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Coordination of Cd(II) by *N*-alkylamino sugars in aqueous solution as studied by potentiometry and NMR spectroscopy

Hendrik Lammers, Herman van Bekkum, Joop A. Peters *

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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Abstract

The Cd(II) coordination of 1-(2-aminoethylamino)-1-deoxy-D-alditols (**1a–b**) and of 1-(2-aminopropylamino)-1-deoxy-D-alditols (**2a–b**) was investigated by means of ^{113}Cd NMR spectroscopy and potentiometry. The influence of the sugar chains on the basicity of the amino groups was determined with ^{13}C chemical shift pH titration curves. It appears that the inductive effects of the sugar moieties give rise to a decrease in pK_a of the secondary amino function. The Cd(II) stability constants for ligands **1a–b** and **2a–b** and the Ni(II) stability constants for **1a** were determined by potentiometry. ^{113}Cd NMR spectroscopy was employed to study the structures of the Cd(II) complexes of **1a–b** and **2a–b**. From the ^{113}Cd chemical shifts for CdL and CdL_2, it could be concluded that at neutral pH both primary and secondary nitrogen atoms are involved in coordination. ^{13}C NMR shows that additional coordination of a hydroxyl group of the carbohydrate chain occurs at high pH (pH 12). © 1996 Elsevier Science Ltd.

Keywords: Metal ion sequestration; ^{113}Cd NMR; ^{13}C NMR spectroscopy; 1-Alkylamino-1-deoxy-D-alditols; Ni(II) complexes

1. Introduction

The growing demand for application of renewable resources for industrial products has lead to an increasing interest in clean procedures to derivatize carbohydrates. Reductive amination of reducing sugars is an attractive and versatile procedure for the

* Corresponding author.

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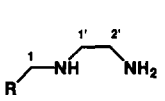
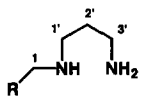
synthesis of *N*-alkyl substituted amino sugars, which are generally readily biodegradable and do not cause skin irritating effects. Therefore, they are being studied as new components for detergents and cosmetics [1]. Further potential applications are as surfactants [2], polymers [3], sweeteners [4], and as liquid crystalline compounds [5].

Recently, we described the synthesis of 1-(2-aminoethylamino)-1-deoxy-D-alditols (**1a–b**) and 1-(2-aminopropylamino)-1-deoxy-D-alditols (**2a–b**) by reductive amination of D-galactose and D-mannose with ethylenediamine (*en*) and propylenediamine (*tn*), respectively, using platinum (5%) on activated carbon as the catalyst [6]. The resulting products may have good chelating properties, particularly for transition metal ions. Sequestering of these ions is of importance in various technological applications, such as in cleaners, in pulp and paper industry, and in photography.

The present paper describes the coordination of Cd(II) and Ni(II), which are considered to be typical representatives of the transition metal ions, by these compounds. The protonation constants of the amino groups, which reflect the affinity of these groups for metal ions were evaluated with ^{13}C NMR spectroscopy and potentiometry. Stability constants of Cd(II) and Ni(II) complexes with **1a–b** and **2a–b** were measured with potentiometry. The structures of the Cd(II) complexes of **1a–b** and **2a–b** were investigated in more detail by ^{113}Cd and ^{13}C NMR spectroscopy. It is shown that the hydroxylic groups of the sugar moiety are involved in the coordination of the transition metal ion at high pH (pH > 12).



1a-c



2a-c

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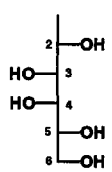
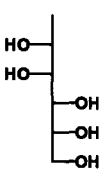


a



b

c

2. Results and discussion

Protonation.—In Figs. 1 and 2, the ^{13}C NMR chemical shift pH titration curves of **1a** and **2a** are presented. Similar plots were obtained with ligands **1b,c** and **2b,c**. The protonation shifts ($\Delta_C = \delta$ protonated form $- \delta$ free base) are upfield, which agrees

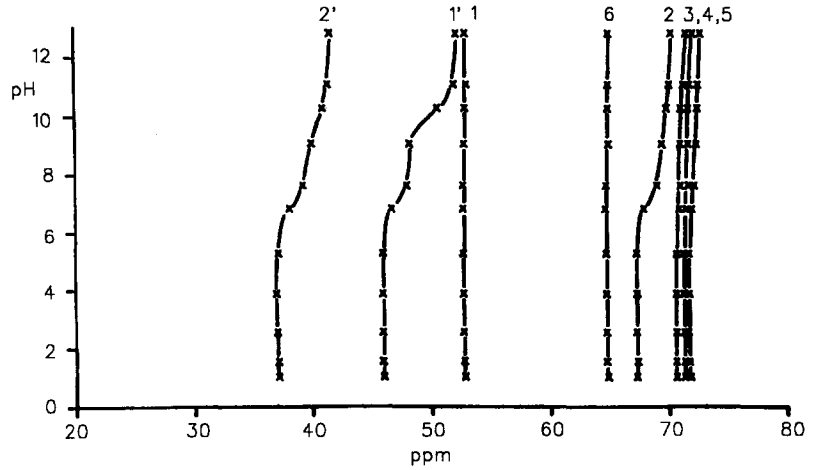


Fig. 1. ^{13}C NMR pH titration curve of a 0.02 M solution of **1a** measured at 50.3 MHz and 293 K.

with the generally observed trend [7,8]. Protonation of the nitrogen atoms has a relatively large influence on ^{13}C chemical shifts of β-positioned carbon atoms owing to electrical field effects [7,8]. Protonation of **1a** occurs initially at the primary amino function as shown by a $\Delta_{C\text{-}1'}$ of -5.9 ppm and relatively small protonation shifts of the ^{13}C nuclei of the sugar chain. Subsequent protonation of the secondary amino function causes substantial shifts of both C-2 ($\Delta_{C\text{-}2} = -2.7$ ppm) and C-2' ($\Delta_{C\text{-}2'} = -4.2$ ppm). The ^{13}C chemical shift titration curve of **2a** (see Fig. 2) shows a large protonation shift of C-2' ($\Delta_{C\text{-}2'} = -7.1$ ppm) because of a double β-effect. Protonation of the secondary amino function results in a protonation shift of C-2 of -2.6 ppm. The pK_a values of the various groups were determined by applying the Henderson–Hasselbach equation [9]

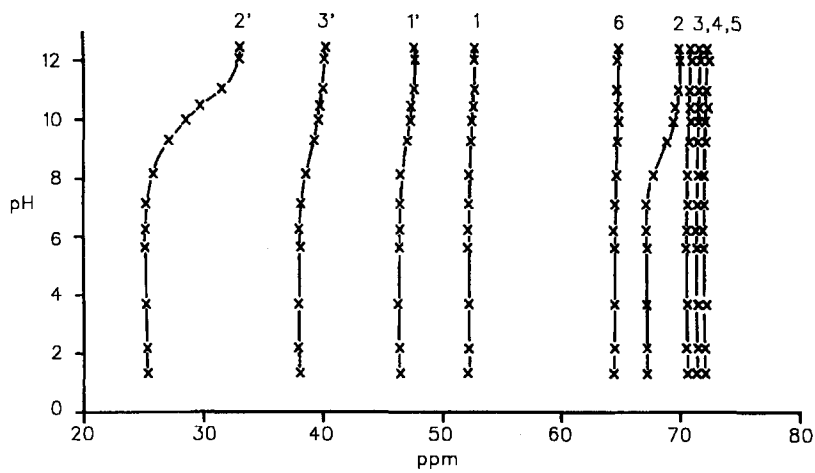


Fig. 2. ^{13}C NMR pH titration curve of a 0.02 M solution of **2a** measured at 50.3 MHz and 293 K.

Table 1
Protonation constants as determined by NMR (measured at 50.3 MHz, $I = 0.25$ M and 295 K) and potentiometry (measured at 295 K and $I = 0.1$ M)

Compound	Method	pK_{a1} [a]	pK_{a2} [a]	ΣpK_a
1a	NMR [b]	9.9	7.2	16.7
	potentiometry [c]	9.48	6.39	15.87
1b	NMR	9.7	7.3	16.6
	potentiometry	9.27	6.59	15.86
1c	NMR	9.8	6.6	16.0
	potentiometry [d]	9.59	6.64	16.23
2a	NMR	10.6	8.9	19.1
	potentiometry	10.63	8.46	19.09
2b	NMR	10.5	8.6	19.0
	potentiometry	10.75	8.52	19.27
2c	NMR	10.3	8.0	17.9
	potentiometry [d]	10.19	7.95	18.14
en	potentiometry [d]	10.0	7.1	17.1
tn	potentiometry [d]	10.5	8.7	19.2

[a] pK_{a1} is assigned to the deprotonation of the primary amino function, and pK_{a2} to that of the secondary one (see text).
[b] Error ± 0.1.
[c] Error ± 0.05.
[d] Ref. [10].

to the δ values near the point of inflection in the ^{13}C NMR titration curves. In Table 1, these pK_a values are compared with values obtained by potentiometry. It can be seen that the agreement is very good.

Comparison of the pK_a values of ethylamine and ethanolamine (10.81 and 9.50, respectively [10]) shows that introduction of a β-hydroxyl group generally results in a decrease of the pK_a. For all ligands under study, the pK_a of the secondary amino function appears to be lower than that of the primary amino function due to inductive effects caused by the 2-hydroxyl group. The pK_{a1} values of **1a–c** and **2a–c** are similar to those of ethylenediamine (*en*) and trimethylenediamine (*tn*), respectively, which indicates that the substituent effect on the primary amino function for all these compounds is of the same order of magnitude. Furthermore, the data show that the configuration of the carbohydrate chain, either D-*galacto* or D-*manno*, does not affect the protonation.

Metal ion sequestering capacities.—A practical way to obtain information on the complexation behaviour and crystal growth inhibition is to carry out metal ion sequestering experiments. The Cd(II) sequestering capacities (CdSC) at ambient temperature and pH 11.6 are presented in Table 2. Ligands **1a–b** possess good CdSC abilities in comparison to **2a–b**. This can be ascribed to a decrease in complex stability of the Cd(II) complexes, caused by increase of the chelate ring size from five- to six-membered as the result of an enthalpy effect [11]. The corresponding model compounds **1c** and **2c** show comparable CdSC properties.

The ligand stability constants for Cd(II) of the ligands under study and their

Table 2
Cd(II) and Ni(II) stability constants [a] and Cd(II) sequestering capacities (CdSC) [b] of **1a–b**, **2a–b**, **1c**, *en* and *tn* as determined by potentiometry at 295 K and $I = 0.1$ M

Ligand	Cd(II)				Ni(II)		
	log β_1	log β_2	log β_3	CdSC	log β_1	log β_2	log β_3
1a	4.54	8.41		224 [c] (0.4) [d]	6.01	10.70	
1b	5.24	9.97		279 (0.6)			
1c [e]	4.9	9.2		650 (0.6)	6.8	12.4	
2a	4.31	7.68		82 (0.2)			
2b	4.50	7.63		68 (0.1)			
2c				175 (0.2)			
en [e]	5.45	9.98	11.74		7.3	13.5	17.7
tn [e]	4.50	7.20	8.0				

[a] $\beta_1 = [ML]/[M][L]$, $\beta_2 = [ML_2]/[M][L]^2$, and $\beta_3 = [ML_3]/[M][L]^3$.
[b] Measured at pH 11.6 and 295 K.
[c] mg Cd/g ligand.
[d] mol Cd/mol ligand.
[e] Ref. [10].

corresponding structural analogues as determined by potentiometry are included in Table 2. The Cd(II) stability constants of **1a** obtained in this way are in excellent agreement with those measured by ^{113}Cd NMR speciation [12]. The complexation constants β_{CdL} and β_{CdL2} of the equilibrium shown in eq (1), are defined in eqs (2a–b).

$$Cd + nL \leftrightarrows CdL_n \ (n = 1, 2) \tag{1}$$

$$\beta_{CdL} = [CdL]/[Cd][L] \tag{2a}$$

$$\beta_{CdL_2} = [CdL_2]/[Cd][L]^2 \tag{2b}$$

There is generally a linear correlation for a series of complexes of a particular M^{n+} ion between ΣpK_a of (multiprotic) ligands (L) and the logarithm of the stability constant β. Comparison of the Cd(II) stability constants of **1a–b** and **2a–b** with those of the parent compounds *en* and *tn*, respectively, shows that **1a** has an exceptional complexation behaviour. The Cd(II) stability constants of **1a** are substantially lower than those of **1b** and *en*, although the ΣpK_a values of all these ligands are similar. This is most likely due to steric effects. The Cd(II) stability constants of **1c** are in between those of **1a** and **1b**. By contrast, **2a**, **2b**, and *tn* (which have similar ΣpK_a values as well) do not have significant differences in Cd(II) stability constants. Apparently, the above described conformational preference involved in the complexation of Cd(II) does not occur in this type of ligands.

The ligands **1a–b** and **2a–b** form complexes with 1:1 and 1:2 metal:ligand stoichiometries; 1:3 complexes are not observed. Probably, the stability of the latter complexes is low due to steric interactions between the polyhydroxy chains. In the parent systems (*en* and *tn*), however, the 1:3 complexes do occur. The magnitude of the stability constants of the 1:1 and 1:2 Cd(II) complexes of the sugar derivatives are the same as those of *en* and *tn*, which indicates that the coordination of Cd(II) is similar for

Table 3
^{113}Cd chemical shifts (ppm) of Cd(II) complexes of **1a–c** and **2a–b** [a] measured at 88.7 MHz and 295 K

Ligand	pH	CdL	CdL_2
1a	7.5	110	240
1a	12.2	231	277
1b	7.5	108	242
1c	7.5	108	239
2a [b]	7.5		209
2b [b]	7.5		212
Model A [c]		126	216
Model B [c]		206	292

[a] 0.1 M $Cd(ClO_4)_2$ is used as external reference.
[b] CdL species could not be observed for **2a–b**.
[c] Calculated chemical shifts (see text), model A: both N atoms of the ligand are bound to Cd(II), model B: as model A but with additional binding of OH^- or an ionized sugar hydroxyl function.

these ligands; probably all ligands coordinate with Cd(II) in a bidentate fashion via the two N atoms.

The ligand stability constants for Ni(II) complexes of **1a**, **1c** and *en* are about two orders of magnitude larger than those of the corresponding Cd(II) complexes (see Table 2). The trends observed among these stability constants, however, are the same as among the Cd(II) complexes [13].

^{113}Cd and ^{13}C NMR spectroscopy.—The observed ^{113}Cd chemical shifts for complexes of ligands **1a–c** and **2a–b** in D_2O solution are presented in Table 3. In the ^{113}Cd NMR spectrum of **1a** at Cd(II)/L molar ratio $\rho = 1$ and pH 7.5, three signals are observed at 0, 110, and 240 ppm. Upon altering ρ between 0 and 2, the chemical shifts of these signals do not change, showing that the corresponding species are in slow exchange on the ^{113}Cd NMR time scale. Based on the intensities of the signals as a function of ρ, these signals are assigned to free Cd, CdL, and CdL_2, respectively.

Owing to precipitation occurring at higher ρ values ($0.6 < \rho < 2$) ^{113}Cd spectra (pH 7) could only be obtained at lower ρ values ($\rho < 0.5$) for **2a** and **2b**. Then a single signal is observed at 240 ppm. Upon altering ρ, the chemical shift of this signal does not change and no other signals are observed, indicating CdL_2 to be the only cadmium complex present.

Summers et al. have shown that the ^{113}Cd chemical shifts of complexes with ligands containing N-donor atoms in D_2O solution can be estimated by eq (3) [14,15]:

$$^{113}\text{Cd chemical shift} = 75A + 51B + 31C - 30D \quad (3)$$

where A, B, and C are the numbers of primary, secondary, and tertiary amino donors, respectively, and $D = 0$ for less than 4-non-O donors and 1 for 4 or more non-O donors. This relationship has been successfully applied to a series of Cd(II) complexes, including those of *en* and *tn* derivatives. The chemical shifts observed for CdL and CdL_2 complexes of ligands **1a–c** and **2a–b** (see Table 3) agree well with values estimated for complexes in which both the primary and secondary nitrogen atoms are involved in coordination (Table 3, model A), which supports the conclusions based on potentiometry (see above).

The pH dependence of the NMR spectra of Cd(II) complexes of ligand **1a** was studied in some more detail. Upon increasing the pH of a solution of **1a** at $\rho = 1$ (starting pH 7.5) initially causes precipitation, but upon further increasing the pH up to 12.2 the precipitate dissolves again and a clear solution results. Several signals between 225 and 240 ppm are observed by ^{113}Cd NMR in this sample. At $\rho = 0.75$ and pH 12.2, two ^{113}Cd signals at 231 and 277 ppm, respectively, are observed. Upon further lowering of ρ, the intensity of the ^{113}Cd signal at 277 increases at the expense of that at 231 ppm. The chemical shifts of these signals do not change, suggesting these species to be in slow exchange on the ^{113}Cd NMR time scale. Based on the intensities as a function of ρ, they are assigned to CdL and CdL_2, respectively. The chemical shifts of these species are higher than calculated with eq (3) assuming that only the primary and secondary nitrogen atoms are involved in the coordination (Table 3, model A). This suggests that an OH^- or an ionized hydroxyl group are involved in the coordination. The ^{113}Cd chemical shift increment for these functions in solution is unknown. The ^{113}Cd chemical shift of solid $Cd(OH)_2$ is 158 ppm and it has been shown that ^{113}Cd chemical shifts in the solid state and in solution are identical [16,17]. Therefore, the shift increment for a HO^- or RO^- function can be estimated to be about 80 ppm. Comparison of experimental and calculated chemical shifts (see Table 3) shows that ionization of Cd(II)-bound water or additional coordination of an (ionized) hydroxyl group of the sugar chain could explain the experimental data. Coordination of both the nitrogen atoms and an ionized sugar hydoxyl group is further shown by ^{1}H–^{113}Cd heteronuclear multiple quantum correlation (HMQC) spectroscopy of a solution at $\rho = 0.66$ and pH = 12.2, which shows cross peaks with the protons of the ethylenediamine unit, the 1-methylene group, and in addition to that a weak cross peak in the sugar region. Due to extensive overlap of the ^{1}H resonances of the sugar chains and exchange broadening, no further assignment of the concerning protons could be made.

The conclusions, based on ^{113}Cd NMR, regarding the coordination of these ligands were substantiated by ^{13}C NMR (see Table 4). Spectra of **1a** at $\rho = 0.4–1$ and at pH 7.5 showed one set of 8 signals indicating the present Cd species and free ligand to be in fast exchange on the ^{13}C NMR time scale. All resonances show a shielding with respect to the free ligand at pH 12. Those of sugar C-1, C-3–C-6 signals are relatively small (< 0.4), whereas the induced shifts of C-2 and C-1′, C-2′ are significant. The relative magnitudes of these induced shifts and the direction are comparable with those upon protonation, which supports the conclusion that both the N atoms are bound to Cd(II). Two-bond ^{13}C–^{113}Cd scalar couplings are usually small and could, unfortunately, not be observed in the ^{13}C NMR spectra. A ^{13}C NMR spectrum of a sample at $\rho = 1$ and pH 12.2 shows several sets of relatively broad signals. At lower ρ values ($\rho < 0.5$), however, two sets of eight resonances are observed at this pH. Based on the intensities obtained at various ρ values one set of signals is assigned to CdL. The other set of signals is assigned to an equilibrium of a CdL_2 species and free ligand, which are in fast exchange on the ^{13}C NMR time scale. One of the ^{13}C resonances in the sugar window (76.7 ppm, see Table 4) assigned to CdL is relatively far downfield compared to the corresponding carbon signals (69.9–72.3 ppm) of free ligand at pH 12.2. This shows that one of the hydroxyl groups of the polyhydroxy chain in the CdL complex is coordinated to Cd(II) under these conditions. The Cd(II) induced shifts in nuclei of the

Table 4
^{13}C chemical shifts (ppm) of **1a** (L) in the absence and the presence of Cd(II) at 298 K

Nucleus	pH 12	pH 7		pH 12	
	L	CdL [a]	CdL_2 [b]	CdL [c]	CdL_2 [c]
1′	52.19	49.33	48.85	47.51	51.10
2′	41.42	39.78	39.48	41.28	40.89
1	52.95	52.61	52.65	54.29	53.29
2	70.19	68.74	68.55	69.90	70.06
3 [e]	71.44	71.25	71.13	72.24	72.16
4 [e]	72.02	71.63	71.61	73.94	72.16
5 [e]	72.72	72.51	72.39	76.67	72.98
6	64.85	64.68	64.72	64.87	64.78

[a] Fast exchange between Cd(II) species. Data obtained at $\rho = 1$.
[b] Fast exchange between Cd(II) species. Data obtained at $\rho = 0.71$.
[c] Slow exchange between CdL_2 and other Cd(II) complexes.
[d] Fast exchange between CdL_2 and L. Data obtained at $\rho = 0.42$.
[e] The assignments of nuclei 3, 4, and 5 may be interchanged.

sugar chain of the CdL_2 complex, however, are much smaller, which suggest that in that complex the sugar chains are not involved in the coordination. Steric effects can account for that. Most likely, in the latter complex a Cd(II) bound water molecule is ionized.

The pK_a of water decreases by about 5 pK_a units upon coordination to Cd(II) [24,25]. A similar effect occurs upon coordination of a hydroxyl group of an alcohol [25]. Apparently, significant coordination of a sugar hydroxyl function of ligand **1a** only occurs with its concomitant ionization. Obviously, the magnitude of the pK_a decrease is also somewhat dependent on the presence of other ligands around Cd(II) ion, since these affect the charge density at the metal ion. This explains why bound water in the resulting CdL complex do not ionize. Similar effects have previously been observed in a study on the effect of pH on the coordination of 2-amino-2-deoxy-D-gluconate, where at low pH the amino and carboxylate groups are coordinated and at elevated pH (10.7) additional coordination of the C-3 hydroxyl group was observed [26].

3. Experimental

Materials.—The organic reagents used were purchased from Janssen Chimica (Analytical Grade). $Cd(ClO_4)_2 \cdot xH_2O$ was obtained from Alfa Products. The Cd content of $Cd(ClO_4)_2 \cdot xH_2O$ was determined using complexometric methods [18]. The synthesis of **1a–b** and **2a–b** has been published elsewhere [6]. These compounds were purified by recrystallization from 1:9 MeOH–H_2O.

Potentiometry.—The potentiometric titrations were conducted at 298 K in a double-walled vessel. Millivolt readings obtained with a glass electrode were converted to pH values using a calibration curve, which was determined from standard buffer solutions. The ionic strength was maintained at 0.1 M using $NaClO_4$. The protonation constants were determined by titration of a 0.01 M ligand solution with 0.02 M HCl. The Cd(II)

and Ni(II) stability constants were determined by titration of 0.01 M $Cd(ClO_4)_2$ or 0.01 M $NiCl_2$ with a 0.01 M ligand solution. All calculations for the potentiometric titrations were performed using a spreadsheet program [19,20]. The speciation and the stability constants were determined for each point in the titration. The obtained stability constant was used in a speciation simulation generating pH values. Always good agreement between the calculated and the experimental pH curve was observed.

Cadmium(II) sequestering capacities.—The Cd(II) sequestering capacities were determined according to a procedure of Mehltretter et al. [21] modified by Akzo Chemicals Research Center in Deventer, The Netherlands [22]. The CdSC values were obtained by adding a 0.1 M $Cd(ClO_4)_2$ to a solution containing 100 mg ligand at room temperature and pH 11.6 using $NaOH/Na_2CO_3$ as the indicator. The point at which the turbidity remained for more than 30 s was taken to be the endpoint of the titration.

NMR spectroscopy.—The ^{13}C NMR spectra were recorded at 295 K on a Nicolet NT-200 WB NMR spectrometer (50.3 MHz) and on a Varian VXR-400 S NMR spectrometer (100.6 MHz) using 98% D_2O (for locking) in water as the solvent with *t*-butanol ($\delta = 31.2$ ppm) as the internal reference. The ^{13}C spectra were recorded using 16K datapoints, a spectral width of 12 KHz, broadband ^1H decoupling and an acquisition delay of 10 s. For ^{13}C NMR 0.02 M solutions of amine were used. The pH was adjusted to 1 using 1 M HCl. Subsequently, the pH was raised from 1 to 12 in intervals of approximately 1 using 1 M NaOD. The pD was measured with a calibrated Z11,344-1 Aldrich combination pH electrode. In the ^{13}C NMR chemical shifts titration curves pH values are used which were obtained by a correction (pH = pD − 0.4) of the pD values.

The ^{113}Cd NMR spectra were recorded on a Varian VXR-400 S NMR spectrometer at 88.7 MHz using 48K datapoints, a spectral width of 50 KHz, and 0.1 M $Cd(ClO_4)_2$ as an external reference. A 60° pulse was applied and the acquisition delay was 2.5 s. Solutions were prepared by dissolving the appropriate amounts of $Cd(ClO_4)_2 \cdot xH_2O$ and ligand in D_2O. The total Cd(II) concentration was 0.1 M. The pH was adjusted to 7 using diluted solutions of 60% aqueous $HClO_4$. The ionic strength was approximately 0.25 M. The $^1H-^{113}Cd$ correlated spectra were obtained with the HMQC method [23].

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