ions: Ca^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{3+}. "Equivalent" potentiometric titration curves (*i.e.*, potentiometric measurements of systems containing equimolar ratios of metal ion and ligand) are illustrated in Figures 1, 2, and 3.

Table I. Acid Association Constants of the Ligands

Equilibrium constants		Log of equlibrium constant		
		NADMP, H_5L	NAPMP, H_4L	ENTMP, H_8L
$K_1 = \dfrac{[HL]}{[H^+][L]}$		10.80	10.41	10.60
$K_{12} = \dfrac{[H_2L]}{[H^+][HL]}$		6.37	5.59	9.22
$K_{13} = \dfrac{[H_3L]}{[H^+][H_2L]}$		5.01	3.48	7.43
$K_{14} = \dfrac{[H_4L]}{[H^+][H_3L]}$		2.00	2.72	6.63
$K_{15} = \dfrac{[H_5L]}{[H^+][H_4L]}$		1.73		6.18
$K_{16} = \dfrac{[H_6L]}{[H^+][H_5L]}$				5.05
$K_{17} = \dfrac{[H_7L]}{[H^+][H_6L]}$				2.72
$K_{18} = \dfrac{[H_8L]}{[H^+][H_7L]}$				1.46

The general features of the potentiometric titration curves make possible some conclusions about the metal chelates formed in solution. It is obvious that the stability order for the ligands is Ca(II) < Mn(II) < Cu(II) < Fe(III), as expected.[7]

Complex formation with the completely deprotonated form is generally not complete for Ca(II) and Mn(II) below pH 9–10, except for the combination of Mn(II) with IId, which appears to be complete at about pH 8.5.

The Cu(II) and Fe(III) chelates of all three ligands are very much more stable than those of Mn(II) and Ca(II), as can be seen from the separations between the respec-
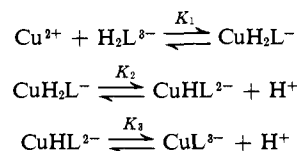
tive titration curves. Also, the presence of a number of protonated forms of the chelates is apparently indicated, as can be seen from the inflections and/or shape of the Cu(II) and Fe(III) curves at low pH. Thus with NADMP (H_5L), Fe(III) apparently forms a protonated chelate, $FeHL^-$, the "normal" chelate FeL^{2-}, and a hydrolyzed form, $FeOHL^{3-}$. By using the usual material balance relationships, the equilibrium constants for the formation of these chelates were calculated, and the values are presented in Table II. For this ligand, the

Table II. Chelate Formation Constants with NADMP (H_5L)[a]

Positive ion	Reaction			Log of constant
Ca^{2+}	$Ca^{2+} + L^{5-}$	⇌	CaL^{3-}	6.17
Mn^{2+}	$Mn^{2+} + L^{5-}$	⇌	MnL^{3-}	7.00 ± 0.5
Fe^{3+}	$Fe^{3+} + HL^{4-}$	⇌	$FeHL^-$	8.65 ± 0.03
	$FeL^{2-} + H^+$	⇌	$FeHL^-$	4.8 ± 0.1
	$Fe^{3+} + L^{5-}$	⇌	FeL^{2-}	14.65 ± 0.05
	$FeLOH^{3-} + H^+$	⇌	FeL^{2-}	7.20 ± 0.05
Cu^{2+}	$Cu^{2+} + H_2L^{3-}$	⇌	CuH_2L^-	5.43 ± 0.05
	$CuHL^{2-} + H^+$	⇌	CuH_2L^-	4.14 ± 0.05
	$CuL^{3-} + H^+$	⇌	$CuHL^{2-}$	5.89 ± 0.02
	$Cu^{2+} + L^{5-}$	⇌	CuL^{3-}	12.53 ± 0.05

[a] At 25°, $\mu = 0.10$ (KNO_3).

Cu(II) titration curve indicates the presence of two acid forms and a normal chelate, CuH_2L^-, $CuHL^{2-}$, and CuL^{3-}. The following equations represent the reaction that may be occurring in solution.

$$Cu^{2+} + H_2L^{3-} \xrightleftharpoons{K_1} CuH_2L^-$$

$$CuH_2L^- \xrightleftharpoons{K_2} CuHL^{2-} + H^+$$

$$CuHL^{2-} \xrightleftharpoons{K_3} CuL^{3-} + H^+$$

Equilibrium constants K_1 and K_2 were evaluated by means of a graphical method details of which are given previously.[8] Calculation of K_2 and K_3 was carried out by means of a modification of the method outlined by Carlson, *et al.*[9] The value of K_2 obtained by the two

(7) The slight reversal between Ca(II) and Mn(II) in Figure 1 is considered anomalous and is probably due to somes ide reaction which would bear further investigation.

(8) K. S. Rajan and A. F. Martell, *J. Inorg. Nucl. Chem.*, **26**, 1927 (1964).

(9) G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1335 (1945).

methods agreed well within the limits of tolerances. Results are presented in Table II.

In the case of NAPMP (H_4L), Fe(III) goes directly to the normal chelate FeL^-, but a number of hydroxo chelates, containing up to three OH^- ions per Fe(III) atom, are obviously formed. The Cu(II) ion, on the other hand, clearly forms a protonated chelate $CuHL^-$, and a very stable normal chelate compound, CuL^{2-}, which does not undergo further hydrolysis even at very high pH. The reactions which take place in the buffer regions between $a = 0$, $a = 3$ and $a = 3$, $a = 4$ are represented by the equations

$$Cu^{2+} + HL^{3-} \rightleftharpoons CuHL^-$$

$$CuHL^- \rightleftharpoons CuL^{2-} + H^+$$
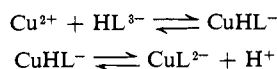
Equilibrium constants for these reactions were then calculated by using the relevant material balance relationships. The results are presented in Table III.

Table III. Chelate Formation Constants with NAPMP (H_4L)[a]

Positive ion	Reaction	Log of constant
Ca^{2+}	$Ca^{2+} + L^{4-} \rightleftharpoons CaL^{2-}$	4.88
Mn^{2+}	$Mn^{2+} + L^{4-} \rightleftharpoons MnL^{2-}$	7.24
Fe^{3+}	$Fe^{3+} + L^{4-} \rightleftharpoons FeL^-$	16.3 ± 0.4
Cu^{2+}	$Cu^{2+} + HL^{3-} \rightleftharpoons CuHL^-$	7.2 ± 0.1
	$CuL^{2-} + H^+ \rightleftharpoons CuHL^-$	4.71 ± 0.01
	$Cu^{2+} + L^{4-} \rightleftharpoons CuL^{2-}$	13.0 ± 0.1

[a] At 25°, $\mu = 0.10$ (KNO_3).

The Cu(II) chelates of ENTMP (H_8L) are seen to be first formed with three or four protons per ligand, giving rise to compounds such as CuH_4L^{2-}, CuH_3L^{3-}, and further dissociation products. The definite inflection between pH 8 and 10 at 8 equiv. of base indicates that the compound finally formed is CuL^{6-}. Potentiometric titration data obtained in the buffer region between 0 and 5 equiv. of base per mole of the total metal salt were treated in accordance with the assumption of the formation of CuH_3L^{3-} as

$$Cu^{2+} + H_3L^{5-} \rightleftharpoons CuH_3L^{3-}$$
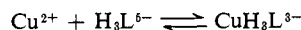
The corresponding equilibrium constant was then calculated by using the usual material balance equations. Dissociation of all the three protons from the species CuH_3L^{3-} takes place in overlapping steps. Equilibrium constants for the dissociation steps were calculated by means of a modification of the method reported by Carlson and co-workers.[9] Results are presented in Table IV.

In the case of Fe(III), on the other hand, the inflections at 6 and 8 equiv. of base indicate the formation of FeH_2L^{3-} and FeL^{5-} as definite entities and, by inference, also the intermediate protonated chelate $FeHL^{4-}$. It is noted that further reaction with base occurs above pH 8 to produce hydroxo chelates of Fe(III). The reactions taking place in the buffer regions between $a = 0$ and $a = 6$, and $a = 6$ and $a = 8$, can be represented as
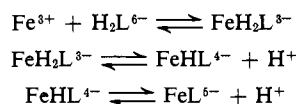
$$Fe^{3+} + H_2L^{6-} \rightleftharpoons FeH_2L^{3-}$$

$$FeH_2L^{3-} \rightleftharpoons FeHL^{4-} + H^+$$

$$FeHL^{4-} \rightleftharpoons FeL^{5-} + H^+$$

Table IV. Chelate Formation Constants of ENTMP (H_8L)[a]

Positive ion	Reaction	Log of constant
Ca^{2+}	$Ca^{2+} + L^{8-} \rightleftharpoons CaL^{6-}$	5.74
Mn^{2+}	$Mn^{2+} + L^{8-} \rightleftharpoons MnL^{6-}$	9.40
Cu^{2+}	$Cu^{2+} + H_3L^{5-} \rightleftharpoons CuH_3L^{3-}$	9.14 ± 0.3
	$H^+ + CuH_2L^{4-} \rightleftharpoons CuH_3L^{3-}$	5.85 ± 0.06
	$H^+ + CuHL^{5-} \rightleftharpoons CuH_2L^{4-}$	6.71 ± 0.02
	$H^+ + CuL^{6-} \rightleftharpoons CuHL^{5-}$	7.77 ± 0.05
	$Cu^{2+} + L^{8-} \rightleftharpoons CuL^{6-}$	16.09 ± 0.4
Fe^{3+}	$Fe^{3+} + H_2L^{6-} \rightleftharpoons FeH_2L^{3-}$	13.2 ± 0.4
	$H^+ + FeHL^{4-} \rightleftharpoons FeH_2L^{3-}$	6.32 ± 0.07
	$H^+ + FeL^{5-} \rightleftharpoons FeHL^{4-}$	7.14 ± 0.07
	$Fe^{3+} + L^{8-} \rightleftharpoons FeL^{5-}$	19.6 ± 0.5

[a] At 25°, $\mu = 0.10$ (KNO_3).

Equilibrium constants for the above reactions are presented in Table IV.

Discussion

The acid dissociation constants given in Table I are about what would be expected on the basis of the arrangements of protons indicated in structures Ia–c, IIa–c, and IIIa–c. The only apparently unusual behavior is the relatively small difference of 1.4 in the first two association constants of ENTMP, compared to 4.0 in EDTA and 1.7 in ethylenediamine, and intermediate values for other ethylenediamine derivatives substituted with negative groups. The decreased charge repulsion between the two positive nitrogen atoms in IIIc may be due in part to the high negative charge of the anion and the partial electrostatic binding (weak hydrogen bonding) of the ammonium hydrogens to the negative phosphonate oxygens, as indicated by IIIe.
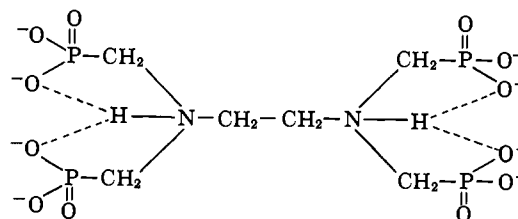
IIIe

In view of the original purpose of this work, the magnitudes of the metal chelate stability constants seem relatively disappointing. It is apparent now that it is not possible to extrapolate on the basis of the information obtained through the substitution of one acetate group in nitrilotriacetic acid (NTA) by a methylenephosphonate group. Thus the increase in stability of the Ca(II) chelate obtained in going from NTA to nitrilotriaceticmethylenephosphonic acid[2] is not continued in going to NADMP. A possible explanation for this behavior is that the rather large negative charges of the phosphonate groups prevents them from all coming together about a single positive (divalent) metal ion. Thus the structures in aqueous solution of the Ca(II) chelates of Id and IIId probably are IV and V.

In the case of Fe^{3+}, the stability data in this paper, while showing no advantage of polyamine polymethylenephosphonates over polyaminopolyacetates, indicate

IV

V

VI

VII
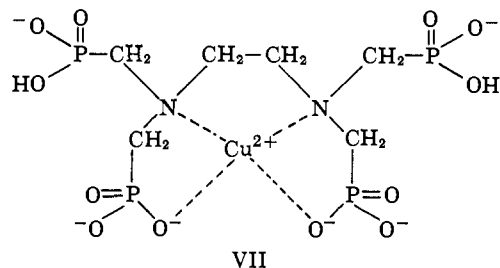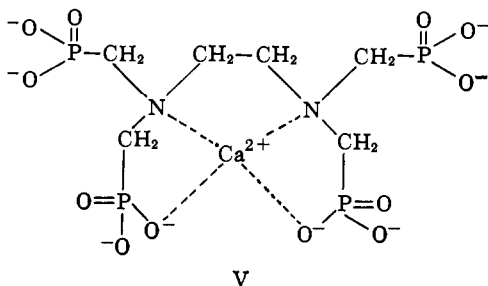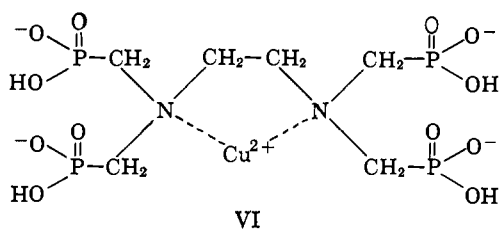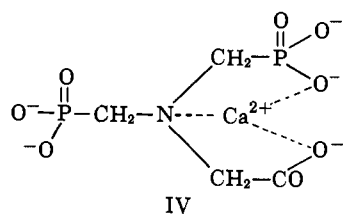
a much more favorable situation than for the divalent metal ions. On the basis of the *a priori* reasoning given above for the low stabilities of the chelates of divalent metal ion, this is not an unreasonable result. Therefore it seems that the ligands of the type described in this paper may have exceptionally high affinities for metal ions of +4 charge. In order to investigate this idea, work on the synthesis and thermodynamic study of these and similar ligands is being continued in these laboratories.

The combination of Cu(II) and ENTMP, with the displacement of two additional protons over that occurring with the free ligand at the same pH, suggests structure VI for the initial metal–ligand bonding. Four subsequent proton dissociation steps, indicated by the potentiometric curves, suggest increasing engagement of the phosphonate oxygen atoms as indicated by VII. This process leads ultimately to the Cu(II) chelate of the completely dissociated ligand, shown clearly by the potentiometric curve. This compound probably involves tetragonal (hexadentate) coordination of the Cu(II) ion.

Steric and Electronic Effects in the Dissociation of Cobalt Carbonyl Derivatives. IV. Rates of Dissociation of Mono(trimethylolpropane phosphite) Derivatives and π-Allylcobalt Carbonyl Bis(trimethylolpropane phosphite) Complexes

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π-Allylcobalt tricarbonyl complexes react with 2 moles of trimethylolpropane phosphite to produce π-allylcobalt carbonyl bis(trimethylolpropane phosphite) derivatives. Cobalt hydrocarbonyl reacts similarly producing cobalt hydrodicarbonyl bis(trimethylolpropane phosphite). The kinetics of replacement of carbon monoxide in these complexes and the related acetylcobalt carbonyl complexes have been studied. All appear to react by first-order dissociation mechanisms.

Introduction

Phosphite esters successively replace two coordinated carbon monoxide groups from acylcobalt tetracarbonyls.[1] The mechanism of replacement of the first carbon monoxide has been shown to involve a first-order dissociation process.[2] The mechanism of replacement of the second carbon monoxide has now been studied to determine the influence of the phosphite group upon the second replacement reaction. A similar replacement of two coordinated carbon monoxide groups by phosphite esters has also been found to take place with π-allylcobalt tricarbonyl complexes. The kinetics of these replacement reactions are reported in this paper along with several examples of the preparation of π-allylcobalt carbonyl bis(phosphite) complexes. Cobalt hydrotricarbonyl trimethylolpropane phosphite also reacted with a second mole of trimethylolpropane phosphite. The mechanism of this

(1) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1220 (1963).

(2) R. F. Heck, *ibid.*, **85**, 651 (1963).