POTENTIOMETRIC AND NMR STUDY OF ETHYLENEDIAMINE--N,N,N',N'-TETRAKIS [METHYLENE(PHENYLPHOSPHINIC)] ACID AND ITS COMPLEXING PROPERTIES

Ivan LUKEŠ[a], Petr HERMANN[a] and Pavel PECH[b]

[a] *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2 and*
[b] *Laboratory of Nuclear Magnetic Resonance,*
Prague Institute of Chemical Technology, 166 28 Prague 6

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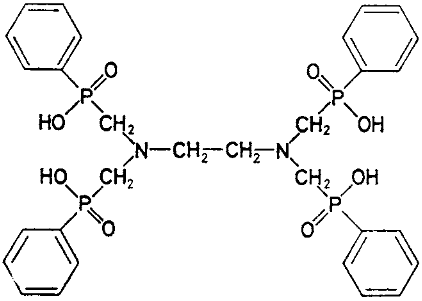
The dissociation constants of ethylenediamine-tetrakis-[methylene(phenylphosphinic)] acid (H_4edtmpPh) and its stability constants with Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} have been determined. Study of the dependence of the ^{1}H, ^{31}P and ^{13}C NMR spectra of H_4edtmpPh solutions on the pH indicates that it is more similar to H_4edta than to analogous phosphonic acids.

Aminoalkylphosphinic acids are the phosphorus analogues of the better known aminocarboxylic acids. Interest in these substances is increasing, similar to aminoalkylphoshonic acids, because of their biological activity, presence in microorganisms and use in analytical chemistry.

Of the phosphinic analogues of common complexones, so far only ethylenediamine-tetrakis(methylenephosphinic) acid (H_4edtmpH) has been studied. Motekaitis et al.[1] have described a potentiometric study of this ligand in solution. It was found that, compared, for example, with ethylenediamine, H_4edta, and ethylenediamine--tetrakis(methylenephosphonic) acid, H_8edtmp, the nitrogen atoms of H_4edtmpH are very weakly basic. The complexes of H_4edtmpH have much lower stability



I

constants and, in addition, do not form protonated complexes, probably because of the high acidity of the PO_2H_2 group.

Plaza and Grim[2] prepared another phosphinic complexone, H_4edtmpPh, i.e. ethylenediamine-tetrakis[methylene(phenylphosphinic)]acid (*I*), but have published no information on its behaviour and properties. This work is concerned with study of H_4edtmpPh in solution by the NMR and potentiometric methods.

EXPERIMENTAL

Preparation and Characteristics of H_4edtmpPh and Chemicals

H_4edtmpPh was prepared by three-step synthesis from PCl_3. First $C_6H_5PCl_2$ was prepared by the method of Gefter[3] and was characterized by analysis for phosphorus and chlorine, the refractive index and the boiling point. The values found agree with the literature data[3,4]. Hydrolysis[6] with $PhPCl_2$ yielded $PhPO_2H_2$, which was characterized by the ^{31}P NMR spectrum, which contained a clearly resolved triplet or doublet whose $\delta(P) = 23{\cdot}53$ value and interaction constants $^1J(PH) = 563$ Hz agree with the published data[5,6] ($\delta(P) = 23$, $^1J(PH) = 565$ Hz). In addition, a multipet was observed, corresponding to pairing of the H atoms of the phenyl group, with an interaction constant of $^3J(PCCH_{ar}) = 14{\cdot}2$ Hz. H_4edtmpPh was prepared by the Mannich reaction according to Grim and Plaza[2]. Repeated syntheses yielded amounts corresponding to 48—59% of the theoretical value. The melting point of the crude product, 234°C, increased on recrystallization by 1—1·5° and no longer changed on further recrystallization. Recrystallization was carried out by dissolving the acid in a dilute NaOH solution and acidification with conc. HCl. The ^{1}H NMR spectrum indicated that H_4edtmpPh prepared by this method contained a maximum of 0·1% impurities. The ^{31}P NMR spectra of a solution with pD = 10·38 yielded a chemical shift value of $\delta(P) = 29{\cdot}76$ (ref.[2], $\delta(P) = 29{\cdot}3$ for the tetrasodium salt). Analysis for phosphorus was carried out spectrophotometrically[7]; calculated 18·31%, found 18·1% P. Nitrogen was determined after mineralization by distillation; calculated 4·14%, found 4·12% N.

The stock solutions of the individual cations were the acidified solutions of the perchlorates, prepared by reaction of the oxides or carbonates (p.a.) of the metals with a slight excess of p.a. purity perchloric acid (Merck). The metal content in the solution was determined by titration of the solution with an edta solution and excess perchloric acid was determined by pH metric titration using a DTS 833 titrator with the recommended program.

Procedures

The NMR spectra were measured using the AM 400 instrument from the Bruker company with Fourier transformation of the spectra at a temperature of 24°C. The ^{1}H NMR spectra were measured at a working frequency of 400·13 MHz with DSS as an internal standard; ^{31}P NMR spectra were measured at a working frequency of 161·07 MHz with 85% H_3PO_4 as an external standard; ^{13}C NMR spectra were measured at a working frequency of 100·62 MHz with DSS as an external standard. The $C^{13}\{^1H\}$ and $^{31}P\{^1H\}$ spectra were measured using wide-band proton decoupling. Samples were prepared by dissolving H_4edtmpPh in a 10% NaOD solution in D_2O. The pD value was adjusted by addition of a 25% $DClO_4$ solution in D_2O or NaOD in D_2O. The pD value was calculated from the formula pD = pH + 0·40 (ref.[8]), where pH is the value read on the pH meter calibrated according to instructions. The measured solutions had concentrations of 0·37 mol dm^{-3} except for solutions for measurement of the concentration dependence, whose concentrations were gradually decreased. The NaOD solution was prepared by the reaction of Na with D_2O; $DClO_4$ (Apolda, G.D.R.) was of isotopic purity 99·2% and D_2O (Reachim, U.S.S.R.) 99·8%.

Potentiometric measurements were carried out using the DTS 833 digital titration system from the Radiometer company using a combined GK 2401 B electrode from this company. The measurements were carried out in a glass vessel with a volume of 150 cm^3 tempered using a thermostat at 25 ± 0·1°C at an ionic strength of $I(NaClO_4) = 0{\cdot}1$ mol dm^{-3}. Inert atmosphere was ensured by constant passage of argon saturated with solvent vapours. Prior to each series of measurements, the pH meter was calibrated using borax and oxalate buffers[9,10]. The calibration was controlled using buffers from the manufacturer; deviation of the pH from the calibrated values was always less than 0·005 pH units. The calibration was carried out so that the pH meter yielded $-\log [H^+]$ values (ref.[11]).

Titrations were carried out using the Mode = 1·2, Speed 15 programs, yielding 50—70 points per titration.

The initial solution volume was 50 ml and the H_4edtmpPh concentration was 0·001 or 0·005 mol dm^{-3}. In the determination of the stability constants of the complexes with the transition metals, the H_4edtmpPh concentration was 0·005 mol dm^{-3} and the ligand: metal ratio was 1 : 1 or 2 : 1.

The protonation constant was determined spectrophotometrically using a 0·0005 mol dm^{-3} H_4edtmpPh solution. The ionic strength was maintained so that $c(ClO_4) = c(NaClO_4) + c(HClO_4)$. The absorbance was measured against a 0·1 mol dm^{-3} ClO_4^- solution a maximum of 5 minutes after mixing the tempered ligand solution with the $HClO_4$ solution. The absorbance was measured between 230 and 275 nm in steps of 5 nm in the pH range 1·0—2·5 using a UNICAM SP 8 800 instrument.

Data Treatment

The values of n and $-\log [L]$ ([L] = free ligand concentration) were calculated from the measured values and were plotted graphically. The estimated stability constant obtained from these graphs was treated by the MINIQUAD statistical program[12]. First the stability constants of the unprotonated complexes were refined and were then set as fixed values and the stability constants of the protonated complexes were refined. Finally all the constants were refined at once. The protonation constants were determined from the spectrophotometric data using the SQUAD program[13]. This program minimizes the difference between the calculated and experimental values of the molar extinction coefficients of the individual species at a given wavelength.

DISCUSSION

pH *Measurements*

The H_4edtmpPh acid (*I*) is insoluble in all common solvents but is dissolved rapidly in a solution of alkaline hydroxides containing at least 3-equivalent OH^- ions. On acidification the acid again begins to slowly precipitate at pH < 3. Thus, the pH titrations and NMR spectra were measured in dependence on the pH in the range pH 3 – 11. On the other hand, the kinetically slow precipitation of H_4edtmpPh from solution permitted orientative determination of K_1 and K_2 from spectrophotometric data. The pH-metric titration method was employed only to determine the first two protonation constants at two different concentrations of H_4edtmpPh. Their values depend strongly on the concentration (see Table I). Thus, (and as also indicated by NMR spectroscopy, see below) inter- or intramolecular interactions of the H_4edtmpPh molecules are important. Further, the UV absorbance-pH dependence was recorded for the ligand alone. Absorbance bands were found for the ligand in the region 207–218 nm (maximum $\log \varepsilon = 4{\cdot}51$) and 245–272 bm ($\log \varepsilon = 3{\cdot}15-3{\cdot}43$), corresponding to the ^1L_a and ^1L_b transitions of the aromatic ring. The shapes of the spectra measured at $\mathrm{pH} < 6$ were similar to those for Ph_3PO (ref.[14]) and, at $\mathrm{pH} > 7$, are similar to the spectra of $PhPO_2H_2$ (ref.[14]). The difference between the spectra in the acid and alkaline regions can be seen in Fig. 1. A change in the character of the UV spectra of $PhPO_2H_2$ and Ph_2PO_2H with the pH was studied in ref.[14]. As no shifts were observed in the band positions, it can be assumed that there is no resonance between the phenyl and the PO_2^- group. The differences in the band shapes were utilized in the determination of the stability constants. Constants K_1 and K_2 (Table I) were determined with a large error resulting because of the necessity of measuring unstable solutions, with low concentrations. It can be assumed that the K_1 and K_2 values will be much lower at concentrations 10-fold larger, i.e. at the concentrations employed in the pH-metric titrations. As expected, the K_3 and K_4 constants for H_4edtmpPh are higher than for H_4edtmpH (ref.[1]) and lower than for H_4edta (ref.[15]). These results indicate that the phenyl group as an electronegative substituent increases the electron density on the phosphorus atoms and thus on the nitrogen atoms. The stability constants of the complexes of the metals with H_4edtmpPh were determined for Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Mn^{2+} and Ni^{2+} (Table II). The titration curves are depicted in Fig. 2. The stability constants could

TABLE I

Dependence of the dissociation constants of H_4edtmpPh on the concentration

Protonation and dissocation constants	Concentration of H_4edtmpPh, mol dm^{-3}		
	0·0005	0·001	0·005
$\log \beta_1(\sigma)$	–	8·24(2)	7·911 (5)
$\log \beta_2(\sigma)$	–	12·21(5)	11·268(8)
pK_4	–	8·24	7·911
pK_3	–	3·97	3·357
pK_2 (σ)	2·5(4)		
pK_1 (σ)	1·0(5)		

not be determined for Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}. These ions form complexes at pH < 2·5, where errors arise from imprecise knowledge of the K_1 and K_2 values for the acid. The La^{3+} and Al^{3+} ions form a precipitate in the whole pH region.

It follows from Table II that the transition metals also form stable protonated complexes that act as weak acids. The existence of protonated complexes of the alkaline earths could not be demonstrated by calculation because of their low contents in solution. Their presence can be assumed on the basis of analogy with phosphonic acids[10,16].

The stability constants determined for the H_4edtmpPh complexes are higher than for H_4edtmpH (ref.[1]). Comparison with the values for H_4edta (ref.[15]) and for H_8edtmp (ref.[16]) indicates that the nitrogen atoms are coordinated and have basicity increasing in the order H_4edtmpH < H_4edtmpPh < H_4edta < H_8edtmp. In addition, in contrast to H_4edtmpH, H_4edtmpPh forms protonated complexes. For alkaline earth metals, a dependence was found between the cation size and the stability constant value. The stability constants decrease in the order Ba > Sr > Mg. The relatively low stability constant for magnesium and higher value for barium and strontium can be explained on the basis of elimination of bonding interactions in the ligand molecule by the large cation[17]. The relatively high value for calcium is probably a result of interaction of the ion with the nitrogen atom of the ligand.

NMR *Study*

The ^{31}P NMR spectra assumed two different shapes in dependence on the pH. One peak was found in the region pH 3–7·3 and also 9–11, with poorly resolved triplet

TABLE II

Stability constants of H_4edtmpPh with metals $\beta_{pqr} = [M_qH_qL_r]/[M]^p[H]^q[L]^r$

Ion	Stability constants		Dissocation constants of the protonated complexes
	$\log \beta_{101}(\sigma)$	$\log \beta_{111}(\sigma)$	pK_{111}
Mg^{2+}	3·15(1)	—	—
Ca^{2+}	4·666(6)	—	—
Sr^{2+}	3·54(2)	—	—
Ba^{2+}	3·583(7)	—	—
Mn^{2+}	6·55(1)	10·67(3)	4·12
Fe^{2+}	7·71(1)	10·89(3)	3·18
Co^{2+}	8·60(1)	11·27(4)	2·67
Ni^{2+}	9·82(2)	—	—

structure. Abnormal broadening of the "main" original peak was observed in the region pH 7·3 – 9 and an additional "side" peak appeared. This peak has low relative intensity and its position is practically pH-independent (see Fig. 3). At pH ~ 9 the two peaks coalesce in the triplet peak. The character of the spectrum at pH 7·3 – 9 is not time-dependent but depends on the ligand concentration in solution. The relative intensity of the "side" peak relative to that of the broadened "main" peak decreases in the concentration region 0·25 – 0·1 g cm^{-3}. At temperatures 80°C, the very broad peak narrows to the usual width, while the intensity of the "side" peak remains unchanged. Fig. 4 depicts the shapes of the curves of the dependences of $\delta(P)$, $\delta(H)$, and $\delta(C)$ on the pH. The $\delta(P)$ and $\delta(H)$ curves depict the dissociation of the third and frouth protons and the $\delta(C)$ corresponds to the dissociation of only the fourth proton, with respect to the studied pH region. The curves for the dependences of $\delta(P)$ and $\delta(H)$ on the pH agree with the literature data for nitrilo-tris(methy-

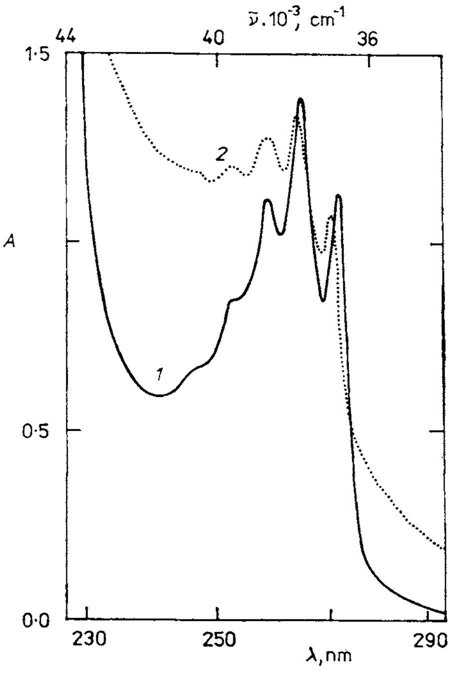


FIG. 1

Part of the spectrum (the $^{1}L_{b}$ transition) of an aqueous solution of H_4edtmpPh with concentration 0·0005 mol dm^{-3}. pH: *1* 2·28, 2 10·78

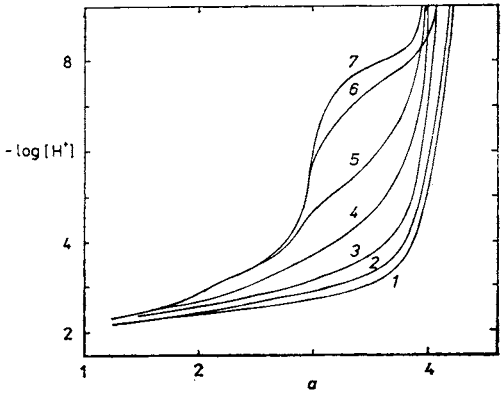


FIG. 2

Titration curves of a H_4edtmpPh solution containing divalent metal ions (value *a* designates equimolar amounts). *1* Ni^{2+}, *2* Co^{2+}, *3* Fe^{2+}, *4* Mn^{2+}, *5* Ca^{2+}, *6* Mg^{2+}, *7* L lenephosphonic) (H_6ntmp) and imino-bis(methylenephosphonic) (H_4ibmp) acids (ref.[18]), H_8edtmp (ref.[19]) and $NH_2(CH_2)_nPO_3H_2$ ($n = 1-3$) (ref.[20]). Except for the dissociation of the last proton, the absolute $\delta(P)$ value decreases in steps corresponding to the pK_n of the acid. The dissociation of the last proton from the nitrogen atoms rapidly changes the electron conditions in these molecules, leading to an increase in the absolute $\delta(P)$ value by 2–10. An increase of about 6 ppm was observed for H_4edtmpPh. The changes in $\delta(H)$ for the hydrogen atoms of the methylene groups correspond to the $\delta(H)$ values for H_4edta (ref.[21]). The decrease in $\delta(H)$ for the hydrogen atoms of the ethylene group by 1 ppm for dissociation of the last H^+ ion is twice as large as that for H_4edta (ref.[21]) and H_8edtmp (ref.[22]); the $\delta(H)$ values for these atoms does not change in the pH region 3–6, i.e. the region for dissociation of the third H^+ ion from the ligand.

The determined $\delta(C)$ values for the methylene and ethylene groups and their changes with changing pH are very similar to the $\delta(C)$ values for H_4edta (ref.[23]). In the ^{13}C NMR spectra of the carbon atoms of the phenyl groups, these changes could be found only after dissociation of the last proton. The peaks were assigned to the individual carbon atoms on the basis of comparison with benzoic acid[24] and benzenesulfonic acid[25] considering the decreasing $^nJ(CP)$ value for the C1 to C4 atoms on the phenyl group.

For simple aminoalkylphosphonic acids, $NH_2(CH_2)_nPO_3H_2$, Appleton et al.[20] assumed a conformation that is stabilized by intramolecular N···H···O bonds. Quantum chemical calculations[26] indicate that this conformation can be assumed for

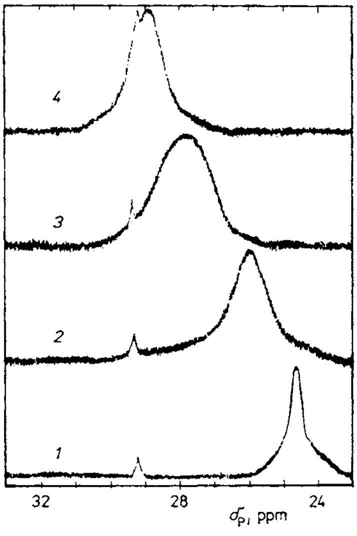


FIG. 3

^{31}P NMR spectra of solutions with pD: *1* 7·30, *2* 7·90, *3* 8·21, *4* 8·71 phosphonoglycine, also in the gas phase. Similar intermolecular interactions can be assumed for H_4edta. With increasing deprotonation, the H^+ ions are first dissociated on the carboxyl groups. The last H^+ ion in the $Hedta^{3-}$ anion is bonded to the nitrogen atom and the carboxyl group does not participate in intermolecular hydrogen bonding[21,27]. Chapman et al.[28] have assigned anticlinal conformation to the $Hedta^{3-}$ ion on the basis of the NMR and infrared spectra; this conformation is

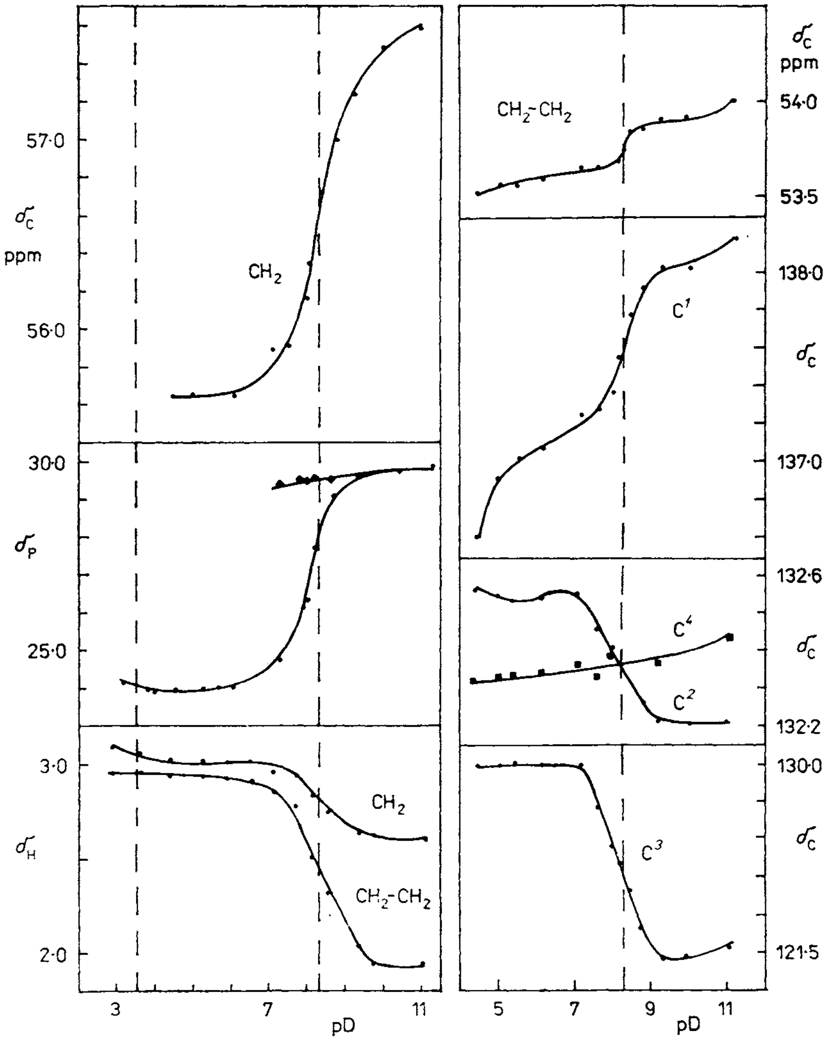
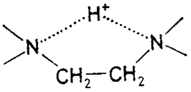


FIG. 4

Curves for the dependences of δ(P), δ(H) and δ(C) on pD; C^1 — C^4 are aromatic carbon atoms stabilized by the N···H^+···N bond. Our results obtained from the NMR spectra indicate a certain similarity with the above acids, especially with H_4edta. Thus anticlinal conformation of the ethylenediamine skeleton can also be considered for the HedtmpPh^{3-}anion, which is stabilized by a hydrogen bond (*II*). The phenyls of



II

the phosphinic groups apparently sterically hinder the formation of more stable hydrogen bonds N···H^+···O. On dissociation of the fourth H^+ ion, this conformation probably changes to anti-periplanar. The large change in δ(H) in this region also reflects this change. If slower exchange occurs between these conformations in concentrated viscous solutions, these changes would be observed in the ^{31}P NMR spectrum at pH 7·3 – 9.

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