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FULL PAPER

pH-metric and NMR studies of the complexation of Zn^{2+}, Cd^{2+}, and Pb^{2+} with diazacrown ethers having dangling phosphonate groups

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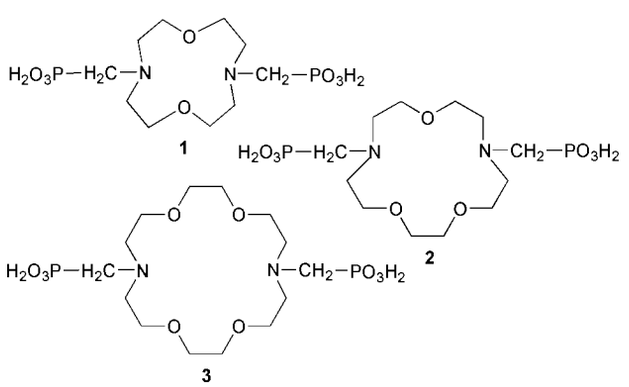
The complexation of 4,10-bis(phosphonomethyl)-1,7-dioxa-4,10-diazacyclododecane **1**, of 7,13-bis(phosphonomethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane **2**, and 7,16-bis(phosphonomethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane **3** with Zn^{2+}, Cd^{2+}, and Pb^{2+} was studied by potentiometric pH titrations and ^{1}H and ^{31}P NMR techniques using a fully automated pH–NMR titration set-up and selected single spectra. The potentiometry allowed one to identify the species and to determine their stability constants. All three metal ions form a series of more or less strongly protonated 1 : 1 complexes (MLH_n, $n = 3$, 2, 1 or 0) as well as 2 : 1 species (M_2LH_m, $m = 1$, 0, −1 or −2). The stabilities of ML follow the order $Pb^{2+} > Cd^{2+} > Zn^{2+}$ for **2** and **3**, whereas the smaller ring **1** shows a different sequence ($Cd^{2+} > Pb^{2+} > Zn^{2+}$), being selective for Cd^{2+}. The same order is also found for coordination of a second metal ion to give M_2L. The NMR studies showed in all cases, except for Cd^{2+} with **2,** only one ^{31}P resonance for the phosphonate groups, which clearly interact with the metal ion since the signals show satellites with metal isotopes having $I = \frac{1}{2}$. Two resonances were observed for Cd^{2+} with **2**. Both have satellites indicating that both are coordinated, but not equivalent. In the ^{1}H NMR spectra one observes signals for both the ligand and the complexes in slow exchange. At some pH values the resonances are broad and indicate that dynamic processes are taking place.

Introduction

Many powerful programs for the determination of protonation and stability constants from potentiometric pH measurements have been developed.[1,2] Based on a model they generally allow one to determine the stoichiometry and equilibrium constants of the species present in solution and thus to calculate distribution diagrams as a function of pH (speciation). From potentiometric titrations it is practically impossible to propose structures for the species except in very simple cases, in which knowledge of analogous systems can be of help. However, when UV-VIS measurements are used in spectrophotometric titrations to study equilibria, spectra of the individual species are obtained besides stability constants and can be used to discuss the structure of the complexes in solution.[3] This is often based on the number of bands in the spectrum, which results from the coordination symmetry, and on their positions, which is determined by the ligand field strength of the donor atoms.[4]

Whereas structural studies in the solid state have been improved so much that a structure determination by X-ray diffraction has become more or less routine, the development of methods which permit one to gain structural information in solution has been less rapid.[5] NMR measurements are a powerful technique to obtain such information as shown by many examples in organic chemistry[6] and biochemistry.[7] For metal complexes, however, several problems must be taken into account. For one equilibria between the species are present. If they are fast on the NMR timescale spectra result which are the mean of those of the single species, whereas if they are slow separate signals of each species can be observed. Secondly, very often the existence ranges of species overlap, so that it becomes difficult to separate individual spectra. Thirdly the method can mainly be used for diamagnetic systems, thus excluding measurements of this type for many transition metal ions.

In an attempt to make better use of NMR techniques we have developed a fully automatic pH–NMR titration set up, with which we can cover with a relatively little amount of the compound the whole pH range and obtain ^{1}H as well as ^{31}P NMR spectra from the same solution.[8] We present here a study of the complexation of three diazacrowns substituted with methylphosphonate groups (**1**–**3**) with Zn^{2+}, Cd^{2+} and Pb^{2+}. The combination of pH titrations and NMR spectra will be used to obtain structural information of the species in solution.



Experimental

Ligands were synthesized as described.[8] NMR titrations were run on a 250 MHz Bruker instrument equipped with a LC probe (Bruker PH LCTXO250SB P/C-H-D-5 O).[8] Single spectra were taken on a 400 MHz Bruker dpx400 instrument. The ^{1}H chemical shifts are referred to 2-(trimethylsilyl)-propanesulfonate and the ^{31}P shifts to 5% H_3PO_4 in D_2O, both used as external standards.

NMR Titrations

Solutions of the complexes (ligand 5×10^{-3} mol dm^{-3} and metal ion 4×10^{-3} mol dm^{-3}) for the pH–NMR titrations were

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Table 1 Stability constants of the Zn^{2+}, Cd^{2+}, and Pb^{2+} complexes with ligands **1**–**3** at $I = 0.1$ mol dm^{-3} ($[Et_4N]NO_3$) and 25 °C

	1			**2**			**3**		
	Zn^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
$\log \beta_{110}$	12.97(1)	14.49(1)	13.49(2)	13.10(2)	13.30(2)	14.39(3)	9.34(2)	11.30(2)	14.26(2)
				(13.25)[a]	(10.93)	(11.78)	(9.78)	(10.73)	(13.06)
$\log \beta_{111}$	18.80(2)	20.50(2)	19.86(2)	19.84(2)	20.06(2)	21.23(2)	16.84(1)	19.60(2)	22.08(1)
$\log \beta_{112}$	23.80(2)	25.02(5)	25.12(2)	25.48(3)	25.58(1)	25.89(5)	22.96(2)	24.54(2)	27.04(3)
$\log \beta_{113}$									30.11(2)
$pK_{H,1}$	5.83	6.01	6.37	6.74	6.76	6.84	7.50	8.30	7.82
				(6.66)[a]	(7.53)	(6.81)	(6.45)	(8.97)	(10.95)
$pK_{H,2}$	5.00	4.52	5.26	5.64	5.52	4.66	6.12	4.94	4.96
				(5.56)[a]	(4.02)	(4.98)	(3.43)	(4.46)	(6.81)
$\log \beta_{11-1}$	1.84(3)	3.34(2)					−1.27(3)		
$\log \beta_{210}$	16.34(2)	19.55(2)	18.36(2)	16.10(2)	17.38(1)	20.18(1)	[b]	15.31(2)	19.84(2)
$\log \beta_{211}$		24.51(5)				25.40(2)			
$\log \beta_{21-1}$	8.29(3)	9.76(3)	10.12(2)	8.39(2)	7.69(1)	11.65(3)	5.82(1)	5.46(3)	11.56(2)
$\log \beta_{21-2}$		−1.18(3)	−0.35(3)				[b]	−4.22(2)	0.76(3)

[a] Values in brackets from ref. 11. [b] The 2:1 titration could only be measured to about pH 8, after which $Zn(OH)_2$ precipitation occurred.

made up in D_2O–H_2O (20%) for the ^{31}P measurements and in D_2O (99.8%) for the combined ^1H and ^{31}P NMR spectra. As base $[Et_4N]OH$ in water was used for the ^{31}P experiments and KOD in D_2O for the combined spectra. pH values in D_2O were calculated from the equation $pH = pD - 0.4$.[9] In the fully automatic NMR titration 10 ml of the ligand–metal solution in the thermostatted vessel were titrated with 0.005 ml base addition up to 0.3 ml total base. For a combined ^1H and ^{31}P measurement it takes about 20 h to run a complete titration.

Potentiometric measurements

pH titrations were run under N_2 on the automatic titrator previously described,[10] consisting of a Metrohm 605 pH-meter, a 665 burette, a thermostatted titration vessel (25 EC) and a 286-AT PC controlling the set up. Calibration of the electrode and control titrations to check the calibration were done as described.[10] The activity coefficient of the proton, γ_H, and the pK_W value were determined separately as 0.95 and 13.92, respectively.

Ligand hydrochloride (5.5×10^{-4} mol dm^{-3}) and metal nitrate (5×10^{-4} or 1×10^{-3} mol dm^{-3}) were dissolved after addition of $[Et_4N]NO_3$ to $I = 0.1$ mol dm^3 and titrated with 0.1 mol dm^{-3} $[Et_4N]OH$, the exact concentration of which was determined using potassium hydrogenphthalate. 20 ml of the solution were titrated with 0.01 ml base increments up to 1 ml total addition. The fitting of the curves was done with the program TITFIT,[2] whereby σ_{ml} was smaller than 3×10^{-3} ml. The results are the mean values of two separate sets of titrations each consisting of two curves with different metal to ligand ratio. The protonation constants of the ligands were taken from ref. 8. The role of the hydrolysed species MOH^+ was studied. Since they do not appear in the species distribution below pH 11 they are not shown in the results in Table 1.

Results and discussion

The complexation of the three ligands **1**–**3** with Zn^{2+}, Cd^{2+}, and Pb^{2+} has been studied by potentiometry and NMR techniques. The fitting of the pH-titration curves with TITFIT[2] has allowed us to determine the species involved in the equilibria as well as their stability constants (Table 1). In order simultaneously to fit the 1:0.9 as well as the 1:1.8 ligand to metal titration curves (batch calculation) the introduction of 2:1 complexes was necessary although a previous investigation[11] of two of these systems did not indicate any such species. The different models used by us and others are the main cause for the large differences in the values found for some of the systems. In the case of **2** with Zn^{2+} the results compare well, since the 2:1 species are of low stability and do not show up in a 1:0.9 mixture. However, when the stabilities of the 2:1 species become higher the discrepancies between our results and those already published become significant (Table 1).

The 1:1 species occur with different protonation degrees (ML, MLH, MLH_2) indicating that in ML either not all basic donor groups are coordinated or that the proton can easily compete for the metal ion. The selectivity of the three macrocycles in forming ML is $Pb^{2+} > Cd^{2+} > Zn^{2+}$ for ligands **2** and **3**, whereas the smaller ring **1** gives $Cd^{2+} > Pb^{2+} > Zn^{2+}$. Interesting is also the observation that ligand **3** is more selective than the other ones, the difference between Pb^{2+} and Zn^{2+} being nearly 6 log units. This might be due either to the fact that Pb^{2+} can achieve higher coordination numbers and ligand **3** can offer up to eight donor atoms, or to the larger cavity of **3** which can better accommodate a large cation such as Pb^{2+} or to both.

The $pK_{H,1}$ values for MLH (Table 1) range from 5.8 to 8.3, being in the lower range for the smallest macrocycle **1** and at the higher side for the largest ring **3**. From an electrostatic point of view this is expected since the distance between the positive charges of the metal ion and that of the proton increases from **1** to **3**. The questions of the structures of the species MLH and in particular where the proton is bound are not easy to answer. It is, however, worth pointing out that all $pK_{H,1}$ values for MLH are larger than the third protonation constant of the ligands which describe the protonation of a phosphonate group.[8] This could indicate that the proton in MLH is sitting at one of the nitrogens, whereas the metal coordinates to the other half of the molecule.

The tendency to form dinuclear species M_2L is not very high but significant. The ligands show for these species the same trend in stability as for ML, the dinuclear Cd^{2+} complex being the most stable for **1** and the Pb^{2+} complex for **2** and **3**. In the case of **3** with Zn^{2+} the pH titration can only be followed up to pH 8 after which precipitation occurs. This indicates a relatively low stability for the 2:1 species M_2L, which in fact could not be observed, although M_2LH_{-1} was found in smaller amounts. The tendency for protonation of M_2L is given but is much smaller than that for ML. All species M_2L can be hydroxylated to M_2LH_{-1} and sometimes even to M_2LH_{-2}, which is observed in the case of **1** and **3** for Cd^{2+} and Pb^{2+}. The formation of mono- and di-hydroxo 2:1 species is an indication that the coordination sites of the metal ions are not completely taken up by the ligand. In fact in the 2:1 species the phosphonate and the amino groups on each side of the macrocycle and the ether oxygen(s) are involved. In M_2LH_{-1} the OH^- group can bind either to one metal or be symmetrically coordinated between the two metal centres as a μ-hydroxo bridge. As an example the speciation of the Cd^{2+} complexes with **1** is shown in Fig. 1. One can see that in the 1:0.9 mixture complexation begins around

pH 4 with the protonated complexes (MLH_2, MLH), that between pH 7 and 10 ML is the main compound and that at pH > 10 the hydrolysed complex MLH_{-1} is formed. In the 1 : 1.8 mixture M_2L is the dominant species between pH 5 and 9, whereas at higher pH the hydrolysed complexes M_2LH_{-1} and M_2LH_{-2} are present.

The pH–NMR studies show that exchange between the ligand and complex is slow on the NMR timescale and that at certain pH a significant line broadening occurs indicating dynamic processes. In all cases the ^{31}P spectra start at low pH with the signal of the "free" ligand, which then disappears with increasing pH to give rise to a new signal at lower field corresponding to that of the metal complexes (Fig. 2a). Thereby the chemical shift of this new peak is pH dependent between pH 4 and 7, as expected since the protonated species MLH_2, which is the first formed, is stepwise deprotonated to give MLH and ML (Fig. 1). For **1** and **3** only one ^{31}P signal is observed over the range studied (Table 2). This implies equivalence of the two phosphonate groups in all metal complexes, either because the species are symmetrical, *i.e.* both phosphonate groups bind to the metal ion, or because of rapid exchange between a structure in which the metal ion, bound on one side of the ring, changes to that with the metal ion on the other side (see below). The observation that in the case of Cd^{2+} and Pb^{2+}, which have isotopes with nuclear spin $I = \frac{1}{2}$, the signals have satellites is clear proof that these metal ions interact with the phosphonate groups. For **2** and Cd^{2+} two phosphonate signals can be observed at high pH, both with satellites due to $^{111}Cd^{2+}$ and $^{113}Cd^{2+}$ (Fig. 3). So both phosphonate groups must be coordinated, but are magnetically not equivalent and exchange slowly on the NMR timescale.

The ^1H NMR spectra as a function of pH show that at the beginning of the titration at low pH the signals of the "free" protonated ligand are present (Fig. 2b). By increasing the pH complexation occurs producing new signals due to the complexes, whereas the ligand signals become weaker. On the NMR timescale the complexation process is slow so that at the same time both sets of signals can be seen. In contrast the equilibria between the different protonated metal complexes are fast so that only one set of resonances for the complexes results. In the case of **1**, for which most of the measurements were done, the relatively simple spectrum of the ligand, consisting in alkaline solution of a doublet (CH_2P) and two triplets (CH_2O, CH_2N),[8] becomes more complicated upon complex formation. Whereas the doublet remains intact (except for satellites in the

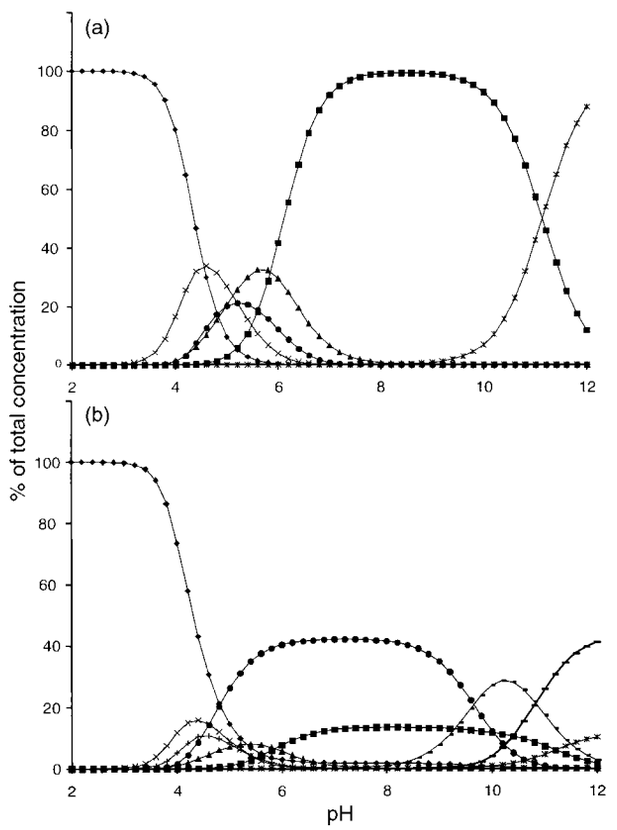

Fig. 1 Calculated species distribution for Cd^{2+} with compound **1**: (a) $[Cd^{2+}] = 5 \times 10^{-4}$ mol dm^{-3}, [ligand] = 5.5×10^{-4} mol dm^{-3}; (b) $[Cd^{2+}] = 1 \times 10^{-3}$ mol dm^{-3}, [ligand] = 5.5×10^{-4} mol dm^{-3}. ◆ M^{2+}, × MLH_2, ▲ MLH, ■ ML, * MLH_{-1}, ● M_2L, + M_2LH, − M_2LH_{-1}, ─ M_2LH_{-2}. Percentages relative to the total amount of Cd^{2+}.

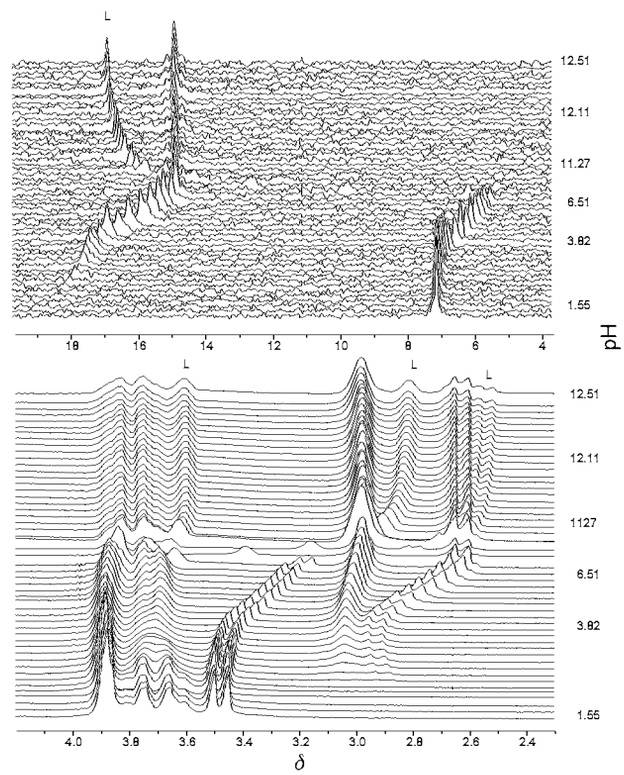

Fig. 2 ^{31}P (a) and ^1H (b) NMR spectra of the Cd^{2+} complexes with compound **1** as a function of pH (L = ligand peaks; $[Cd^{2+}] = 3.56 \times 10^{-3}$ mol dm^{-3}, $[L] = 4.5 \times 10^{-3}$ mol dm^{-3}).

Table 2 ^{31}P chemical shifts in ppm (coupling constants in Hz) of the metal complexes with ligands **1**–**3** in D_2O

	1			**2**	**3**	
Species	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Cd^{2+}	Pb^{2+}
MLH_2						28.39 (br)
MLH					16.86 (42)	27.49 (br)
ML	14.92 (46)	18.96 (42)	14.37	14.50 (48), 14.91 (72)	14.54 (58)	22.97
MLH_{-1}	14.91 (46)		14.38			
M_2L	14.99 (46)					
M_2LH_{-2}	14.03					

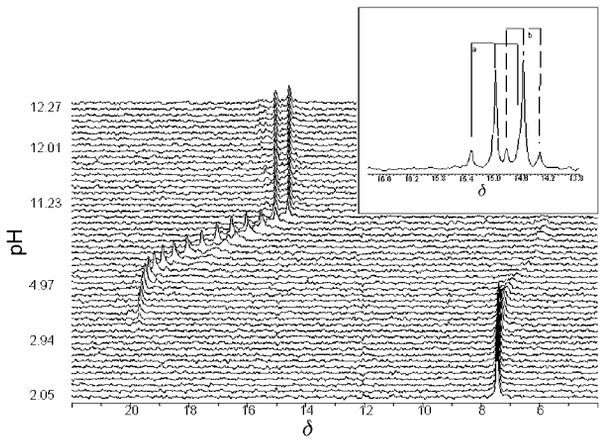

Fig. 3 ^{31}P NMR spectra of the Cd^{2+} complexes with compound **2** as a function of pH. Inset: ^{31}P spectrum at pH 10.6 ($[Cd^{2+}] = 4 \times 10^{-3}$ mol dm^{-3}, $[L] = 4.5 \times 10^{-3}$ mol dm^{-3}) with coupling a = 72 Hz and b = 48 Hz.

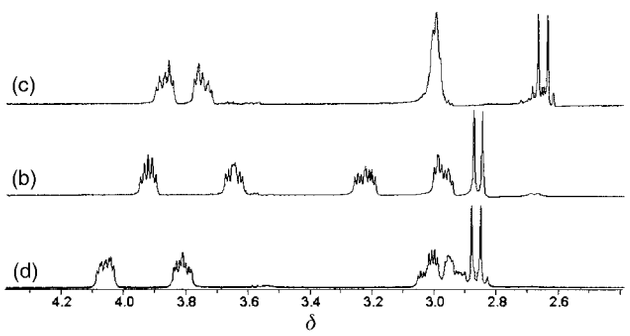

Fig. 4 ^{1}H NMR spectra of the Pb^{2+} (a), Zn^{2+} (b) and Cd^{2+} (c) complexes with compound **1** at pH 12 ($[ML] = 5 \times 10^{-3}$ mol dm^{-3}).

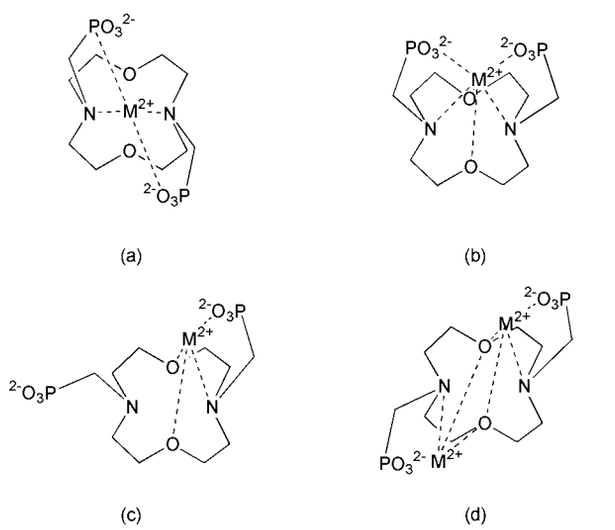

Fig. 5 Suggestions for the structures of ML and M_2L with L = **1**.

case of Cd^{2+} and Pb^{2+}), the two triplets give rise to multiplets which stem from the non-equivalence of the methylene protons in the five membered chelate rings (Fig. 4). If one compares the three metal complexes one finds the largest differences for the CH_2 in α position to the nitrogens, whereas the CH_2 in α position to the oxygens split more or less in the same way.

For the species ML the structures depicted in Fig. 5 can be proposed: (a) metal ion at the centre of the macrocycle with phosphonates coordinated in *trans* position; (b) metal ion sitting atop the macrocycle with phosphonates coordinated *cis*; and (c) metal ion bound to only one half of the macrocycle by two ether oxygens, the amino and the phosphonate group, the other half being not metallated. Whereas structure (a) is

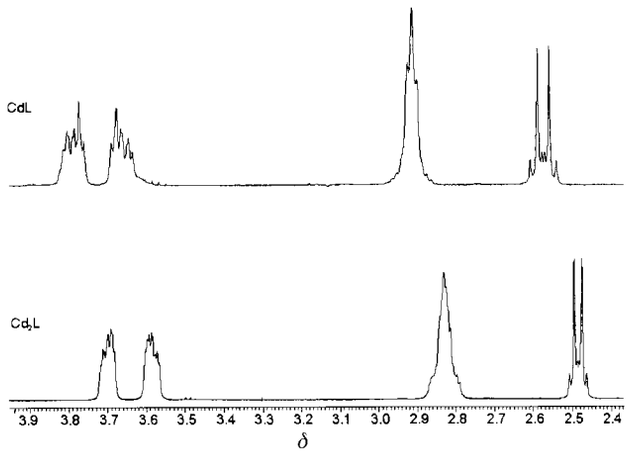

Fig. 6 Comparison of the ^{1}H NMR spectra of CdL and Cd_2L with L = **1** at pH 7 ($[CdL] = 5 \times 10^{-3}$ mol dm^{-3}, $[Cd_2L] = 5 \times 10^{-3}$ mol dm^{-3}).

very improbable since no structures of metal complexes with derivatives of 1,7-dioxa-4,10-diazacyclododecane are known in which the metal ion is sitting in the centre of the ring,[12] the other two possibilities must be analysed in detail. That the phosphonate groups are coordinated is well documented by the observation of satellite peaks in the ^{31}P spectra with Cd^{2+} or Pb^{2+}, both of which have isotopes with $I = \frac{1}{2}$. In (b) the two phosphonates are equivalent and thus give rise to one ^{31}P resonance. In (c) a rapid on/off process could take place and average the two signals of the phosphonate groups. Similarly the fact that in the ^{1}H spectra there is only one signal for the methylene groups in α position to the phosphonate also is an indication that both side chains are equivalent on the NMR timescale.

The ^{1}H NMR spectra of the ethylene bridges have no longer the symmetry observed for the "free" ligand, but can be explained by an ABCD system, which results through the fixation of the ethylene protons in the five membered chelate rings. This strongly speaks for structure (b), with a low interconversion of the ethylene protons. In (c) the rapid movements of the metal ion from one side of the ligand to the other one could average the two forms of the molecule, but one would then perhaps expect an A_2B_2 spectrum similar to that of the "free" ligand.

Interesting is that for the 2:1 complex of ligand **1** the ^{1}H NMR spectrum is very similar to that of the 1:1 species ML, although the chemical shifts are different (Fig. 6). For M_2L we propose structure (d) with a structurally fixed macrocycle so that an ABCD spectrum results for the ethylene protons.

For ligand **2** we have studied the Cd^{2+} complex (CdL) which shows two ^{31}P resonances both with satellites. A very unsymmetrical structure is therefore expected and this is in fact also shown by the ^{1}H NMR spectrum. There are several very complicated multiplets in the ranges δ 4.05–3.60, 3.35–3.00 and 3.00–2.40, which do not allow one to associate signals with specific protons in the structure.

The ^{31}P and ^{1}H NMR spectra of the Zn^{2+}, Cd^{2+}, and Pb^{2+} complexes with compound **3** are all relatively broad. In the ^{31}P spectra all complexes show only one resonance (in the case of Cd^{2+} with satellites) at alkaline pH (Table 2). In the ^{1}H spectra of the Pb^{2+} complexes one can observe that the resonances are pH dependent and that at pH 12 a non-well structured spectrum with a doublet at δ 2.72 and 2.75 (intensity 4, CH_2P) and three broad multiplets (each of intensity 8) at δ 2.94 (CH_2N), 3.74 and 3.81 (CH_2O) are present, from which no structural data, however, can be derived.

In conclusion we can say that the combination of pH titrations and NMR spectra is a very powerful method to study metal complexes, to determine their stoichiometry and stability but also to gain information on their structure.

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