STUDY OF THE FORMATION OF COMPLEXES OF 2-HYDROXY-1,3-PROPANEDIAMINE-N,N,N',N'-TETRAACETIC ACID WITH Zn(II), Cd(II) AND Pb(II) IONS USING NMR SPECTROSCOPY*

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2-Hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid (HPDTA) forms complexes of the ML type with Zn(II) and Cd(II) ions in the pDH ranges 5·0—11·5 and 7·3—8·6, respectively. In these complexes, there are coordinated oxygen atoms of four carboxylate groups and nitrogen atoms of two amino-groups. Formation of the Pb_2L type complex was observed in the pDH region 5·9—11·5. HPDTA is a heptadentate ligand in this complex. The two glycinate rings correspond to one Pb(II) ion and are nonequivalent. During formation of the hydroxocomplexes of Pb_2L and CdL in alkaline solutions, the HPDTA carboxylate groups become substituted by OH^- ion in the coordination sphere of the metal ion.

2-Hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid (HPDTA) is a structural analogue of EDTA. In contrast to EDTA, however, it is potentially a heptadentate ligand. Potentiometric[1], spectrophotometric[2] and electrophoretic[3] studies have shown that, in contrast to the complexes with Zn(II) and Cd(II) ions, HPDTA forms a binuclear complex with Pb(II), in which coordination of the oxygen of the hydroxyl group is assumed.

This work is concerned with the formation of complexes of HPDTA and Zn(II), Cd(II) and Pb(II) ions in aqueous solutions using ^1H NMR spectroscopy, in order to verify this hypothesis.

EXPERIMENTAL

HPDTA was prepared by the procedure described in ref.[2] and 1,3-propanediamine-N,N,N',N'-tetraacetic acid (PDTA) according to ref.[4]. The purity of these substances was verified by elemental analysis and potentiometric titrations. Samples for spectral measurements were prepared from HPDTA or PDTA and the nitrates of the particular metal ion in D_2O; the ligand concentration in the measured solutions was about 0·3 mol dm^{-3}. KOD and DCl were used to adjust the pDH of the solutions. The value was found from pH_m, recorded on a pH-meter[5]:

$$pDH = pH_m + 0{\cdot}44\,.$$

The ^1H NMR spectra were measured on a Tesla BS 487 A spectrometer; deuterated tert-butyl

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alcohol $(CH_3)_3COD$ (TBA) was used as an internal standard. The chemical shifts of the signals are given with respect to DSS ($\delta_{TBA} = 1{\cdot}233$ ppm). The precision of reading of the resonance frequencies was greater than $\pm 0{\cdot}2$ Hz ($\pm 0{\cdot}0025$ ppm), where not given otherwise.

RESULTS AND DISCUSSION

The ^1H NMR spectra of HPDTA in D_2O, their interpretation and the dependence of the chemical shifts on the pDH value are described in detail in earlier works[6,7]. Designation of the HPDTA protons is apparent from the following structural formula

$$(^-OOC—CH^aH^b)_2{\cdot}N—CH^cH^d—CH^e(OH)—CH^cH^d—N{\cdot}(CH^aH^b—COO^-)_2 .$$

The ^1H NMR spectra of solutions with a molar ratio of Zn(II):HPDTA = 1 : 1 were measured in the range 2·90 < pDH < 13·32. A typical spectrum of this solution is given in Fig. 1 (pDH = 9·27). The spectrum consists of several overlapping multiplets that were identified using the INDOR technique. Assignment of the signals to the individual protons is apparent from the figure. The following values

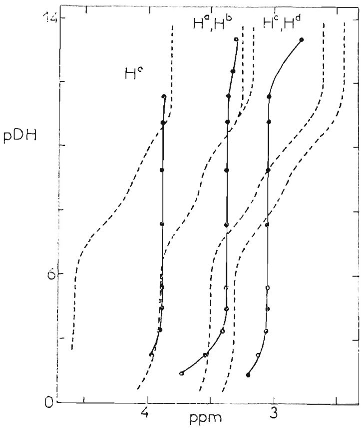

FIG. 1

The ^1H NMR spectrum of the Zn(II) HPDTA complex, pDH = 9·27, t = 25°C

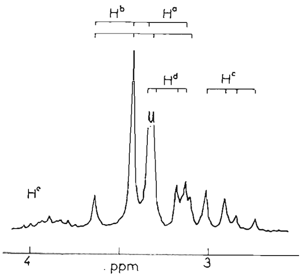

FIG. 2

Dependence of the chemical shifts of the Zn(II) : HPDTA = 1 : 1 system on the pDH of the solution of the chemical shifts (ppm) and coupling constants (Hz) were calculated for the spectrum of a solution with pDH = 8·30, t = 25°C:

$$\delta_{H^a} = 3{\cdot}27 \quad \delta_{H^b} = 3{\cdot}48 \quad J_{H^aH^b} = 16{\cdot}5$$

$$\delta_{H^{a'}} = 3{\cdot}24 \quad \delta_{H^{b'}} = 3{\cdot}48 \quad J_{H^{a'}H^{b'}} = 16{\cdot}6$$

$$\delta_{H^c} = 2{\cdot}90 \quad \delta_{H^d} = 3{\cdot}21 \quad J_{H^cH^d} = 13{\cdot}2$$

$$\delta_{H^e} = 3{\cdot}87 \quad J_{H^cH^e} = 8{\cdot}7$$

$$J_{H^dH^e} = 3{\cdot}3$$

It can be seen from the dependence of the chemical shifts of the nonlabile protons of equimolar solutions of Zn(II) and HPDTA on pDH (Fig. 2) that HPDTA is completely bonded in the Zn(II) HPDTA complex in the region 5·0 < pDH < 11·5. The spectrum of the Zn(II) PDTA complex was also measured for comparison of changes in the chemical shifts during coordination of HPDTA. The chemical shifts of the signals of this complex, determined by finding the centre of the multiplet in the spectrum, are listed in Table I. Comparison of the $\Delta\delta$ values indicates that HPDTA is coordinated to Zn(II) similarly to PDTA. It is bonded to the central ion through two nitrogen atoms and oxygen atoms from four carboxyl groups. The separate signals of the carboxymethyl protons (H^a, H^b) indicate zinc–nitrogen nonlabile bonds in the Zn(II) HPDTA complex. This complex contains two types of chemically non-equivalent glycinate rings, corresponding to the two AB quartets for the protons of the carboxymethyl groups in the spectrum.

TABLE I

Chemical shift values for the nonlabile protons (ppm) in the complexes of Zn(II), Cd(II), Pb(II) with HPDTA and PDTA $\Delta\delta = \delta_{ML} - \delta_{L^{4-}}$

Complex	$\delta_{H^{a,b}}$*	$\Delta\delta_{H^{a,b}}$	$\delta_{H^{c,d}}$*	$\Delta\delta_{H^{c,d}}$	δ_{H^e}	$\Delta\delta_{H^e}$
ZnPDTA	3·29	0·10	2·98	0·44	1·68	0·04
ZnHPDTA	3·37	0·17	3·05	0·53	3·89	0·06
CdPDTA	3·11	−0·08	2·83	0·29	1·82	0·18
CdHPDTA	3·25	0·05	2·86	0·34	3·93	0·10
Cd(OH)HPDTA	3·20	0·00	2·56	0·04	3·93	0·10
PbPDTA	3·64	0·45	2·90	0·37	1·76	0·12
Pb_2HPDTA	3·86	0·66	2·99	0·47	4·25	0·42

* When the separated signals of H^a,H^b or H^c,H^d were observed, the averaged chemical shift value is given.

HPDTA exists in various forms in Zn(II) : HPDTA = 1 : 1 solutions with $\text{pDH} < 5$ and $\text{pDH} > 11{\cdot}5$ (hydrogen or hydroxy complexes, free HPDTA), between which exchange occurs and broad signals with chemical shifts dependent on the pDH are observed (Fig. 2).

The shape of the signals of the nonlabile protons of equimolar solutions of Cd(II)-HPDTA does not change at laboratory temperature over the whole pDH interval (2·60–13·55) (Fig. 3). The dependence of the chemical shifts of these signals on the pDH is given in Fig. 4. The values of the chemical shifts do not change with a change of the pDH in the region $7{\cdot}3 < \text{pDH} < 8{\cdot}6$ and $\text{pDH} > 9{\cdot}7$. In the region $7{\cdot}3 < \text{pDH} < 8{\cdot}6$, the solution contains HPDTA bonded to Cd(II) in a complex with composition CdL; the structure of this complex is analogous to that of the ZnL complex. It is apparent from comparison of the values of the chemical shifts of these complexes (Table I) that the electron density is considerably greater on the H^a, H^b and H^c, H^d protons in the CdL complex, which are located close to the donor atoms, as a result of the greater ionic radius of Cd(II) and the greater length of the M—N and M—O bonds. The broad, unresolved multiplets observed in the spectra of the samples measured at laboratory temperature and on cooling to 0°C become narrower and split at temperature above 60°C. The signal of the protons of the carboxymethyl groups (H^a, H^b) is an AB quartet with coupling constant $J = 16{\cdot}3$ Hz (Fig. 3).

The shift of the signals in solutions with $\text{pDH} < 7{\cdot}3$ depends on the decreasing electron density to roughly the same degree for all the nonlabile protons of HPDTA. The signal of the H^a, H^b protons in solutions with $\text{pDH} = 6{\cdot}55$ and $t = 80°\text{C}$ is

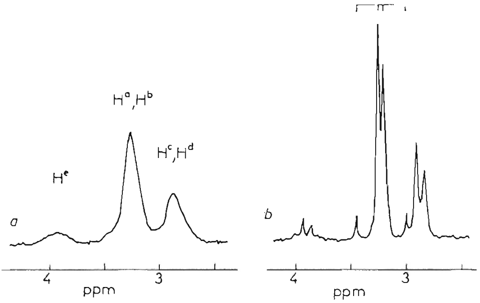

FIG. 3

The ^1H NMR spectra of the Cd(II)HPDTA complex, pDH = 7·75, $t = 25°\text{C}$ (*a*), 60°C (*b*) observed as an AB quartet, indicating that the CdL complex is still present in solution. In solutions with lower pDH values, the signal of these protons is simplified to a singlet. The spectra of solutions with Cd(II) : HPDTA = 1 : 1 in this pDH region indicate that HPDTA is present in solution as a hydrogen complex and also as a free ligand. Rapid exchange occurs between these two forms. It can be assumed on the basis of changes in the chemical shifts in this pDH region that the nitrogen atom is protonated in the hydrogen complex.

In the region 8·6 < pDH < 9·7, different changes were observed in the spectra for each of the signals. The position of the signal of the proton for the methine group (H^e) does not change and the chemical shift of the signals of protons H^a, H^b decreases to a value observed for these protons in the free ligand L^{4-}. A single signal with lower intensity is observed for the H^c and H^d protons, with the same chemical shift as in the CdL complex; the second more intense signal is located at higher magnetic field intensities. It is thus apparent that, in this pDH region, the solution contains not only the CdL complex, but also a further complex of Cd(II) with HPDTA. HPDTA is completely bonded in this complex at 9·7 < pDH < 13·55, where the chemical shifts of the signals do not change (Fig. 4). The chemical shifts of the protons of this complex compared to those for CdL and L^{4-} (Table I) can be explained through formation of the hydroxocomplex Cd(OH)L, in which a hydroxyl

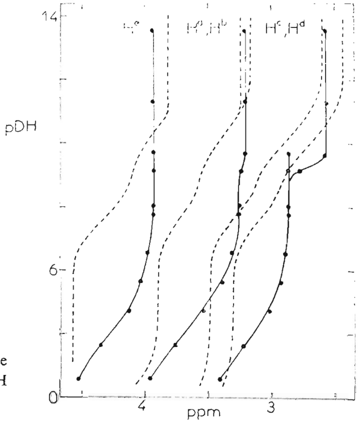

FIG. 4

Dependence of the chemical shifts of the Cd(II) : HPDTA = 1 : 1 system on the pDH of the solution group rather than HPDTA is coordinated to cadmium through a carboxylate group. Rapid exchange occurs among all the carboxylate groups of HPDTA as a result of the labile Cd—O bonds.

The ^{1}H NMR spectrum of the Pb(II) : HPDTA = 2 : 1 (pDH = 7·10) system is depicted in Fig. 5. The signals of all the protons are multiplets located in a narrow proton spectral region and overlapping except for the signal of the H^C protons, which is located at a much higher magnetic field intensity than the other signals. The identification of the individual multiplets was carried out using the INDOR technique; assignment of the protons to the signals in the spectrum is apparent in Fig. 5.

It is apparent from the δ-pDH dependence (Fig. 6) that the spectrum corresponds to the Pb_2L complex which is stable in solution at $5·9 < pDH < 11·5$. The signals of the protons of the carboxymethyl groups appear in the spectrum as two AB quartets (J_{AB} = 16·0 and 16·5 Hz, respectively); the signals of the other protons appear in the spectrum as relatively broad and unresolved multiplets and thus their chemical shifts and coupling constants could not be calculated with precision. Increasing the temperature of the measured solution has no noticeable effect on the shape and position of the signals in the spectrum.

A marked decrease in the electron density on the H^c proton during coordination of HPDTA is apparent from the chemical shifts of the signals for the Pb_2L and L^{4-} protons (Table I), confirming the assumption of coordination through the oxygen of the hydroxyl group. The positions of the signals of the H^a, H^b protons indicate coordination through the carboxylate groups; the small difference in the centres of the AB quartets (0·02 ppm) indicates that all the carboxylate groups are included in the coordination.

The two chelate rings formed by coordination of the iminodiacetate fragment of the HPDTA molecule to a single Pb(II) ion are, however, non-equivalent (two AB

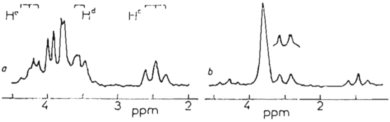

FIG. 5

The ^{1}H NMR spectra of the Pb(II) : HPDTA = 2 : 1 system, *a*) pDH = 7·10; t = 25°C, *b*) pDH = 12·30; t = 25°C (upper signal H^d : t = 80°C) quartets). The Pb—N bonds are nonlabile and inversion of the nitrogen atoms is retarded, leading to separate signals for protons H^a and H^b. The difference in the chemical shifts of protons H^c and H^d of the coordinated ligand is unusually large (1·05 ppm). A similar difference was not observed in other complexes. As these protons are bonded to a single carbon atom, the induction effects acting on them should be identical. The difference in their chemical shifts must thus be a result of anisotropy in the surrounding bonds, with the greatest contribution probably coming from the bond between the oxygen of the hydroxyl group and lead.

At values of pDH > 11·5, a change occurs in the chemical shifts of the signals and in the shape of the signals of the carboxymethyl protons, with the two AB quartets merging into a singlet (Fig. 5). On increasing the temperature, this signal becomes narrower and the signal of the H^d protons is further split. The changes in the ^{1}H NMR spectra in this pDH region can be explained through formation of a hydroxocomplex. The relatively greatest increase in the electron density was observed for the H^a, H^b protons, probably as a result of replacement of the carboxylate groups of HPDTA by OH$^-$ ions in the coordination sphere of the Pb(II) ion. The Pb—N bonds are more labile than in the normal Pb_2L complex and rapid exchange occurs between the carboxylate groups of HPDTA. In this region, the signal of the H^e proton is shifted to lower magnetic field intensities (Fig. 6). The decrease in the electron density on this proton indicates that the bond between the oxygen of the hydroxyl group of HPDTA and lead is retained in the hydroxo complex and that the Pb—O distance is less than in the normal Pb_2L complex.

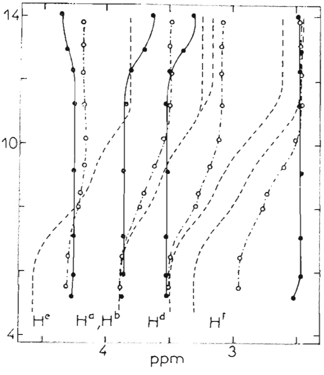

FIG. 6

Dependence of the chemical shifts of the Pb(II)–HPDTA signals on the pDH of the solution, ● M : L = 2 : 1, ○ M : L = 1 : 1, ----- free HPDTA

The data in the literature[3] indicate that Pb(II) forms only a binuclear complex with HPDTA. Consequently, the Pb_2L complex and uncoordinate L ligand should be present in a ratio of $Pb_2L : L = 1 : 1$ in the system containing Pb(II) : HPDTA = = 1 : 1 in the pDH region favourable for the formation of the Pb_2L complex. The ^1H NMR spectrum of this system should thus contain separate signals for Pb_2L and L at slow ligand exchange or average signals for the Pb_2L and L protons at rapid ligand exchange. Only a single system of signals was observed in the spectra for the Pb(II) : HPDTA = 1 : 1 system. Thus rapid exchange occurs between the HPDTA forms present in solution. The observed values of the chemical shifts are apparent from Fig. 6. It can be seen from this figure that the chemical shift values are not the average values for the chemical shifts of the Pb_2L and L signals. Thus this solution is not a mixture (with a ratio of 1 : 1) of the free ligand and the Pb_2L complex or the hydroxocomplex (pDH > 11·5), observed in solutions with Pb(II) : HPDTA = = 2 : 1. No further information can be obtained from the experimental data for the Pb(II) : HPDTA = 1 : 1 system.

For comparison with previously studied metal ion–ligand systems, the ^1H NMR spectra of the Pb(II) : PDTA = 1 : 1 system were also measured. A complex with composition PbL was observed in the region $6 < pDH < 13$; the chemical shifts of the signals for this complex are given in Table I. The difference in the δ_{H^c} values for the Pb(II) complexes also confirms coordination through the oxygen of the hydroxyl group of HPDTA.

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