

New complexanes
XLII. PMR study of interaction
of 2-hydroxy-1,3-propanediamine-*N,N,N',N'*-tetraacetic acid
with alkaline earth metal ions in aqueous solutions

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The complex formation of 2-hydroxy-1,3-propanediamine-*N,N,N',N'*-tetraacetic acid (HPDТА) with Mg(II), Ca(II), Sr(II), and Ba(II) ions in equimolar aqueous solutions was found to be of 1 : 1 stoichiometry on the basis of the dependence of the chemical shifts of nonlabile protons in the ligand on *pD*. It was found that in MgHPDТА, CaHPDТА, and SrHPDТА complexes the nitrogen atoms of amino groups and the oxygen ones of carboxyl groups are coordinated to the central ion, in BaHPDТА also an oxygen atom of hydroxyl group is coordinated. In solutions with an excess of ligand the complex formation of 1 : 2 composition is supposed as well.

Из зависимости химических сдвигов ПМР сигналов нелабильных протонов 2-гидрокси-1,3-пропандиамин-*N,N,N',N'*-тетрауксусной кислоты (HPDТА) в эквимольных водных растворах с ионами Mg(II), Ca(II), Sr(II) и Ba(II) на *pD* было установлено образование комплексов со стехиометрическим соотношением 1:1. В комплексах MgHPDТА, CaHPDТА и SrHPDТА координируют атомы азота аминогрупп и кислорода карбоксильных групп, в комплексе BaHPDТА и кислород гидроксильной группы. В растворах с избытком лиганда предполагается и образование комплексов с соотношением 1:2.

The 2-hydroxy-1,3-propanediamine-*N,N,N',N'*-tetraacetic acid is a significant structural analogue of EDTA which found its use in the analytical chemistry as titrating or masking agent [1, 2], in chromo-photography [3—5], in textile industry as stabilizer of detergents and bleaching agents [6], and in agriculture it aids the tobacco growing [7]. With respect to its wide-spread applications, a great attention is devoted to the study of complex formation equilibria of HPDТА. In the previous paper of our series [8] the stability constants of HPDТА complexes with a number of divalent metal ions were determined. The stability of these complexes is substantially lower when compared with that of EDTA, which is probably

influenced by the presence of energetically less advantageous six-membered ring formed in the HPDTA complexes. They are even less stable than those of 1,3-propanediamine-*N,N,N',N'*-tetraacetic acid (PDTA) in which the six-membered ring is also present. The probable reason of this phenomenon is the drop in energy of the metal bond to nitrogen atoms of HPDTA having lowered electron density due to $-I$ effect of the hydroxyl group. In the case of alkaline earth metal ions, the BaHPDTA complex is an exception, because it is more stable than the BaPDTA one. The aim of our present work is to explain this anomaly by studying the interactions of HPDTA with alkaline earth metal ions in aqueous solutions by means of p.m.r. spectroscopy.

Experimental

HPDTA was prepared by reacting the iminodiacetic acid with 1,3-dichloropropane-2-ol [9]. Crude product was three times crystallized from hot water and dried under the reduced pressure at 80°C. The identity and purity of the product obtained was verified by p.m.r. measurements, elemental analysis, and potentiometric neutralizing titration.

The p.m.r. spectra were measured on a Tesla BS 847 A spectrometer (80 MHz with frequency sweep). The *tert*-butanol (CH₃)₃COD (TBA) served as an internal standard. The chemical shifts are given in p.p.m. of the δ scale with respect to DDS ($\delta_{\text{TBA}} = 1.233$ p.p.m.). The accuracy of the chemical shift values is better than 0.02 p.p.m. and they are independent of the concentration of HPDTA.

The solutions were prepared by dissolving the calculated amounts of HPDTA and metal ion salts in D₂O, in which the pD values were adjusted by adding KOD or DCl solutions in D₂O to the samples. The ligand concentration was 0.3 and 0.15 mol dm⁻³, respectively and that of TBA in samples 5 volume %. The pD of solutions was measured by a combined electrode EA 125 and pH-meter Compensator E 388 (Metrohm) at 25°C. The pH-meter readings thus obtained were recalculated to pD according to *Mikkelsen and Nielsen* [10] using the expression $pD = \text{pH}_m + 0.40$.

Results and discussion

The p.m.r. spectra of noncoordinated HPDTA studied in dependence on pD of solutions together with their interpretation with regard to acid-base properties have been published in our previous paper [11]. In this paper we report on the dependence of chemical shifts of nonlabile protons on pD (Figs. 2, 4, 5, and 7) for comparison with chemical shifts of protons in HPDTA solutions containing the metal ions:

The p.m.r. spectra of equimolar solutions of the metal ions and HPDTA were measured at various pD within 0–90°C. Fig. 1 shows examples of the typical

spectra of $\text{Mg(II)}:\text{HPDTA} = 1:1$ solutions together with denotation of the individual nonlabile protons used in the following text. The signals obtained at lower temperatures (up to 25°C) were relatively broad and the multiplets unresolved. On warming up the solutions, the signals became narrower and for the spin system of protons H^c , H^d , H^e at $\text{pD} = 9-10$ the similar multiplets may be observed as those in the case of free HPDTA in L^{4-} form. The signal of H^a , H^b protons in all

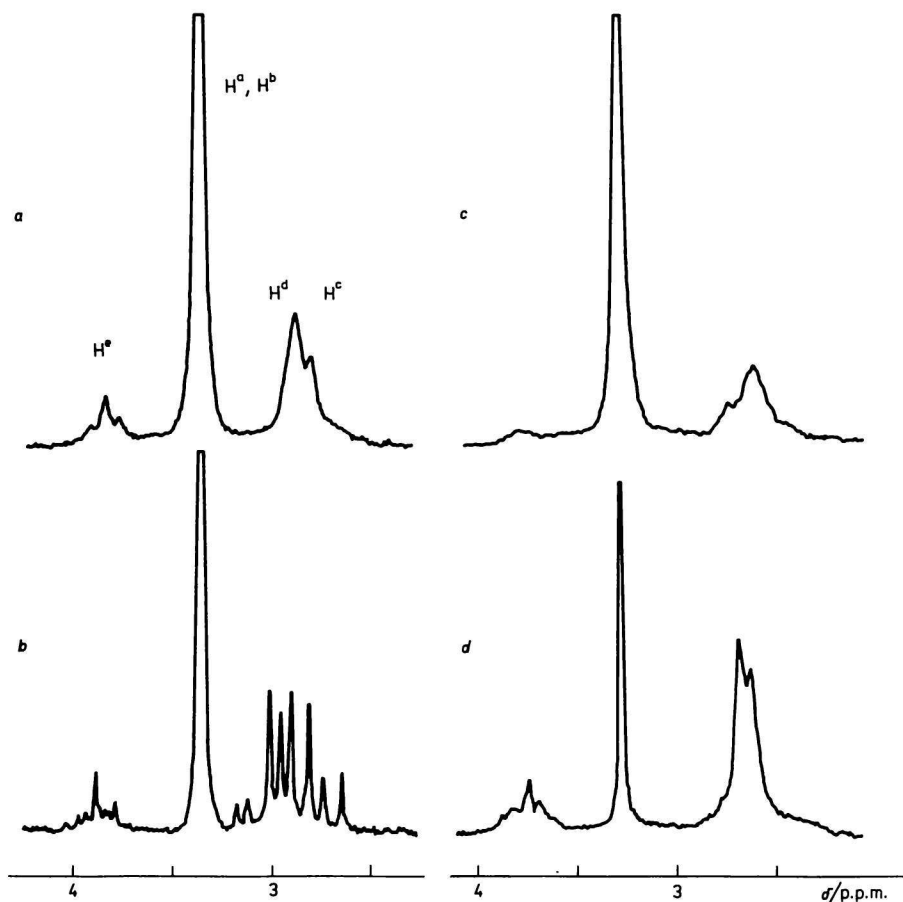
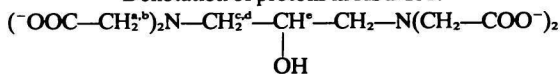


Fig. 1. PMR spectra of $\text{Mg(II)}:\text{HPDTA} = 1:1$ solution.

- a) $\text{pD} = 9.19$, $t = 25^\circ\text{C}$; b) $\text{pD} = 9.19$, $t = 60^\circ\text{C}$; c) $\text{pD} = 12.22$, $t = 25^\circ\text{C}$;
d) $\text{pD} = 12.22$, $t = 60^\circ\text{C}$.

Denotation of protons in HPDTA:



the spectra of $\text{Mg(II)} : \text{HPDTA} = 1 : 1$ solutions was observed as a singlet. Day and Reilly [12, 13] have found that multiplicity of signals of certain ligand bonded in complexes with various ions depends on the lability of individual metal ion—donor atom bonds. Basing on this, they have divided the complexes into three groups :

- complexes with labile both the M—N and M—O bonds,
- complexes with nonlabile M—N bonds and labile M—O ones,
- complexes with nonlabile both the M—N and M—O bonds.

The signals observed in the spectra of the first group reveal the same multiplicity as those of free ligand, because there is possible a quick inversion of the nitrogen atoms due to a short life-time of M—O and M—N bonds. The common signal for two carboxymethyl groups joined to the given nitrogen atom is observed, which may be shaped as a singlet or AB quartet depending on the ligand symmetry. Thus the singlet observed in the case of the MgHPDTA complexes indicates the lability of both the Mg—O and Mg—N bonds.

The values of chemical shifts of nonlabile protons observed with $\text{Mg(II)} : \text{HPDTA} = 1 : 1$ solutions in dependence on pD are given in Fig. 2. It was

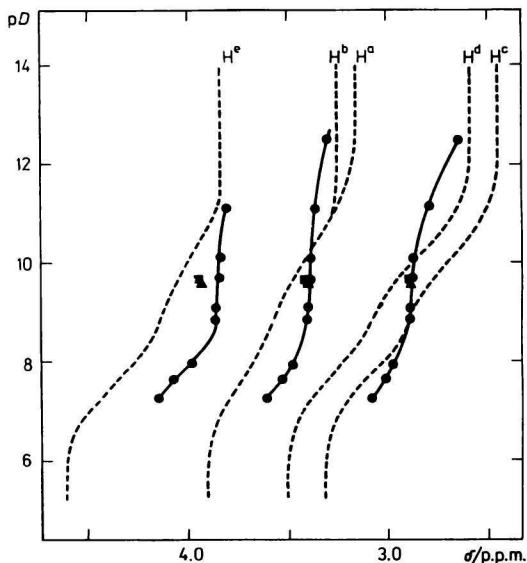


Fig. 2. Dependence of the chemical shifts of resonance signals of HPDTA in $\text{Mg(II)} + \text{HPDTA}$ solution on its pD .

Concentration of HPDTA ca. 0.3 mol dm^{-3} , $t = 25^\circ\text{C}$.

● $\text{M} : \text{L} = 1 : 1$; ■ $\text{M} : \text{L} = 1 : 3$; ▲ $\text{M} : \text{L} = 1 : 2$;

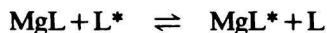
--- the free HPDTA.

impossible to determine the values of H^e and H^d proton chemical shifts in all the spectra as their multiplets were overlapped and not well resolved. Therefore the average value of chemical shifts of the proton signals in question is reported in this dependence and in the following ones as well. Those values were determined as the middle of the multiplet or broad singlet in the spectrum. The complex of MgHPDTA composition is stable only in the narrow range of pD $8.8 < pD < 10.2$. Outside of this range, the values of chemical shifts and shapes of spectra are changed, because in the solutions also other forms of HPDTA (hydroxo- and/or hydrogen complexes, the free HPDTA) are present besides the one under study, and a quick exchange proceeds among them. Alike to solutions with metal—ligand ratio 1:1, the only system of resonance signals is observed in the spectra of Mg:HPDTA = 1:2 or 1:3 solutions. If there is only the MgHPDTA (MgL) complex, the free HPDTA (L), and a quick ligand exchange, for the observed value of chemical shift δ_{aver} should be written

$$\delta_{aver} = (\delta_{MgL} + \delta_L)/2 \quad \text{for 1:2 ratio}$$

$$\delta_{aver} = (\delta_{MgL} + 2\delta_L)/3 \quad \text{for 1:3 ratio}$$

Since these relationships are not valid for the system Mg—HPDTA (Fig. 2), in the solutions containing an excess of ligand proceeds not only the ligand exchange



but probably also the complex of MgL_2 composition is present and is involved in the ligand exchange reactions.

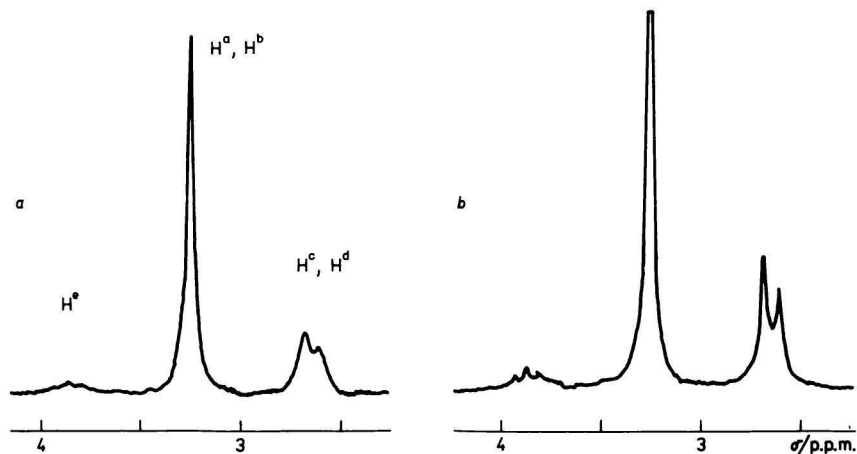


Fig. 3. PMR spectra of Ca(II):HPDTA = 1:1 solution.
 $pD = 9.95$, $t = 25^\circ C$ (a), $t = 80^\circ C$ (b).

The shape of spectra for $\text{Ca(II):HPDTA} = 1:1$ and $\text{Sr(II):HPDTA} = 1:1$ solutions is similar. Fig. 3 shows the spectra of $\text{Ca(II):HPDTA} = 1:1$ solution, $pD=9.95$. The signal of CH_2 in carboxymethyl group (H^a and H^b protons) is a singlet, which is the proof of labile bonds metal—donor atom and of the quick intraligand exchange. The other signals observed at room temperature are unresolved multiplets. On warming up the solution, all the signals become narrower, the signal of H^c and H^d is observed as a doublet, and that of H^e as a triplet (coupling constant $J=6$ Hz). The dependence of chemical shifts on pD (Fig. 4) and the

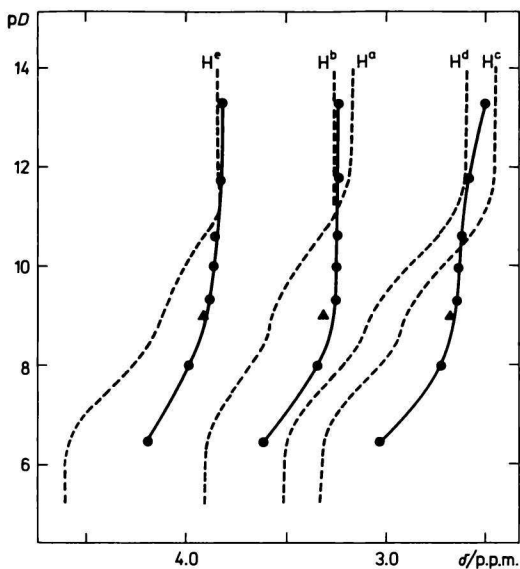


Fig. 4. Dependence of the chemical shifts of resonance signals of HPDTA in $\text{Ca(II)} + \text{HPDTA}$ solution on its pD .

Concentration of HPDTA ca. 0.3 mol dm^{-3} , $t = 25^\circ\text{C}$.

● M: L = 1: 1; ▲ M: L = 1: 2; --- the free HPDTA.

shape of signals showed that the CaHPDTA complex is stable within $pD=9-11$. At higher values of pD , a weak shift of H^e signal position is observed as well as a pronounced one for the H^c and H^d protons towards the higher intensity of magnetic field. The proton signals of $\text{Ca(II):HPDTA} = 1:2$ solution (Fig. 4), similarly as in the case of Mg , indicate the existence of the complex of composition CaL_2 .

Fig. 5 shows the dependence of chemical shifts on pD for the solutions of $\text{Sr(II):HPDTA} = 1:1$ ratio. HPDTA is fully bonded into its Sr complex at $pD=9.5-12.0$. As expected, the signals of H^a , H^b , H^c , and H^d protons, respec-

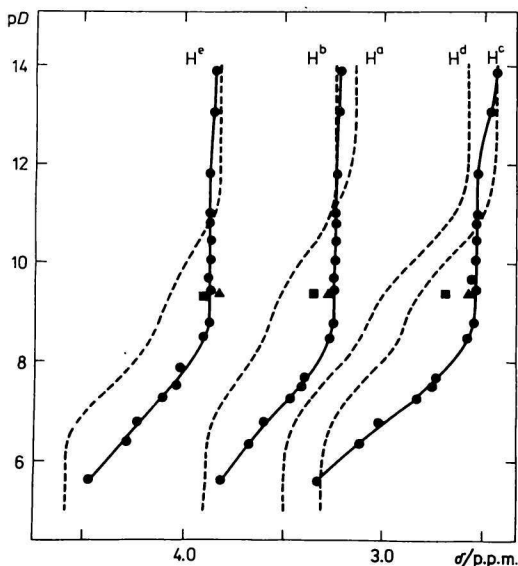


Fig. 5. Dependence of the chemical shifts of resonance signals of HPDTA in Sr(II) + HPDTA solution on its pD .

Concentration of HPDTA ca. 0.3 mol dm^{-3} , $t = 25^\circ\text{C}$.

● M:L = 1:1; ■ M:L = 1:3; ▲ M:L = 1:2;
 --- the free ligand.

tively, observed for Sr(II):HPDTA = 1:2 solutions occur at lower intensity of magnetic field when compared with those of the M:L = 1:1 solutions (Fig. 5). It means that the values of chemical shifts of these protons are lower than those for the free HPDTA at given pD , but higher when compared with the SrL complex. In contrast, the signal of the methine group proton H^e for Sr(II):HPDTA = 1:2 solution is observed at higher magnetic field. The electron density at H^e is higher in comparison with the SrL complex as well as with the free ligand at the same value of pD . The chemical shifts observed may be explained by the SrL₂ complex formation. There is an unexpected mutual position of the H^e proton signals of free HPDTA, SrL, and SrL₂, respectively. This is probably due to a stronger decrease in electron density on that proton in SrL complex than would be caused by coordination of the nitrogen atoms to strontium only. The reason of this effect may be the interaction of oxygen atom in hydroxyl group with Sr(II), whereas such an interaction in the SrL₂ complex would not exist.

The spectrum of Ba(II):HPDTA = 1:1 solution (Fig. 6) substantially differs from those of the other alkaline earth metal complexes. The signal of protons of carboxymethyl groups is AB quartet for all the solutions measured at various values of pD within 25–90°C. It means that the protons of this group (H^a , H^b) are

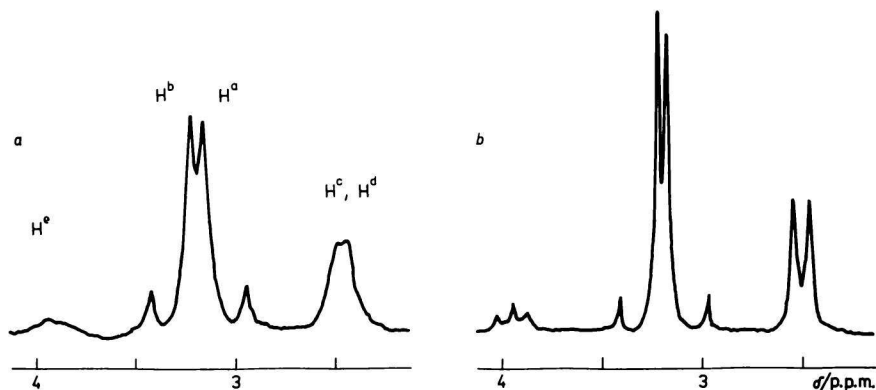


Fig. 6. PMR spectra of Ba(II):HPDTA = 1:1 solution.
 $pD = 11.01$, $t = 25^\circ\text{C}$ (a), $t = 80^\circ\text{C}$ (b).

chemically nonequivalent. With regard to the metal complex classification made by Day and Reilly [12, 13], protons attached to the carbon atom of carboxymethyl group are chemically nonequivalent due to slowing down of the inversion of the nitrogen atoms in complexes having nonlabile M—N bonds. The nonlabile bonds Ba—N were not, however, observed in similar complexes so far [14]. The more probable explanation is that the chemical nonequivalence of H^a and H^b protons is influenced by a lower symmetry of the BaHPDTA complex when compared with the other alkaline earth metal complexes. The H^c , H^d , and H^e proton signals in the spectrum are broad at room temperature. With the increase of temperature the width of these signals becomes smaller with simultaneous appearing of their fine structure. Fig. 7 shows the dependence of chemical shifts on pD for equimolar solutions of Ba(II) and HPDTA. The stable values of chemical shifts together with the unchangeable shape of signals observed for solutions measured at $9.5 < pD < 13.7$ are the proof of the BaHPDTA complex existence in this region of pD .

Table 1 contains the values of chemical shifts of nonlabile protons in HPDTA complexed with alkaline earth metal ions and products $\Delta\delta = \delta_{ML} - \delta_L$, where δ_L is chemical shift for L^{4-} anion of free ligand. Inspecting these values, a remarkable difference between the δ_{H^e} of the Ba(II) complex and the other δ_{H^e} values is seen. The values of chemical shifts of H^a , H^b and H^c , H^d protons decrease in the same order $Mg > Ca > Sr > Ba$ as the ionic radii increase, which is in agreement with the idea of electrostatic interaction of the central ion with donor atoms of ligand, e.g. the nitrogen atoms of amino groups and the oxygen atoms of carboxyl groups [15]. From these statements it is obvious that the lower electron density at the H^e proton of methine group in BaHPDTA complex is influenced by the hydroxyl group in ligand.

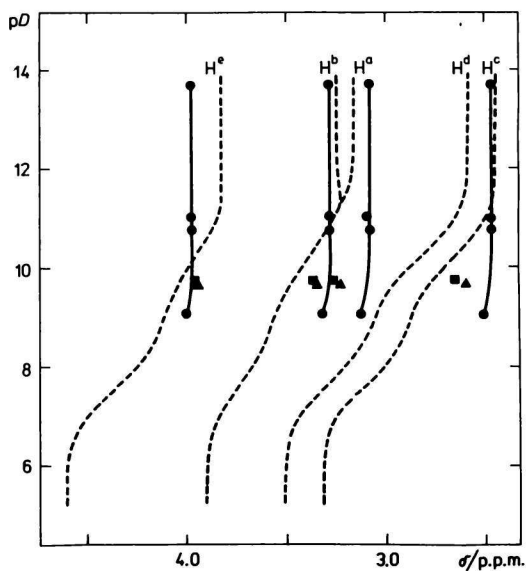


Fig. 7. Dependence of the chemical shifts of resonance signals of HPDTA in Ba(II) + HPDTA solution on its pD.

Concentration of HPDTA ca. 0.3 mol dm^{-3} , $t = 25^\circ\text{C}$.

● M:L = 1:1; ■ M:L = 1:3; ▲ M:L = 1:2;

--- the free ligand.

Table 1

Chemical shifts δ_{ML} of nonlabile protons of HPDTA in its ML complexes
 $\Delta\delta = \delta_{\text{ML}} - \delta_{\text{L}}$ (δ_{L} is the chemical shift of the free ligand anion L^{4-})

Complex	$\delta_{\text{H}^{\text{a,b}}}$	$\Delta\delta_{\text{H}^{\text{a,b}}}$	$\delta_{\text{H}^{\text{c,d}}}$	$\Delta\delta_{\text{H}^{\text{c,d}}}$	$\delta_{\text{H}^{\text{e}}}$	$\Delta\delta_{\text{H}^{\text{e}}}$
MgHPDTA	3.38	0.20	2.85	0.35	3.84	0.02
CaHPDTA	3.24	0.06	2.64	0.14	3.86	0.04
SrHPDTA	3.22	0.04	2.53	0.03	3.86	0.04
BaHPDTA	3.18	0.00	2.47	-0.03	3.97	0.15

* The average values of the H^{a} , H^{b} and H^{c} , H^{d} proton chemical shifts, respectively.

It is also interesting to compare the chemical shifts of Ba(II)—HPDTA solutions with various M:L ratios (Fig. 7). The positions of signals for M:L = 1:2 indicate the BaL_2 complex formation. The values of chemical shifts of H^{a} , H^{b} and H^{c} , H^{d} protons increase with the ligand concentration. There is different situation again in

the case of H^c proton, where the higher electron density is observed for the $M:L = 1:2$ system when compared with that for $M:L = 1:1$ and for noncoordinated ligand as well, at the same value of pD .

The existence of AB quartet of H^a , H^b protons in BaHPDTA, the difference in chemical shift of H^c proton mentioned before, as well as comparison of the latter for $M:L = 1:2$ and $1:1$, respectively, indicate that in BaHPDTA complex the ligand is coordinated to Ba by nitrogen atoms of amino groups, oxygen atoms of carboxyl groups and also by oxygen of hydroxyl group. Using potentiometry it was found that the formation of BaHPDTA is accompanied by dissociating of four protons [8], so that the hydroxyl group is coordinated without deprotonation. HPDTA acts as a heptadentate ligand in its Ba complex. Such a way of coordination of HPDTA enables to explain the magnitude of the stability constant of BaHPDTA which is by an order higher than that of BaPDTA.

The Ba^{2+} ion, as follows from our results, may possess the coordination number of seven in its complexes. This has not been observed, as far as we know, until now. Coordination number of seven of alkaline earths, however, was observed in the case of the complex ion $[Mg(H_2O)EDTA]^{2-}$ [16]. The enlargement of coordination number in complex compounds is explained by the expansion of coordinating sphere. This is caused by an increase of ionic radius together with lowering of energy of the bond between the metal ion and ligand [17]. In the case of EDTA it resulted in coordination of an additional ligand, e.g. attachment of H_2O molecule to Mg^{2+} . One cannot exclude that if the complexone contains another functional group with donor atom, then at appropriate chemical conditions there need not proceed the coordination of an external ligand (as in the EDTA complexes), but the given functional group is coordinated. In order to explain this hypothesis in the case of BaHPDTA complex, we shall continue in our work.

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