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Lateral *cis*-1,3,5,7-Tetraazadecalin Podands and their Complexes: Synthesis, Structure, and Strong Binding with Pb(II) and Other Heavy Metal Ions

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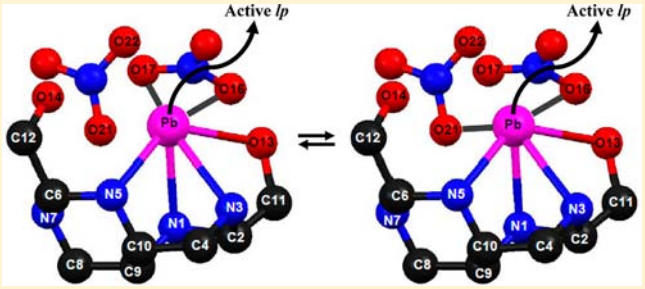
Supporting Information

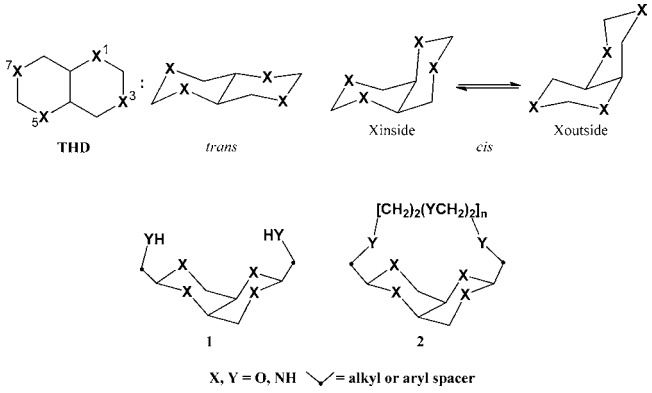
ABSTRACT: The chemistry and complexation behavior of diaminal podands based on *cis*-1,3,5,7-tetraazadecalin (*cis*-**TAD**) were elaborated, reassessed, and extended. The synthesis of 2,6-bis(hydroxymethylene)-*cis*-TAD (**9**) and 2,6-bis(α,α'-dimethyl-β- hydroxyethyl)-*cis*-TAD (**10**) as well as of suitably substituted 2,6-diaryl-*cis*-TAD podands is laid out. For the latter, the effect of electron donating or withdrawing substituents on the benzaldehyde reagents was examined while **9** and **10** were probed and showed considerable propensity for heavy metal-ion chelation. The [Cd^{II}·(**9**)] and [Pb^{II}·(**9**)] complexes stood out indeed, and their structure and properties show a particularly interesting 5-amino-1,3-diazane chelation type and strong ligand-ion binding mode, with intramolecular donor exchange in solution, all strongly influenced by the anomeric effect in the ligand.



INTRODUCTION

In our continuing studies of new 1,3,5,7-tetraheterodecalin (**THD**) stereoisomeric systems (Scheme 1) we had particularly aimed at generating novel supramolecular host systems based on the *cis*-1,3,5,7-THD dissymmetric (C_2) species, which exhibit multiple stereoelectronic effects, intrinsic chirality, and predisposition to intermolecular interactions. The rationale of the latter is the occurrence of a cavity with a built-in high electron lone pair concentration, in any podand (**1**) or macrocycle (**2**) having a *cis*-Xinside-THD core (Scheme 1, bottom).

Scheme 1. 1,3,5,7-Tetraheterodecalin (THD) Diastereomers (top) and the *cis*-THD Podands (1) and Macrocycles (2)



In this framework we had described the synthesis, as well as structural, physical, and chemical attributes (backed up by in-depth theoretical/computational analysis) of a large variety of systems: the *cis*-1,3,5,7-tetraoxadecalin (TOD) podands and macrocycles (Scheme 1, X = O),[1] the respective *cis*-1,3,5,7-diaazadioxadecalin (DADOD) and -dioxadiazadecalin (DODAD) (Scheme 1, X = NH, X′ = O and X = O, X′ = NH, respectively),[1b,c] and the *trans*- and *cis*-1,3,5,7-tetraazadecalins (TAD) (Scheme 1, top, X = NH).[2] We have briefly reported in an early short communication[2a] on some representatives of the latter, double diaminal (TAD) case, followed by a juxtaposition of theoretical/computational data with those secured in experimental/stereochemical studies.[2b] We now elaborate, reassess, and extend our findings on those and additional 2,6-substituted *cis*-1,3,5,7-TAD podands with suitably functionalized termini on the side arms (**1**, X = NH) and their metal complexes, anticipating also that these podands would be, with suitable bridges, good precursors of corresponding macrocyclic host systems with ability of inclusion of metal ions and of potential chiroselective catalytic activity.[1c]

The high and persistent interest, since the related pioneering studies of Lehn, Cram, and Pedersen,[3] in the design of ligand shape and cavity size, which are of particular consideration for monitoring and extracting toxic metal ions such as Cd(II) and Pb(II), has led to a variety of preorganized ionophores, such as

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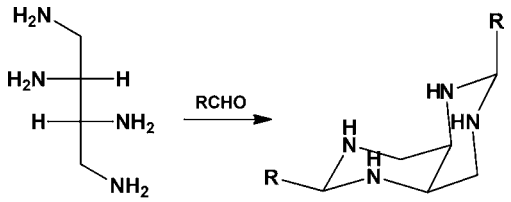
macrocycles,[4] cryptands,[5] and other ligands with high level of preorganization[6] as well as the construction of our other aza-crowns and aza-macrocycles bearing functionalized pendant arms that contain additional donor atoms[7] (see also below). The latter type demonstrated enhancements in the cation binding ability, selectivity, and high coordination number. Notwithstanding, there is a lack of systematic rationalization and understanding of the coordination chemistry of both Cd(II) and Pb(II), *which is not bounded by the requirement constraints for a particular conformation, nor for a specific donor atom type*. Indeed, the coordination number of most Cd(II) and Pb(II) complexes range between 3 and 10, with many and mixed donor atom types (O, N, or S).[8] Another point of interest in the Pb(II) coordination chemistry is the occurrence of the so-called "inert-pair effect",[9] viz. the ability of the pair of the outer shell of electrons on Pb^{II} ($[Xe]4f^{14}5d^{10}6s^2$) to participate in the coordination bond formation.[10]

Thus we now present an in-depth study demonstrating considerable propensity for heavy metal-ion chelation. The Cd^{II} and Pb^{II} complexes were investigated by X-ray analysis, showing a particularly interesting 5-amino-1,3-diazane chelation type and unique ligand-ion binding mode. These observations are corroborated by the heavy nuclei VT NMR study. The close agreement between the results obtained by polarography and ^{113}Cd or ^{207}Pb NMR is remarkable as it gives a clear indication of the stabilities of the complexes.

RESULTS AND DISCUSSION

cis-TAD podands were prepared stereospecifically (Scheme 2) following a known routine,[3] by condensation of *threo*-tetraaminobutane (**3**) with suitably functionalized substituted aldehydes. While transforming the carbonyl function into the corresponding aminal system and to keep the functional group on the aldehyde reactant inert to amine displacement reactions, we sought α- or β-substituted aldehydes with chemically inactive (or masked) functions, to be followed by activation of the termini by chemical manipulation. The simplest models are our earlier reported[2b] 2,6-dialkyl- and 2,6-diphenyl-*cis*-1,3,5,7-TAD derivatives (**4**) (Scheme 2, R = Me, Et, and Ph).

Scheme 2. Preparation of 2,6-Substituted *cis*-TAD Derivatives from D-Tetraaminobutane and Suitably Substituted Aldehydes



3 4

Since tetraaminobutane is all but insoluble in aprotic media we used protic solvents (except water,[11] which reduces the yields and purity of the products) at ambient temperature. Clean products with high yields and selectivity were thus obtained; i.e., only tetraazadecalins[2a] and none of the possible bis(5-imidazolidines) or 1,3-diazolano-1,3-diazepane structures were isolated. Ring−chain tautomeric equilibrium products, *viz.* Schiff-bases (as observed in related systems)[12,13] were also absent.

To attain functionalized 2,6-diaryl-1,3,5,7-TAD derivatives, we examined the influence of electron donating or withdrawing substituents on the behavior of various benzaldehydes toward *threo*-tetraaminobutane (**3**). Reactions were performed in methanol at ambient temperature and with different substituted benzaldehydes (Scheme 3), to discern substituents which lead to 2,6-diaryl-*cis*-TADs from those which provide open-chain structures. In all cases, condensation reactions occurred smoothly under mild conditions.

Thus, benzaldehydes with electron releasing substituents ($-NH_2$, $-OH(R)$) reacted slowly, with dehydration of the aminocarbinol intermediate, to give tetrakis-imine Schiff-bases (Scheme 3, part I-i: **5a**,**b**). These results are in agreement with earlier conclusions[12−14] in related tautomeric systems; namely, such electron donating substituents accelerate the dehydration step and stabilize the C═N bond and are expected, therefore, to hinder the ring-closing step and to form stable conjugated Schiff-bases. In addition, intramolecular hydrogen bonding had been found to stabilize the open-chain Schiff-base structure.[15]

In contrast, benzaldehydes with electron withdrawing substituents (−CN, −NHAc) reacted rapidly to yield the corresponding diaminal system (Scheme 3, part I-ii: **6a**,**b**), indicating that the carbinolamine intermediate underwent either rapid intramolecular −OH displacement by a second amine or dehydration to the Schiff base, followed by rapid intramolecular amine addition to the C═N bond. A striking new structure (**7**) in this series of experiments was obtained with salicylaldehyde (Scheme 3, part I-iii) by intramolecular amidation within the *cis*-tetraazadecalin structure, as proven by elemental analysis, NMR, and mass-spectrometric evidence. Thus, EI-MS and FAB-MS showed molecular peaks, *viz.*, 460 [M^+] or 461 [MH^+], respectively. A strong absorption band at 1690 cm^{-1} in the IR spectrum corresponds to five-membered tertiary lactams, in contrast to the expected[16] absorption band of ArCOOH in the range 1710−1760 cm^{-1}; the OH streching absorption band at 3550 cm^{-1} was also absent. ^{13}C NMR spectrum revealed a characteristic amide signal at δ 166 ppm, and ^1H NMR showed a distinct doublet at δ 5.20 ppm with a large $^3J_{NH\text{-}H2,6}$ = 10.0 Hz, owing to the axial position of the NH bond in a highly rigid system.

The reactions of (*rac*)-1,2,3,4-tetraaminobutane (**3**) with the strong EWG reagents *o*-, *m*-, and *p*-nitrobenzaldehyde at a 1:2 molar ratio, provided the corresponding 2,6-bis(nitrophenyl)-*cis*-TAD products (**6′**) in high yields (Scheme 3, part II). No evidence of ring−chain tautomerism, i.e., no Schiff-base intermediates were obtained, as long as a molar ratio of reactants of 1:2, was maintained (Table 1). Thus, in the case of Ar′ = *o*-nitrophenyl (Table 1), slow addition of *o*-nitrobenzaldehyde to **3**, viz., from 1:1 to higher mole equivalents of aldehyde, revealed the gradual occurrence of the monoaminal intermediate (Scheme 3, part II). As more aldehyde was added, substance **8** gradually appeared becoming the major product at 1:3 ratio (as indicated by both ^1H and ^{13}C NMR spectra including NOE) cf. **8** (Scheme 3, part II), and finally, the tetrakis-imino product (*o*-**5′**) was the major product at a ratio of 1:4 and up. The ^{13}C NMR spectrum of *o*-**6′** contained only nine signals, as expected of a *cis*-TAD C_2-symmetrical structure, whereas the ^{13}C NMR spectrum of **8** reflected the nonsymmetrical structure of the molecule with 25 carbon signals, all of which could be assigned unambiguously, on the basis of chemical shift and DEPT experiments. IR spectroscopy was also of diagnostic value in identification of **8** and *o*-**5′**.

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Scheme 3. (I) Reactions of 3 with Various Substituted Benzaldehydes (2 equiv) and (II) Reactions of 3 with *o*-, *m*-, and *p*-Nitrobenzaldehyde Following Stepwise Addition up to 4 Equivalents

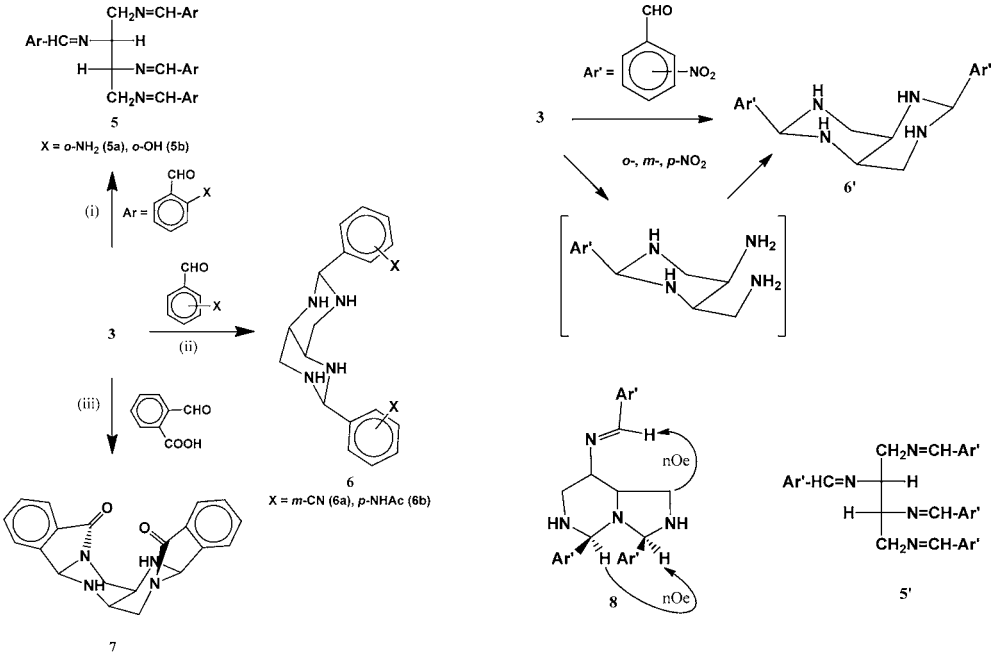


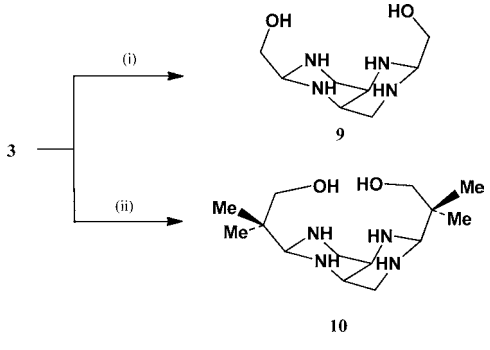
Table 1. Reaction Products from 3 + *o*-Ar′CHO (Room Temperature)[a,b]

3:*o*-Ar′CHO molar ratio	6′	8	5′
[1:1][c]	61%	4%	
[1:2][d]	79%	11%	
[1:2.5]	45%	55%	
[1:3]	10%	80%	10%
[1:4][d]		45%	55%
aldehyde in high excess		25%	75%

[a]Ar′ = nitrophenyl. [b]Determined by ^{1}H NMR at 3−6 h addition intervals. [c]~25% monoaminal present. [d]~10% monoaminal present.

Turning to suitably functionalized alkyls,[2a] the reactions of **3** with glycolaldehyde (Scheme 4, part i) gave within 5 min (room temperature, r.t.) 2,6-bis(hydroxymethyl)-*cis*-TAD (**9**), and with 2,2-dimethyl-3-hydroxypropionaldehyde (Scheme 4, part ii) the expected 2,6-bis(*α*,*α*′-dimethyl-*β*−hydroxyethyl)-*cis*-TAD (**10**) was isolated, albeit more slowly and in 60% yield.

Scheme 4. Synthesis of 2,6-Bis(hydroxyalkyl)-*cis*-TAD Podands: (i) $HOCH_2CHO$/EtOH; (ii) $HOCH_2C(Me)_2CHO$/EtOH at Room Temperature



^{1}H and ^{13}C NMR data of both 2,6-bis(hydroxyalkyl) TAD derivatives (Table 2) were compelling in assigning the tetraazadecalin structures, excluding any possible isomeric bis(5-imidazolidinyl) or 1,3-diazolano-1,3-diazepane systems or ring−chain tautomeric Schiff-bases. Both ^{1}H and ^{13}C NMR (and DEPT) spectra of **9** and **10** reflected the C_2 symmetry of the molecules and CI-MS or FAB-MS spectra exhibited major $[MH]^+$ peaks. Both TAD podands **9** and **10** were anticipated to be good chelating ligands and, therefore, their ability of metal ion inclusion was explored and investigated in detail.

Complexation Studies. Initial experiments to examine the ability of 2,6-bis(hydroxymethyl)-*cis*-TAD (**9**) to chelate various metal ions, based on comparison between ^{1}H NMR chemical shifts of the free ligand and its complexes, indicated that **9** exhibits remarkable binding propensity for heavy metal ions (Table 3). These ions (in particular Pb^{II}) caused large downfield shifts in the spectrum of **9**, while alkali and lanthanum ions showed all but no change in its spectrum. *All complexes exhibited symmetrical spectra, and the aminal ($H_{2,6}$) and angular protons ($H_{9,10}$) were shifted downfield relative to all other signals.* This deshielding effect is taken to imply depletion of electron density from the adjacent atoms and bonds and had been observed in this laboratory in related systems.[1,17]

Electrochemistry. Binding affinity and selectivity in the ligand/cation complexation process are profoundly sensitive to the donor properties of the solvent,[18] due to either its competition with the ligand or intervention in the latter's binding with the cation.[19] In addition, amine ligands are highly sensitive to pH conditions and reasonably exist in partially or fully protonated forms, especially under physiological pH. This has a major influence on binding strength and stoichiometry in cases when nitrogen donor atoms participate in the complex formation. Structural factors such as chelate[20] and pendant donor group effects[21] do also affect coordination number and geometry.

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Table 2. ^{1}H and ^{13}C NMR Data of 2,6-Bis(hydroxyalkyl) *cis*-TAD Derivatives[a]

compd		position					
		2,6	$4,8_{eq}$	$4,8_{ax}$	9,10	CH_2OH	$C(Me)_2$
9 (D_2O)	δ^1H	3.57 (bs)	3.05 (dd)	2.95 (dd)	2.77 (bs)	3.57 (bs)	
			^2J = 14	^2J = 14			
			^3J = 2.4	^3J = 0.9			
9 (D_2O)	^{13}C δ	72.4	51.0	51.0	51.5	66.3	
10 ($CDCl_3$)	δ^1H J	3.48 (m)	3.03 (bd)	2.96 (dd)	2.73 (t)	3.48 (m)	0.98; 0.92 (2s)
			^2J = 13	^2J = 13	^3J = 1.6		
			^2J = 13	^3J = 2.1	^3J = 1.6		
10 ($CDCl_3$)	^{13}C δ	79.1	51.0	51.0	51.5	72.4	37.8
							20.8; 19.5

[a] δ in ppm, J in Hz, (multiplicity).

Table 3. ^{1}H NMR (200 MHz, D_2O, 298 K) Chemical Shift Differences[a] between Free 9 and Its Complexes[b]

ion	r (Å)[c]	$\Delta\delta$ CH_2OH	$\Delta\delta$ $H_{2,6}$	$\Delta\delta$ $H_{4,8eq}$	$\Delta\delta$ $H_{4,8ax}$	$\Delta\delta$ $H_{9,10}$
Pb^{2+}	1.20	0.34, 0.32	2.09	0.18	0.52	1.39
Hg^{2+}	1.10	0.12	0.56	0.15	0.2	0.6
Cd^{2+}	0.97	0.13	0.38	0.135	0.115	0.48
Zn^{2+}	0.74	0.14	0.41	0.15	0.17	0.5
La^{3+}	1.02	0.12	0.25	0.09[d]	0.09[d]	0.26
K^{+}	1.33	0.07, 0.05	0.03	0.04[d]	0.04[d]	0.05
Ba^{2+}	1.34	0.02	0.02	0.01[d]	0.01[d]	0.02
Cs^{+}	1.67	≤0.01	≤0.01	≤0.01[d]	≤0.01[d]	≤0.01

[a] $\Delta\delta$ in ppm. [b] At 1:1 ratio. [c] Crystal ionic radii. [d] Unresolved peak.

To gain comparative insight into the complexation behavior of **9** and its fractional chelating units (*vide infra*), polarographic techniques[22] were compelling. Earlier results[2a] of such efforts for lead are complemented for additional ions, using both normal (NPP) and differential (DPP) pulse polarography in methanol (Table 4). Addition of these ligands to either methanol or aqueous solutions of Cd^{II}, Pb^{II}, and Zn^{II}, in the presence of sodium perchlorate (0.5 M), gave in each experiment a well-defined single polarographic wave shifted toward more negative values, and the limiting currents were not affected by increasing the concentration of any of the ligands. These observations confirmed that the metal ions and their complexes require the same number of electrons.

In principle, **9** can be regarded as being constructed of ethylenediamine (EN) units along with ethanolamine (EA) units, and we compared their complexation behavior with that of **9** (Table 4). To prove the reversibility of the processes under investigation, we carried out a logarithmic analysis of the current–voltage curve as defined by the Heyrovsky–Ilkovic equation:[22]

$$(nF/2.303RT)(E_{1/2} - E) = \log(i/i_d - i) \quad (1)$$

Here n = number of electrons consumed, R = 8.31 V C deg^{-1}, F = 96 500 C, and T = 298 K. The dependence of $\log(i/i_d - i)$ on the potential E must be a straight line whose slope ($nF/2.303RT$) is directly determinable. The reciprocal slope ($2.303RT/nF$) indicates the degree of reversibility for the redox system, and for a two-electron reversible process, the theoretical value obtained for n = 2 is 29.3 mV. Analysis of polarographic measurements, by plotting $\log(i/i_d - i)$ vs $-E$, gave straight lines with reciprocal slope values of 29 ± 3 mV (Table 4), indicating the reversible nature of the reduction processes:

Table 4. Equilibrium Data of M^{II} Ions with 9, EN, and EA[a,b]

solvent	complex (cf. eq 2)	log K[c]	Rc (mV)[e]	ref
9				
DDW[d]	$Cd^{II}L$	NPP: 6.1 ± 0.1	32	this work
water pH = 7	$Cd^{II}L$	NPP: 2.9 ± 0.1	27	this work
water pH = 7		DPP: 3.3 ± 0.1		
water pH = 7	$Pb^{II}L$	NPP: 6.8 ± 0.3	37[f]	this work
water pH = 7		DPP: 7.0 ± 0.3		
MeOH	$Cd^{II}L_2$	NPP: 14.9 ± 0.4	32	this work
MeOH		DPP: 14.6 ± 0.3		
MeOH	$Pb^{II}L$	NPP: ≫ 10	31	this work
MeOH	$Zn^{II}L$	NPP: 6.9 ± 0.1	43[e]	this work
MeOH		DPP: 6.3 ± 0.1		
EN				
DDW	$Cd^{II}L_3$	12.3; 11.89; 12.18	<34	ref 24
DDW	$Pb^{II}L_2$	8.44; 8.66; 8.67	29	refs 25, 26
water pH = 7	$Cd^{II}L_6$	NPP: 13.7 ± 0.5	28	this work
water pH = 7		DPP: 13.8 ± 0.2		
water pH = 7	$Pb^{II}L_6$	NPP: 13.2 ± 0.9	27	this work
water pH = 7		NPP: 13.0 ± 0.9		
MeOH	$Cd^{II}L_2$	NPP: 16.4 ± 0.1	31	this work
MeOH		DPP: 16.0 ± 0.2		
MeOH	$Pb^{II}L_2$	NPP: 10.8 ± 0.2	29	this work
MeOH		DPP: 10.8 ± 0.2		
EA				
DDW	$Cd^{II}L_3$	5.6	N/A	ref 27
DDW	$Pb^{II}L_2$	7.6	30–40	ref 28
water pH = 7	no complex			this work
MeOH	$Cd^{II}L_3$	NPP: 9.8 ± 0.4	30	this work
MeOH		DPP: 8.8 ± 0.2		
MeOH	$Pb^{II}L_2$	NPP: 9.2 ± 0.1	32	this work

[a] Lingane's method[22b–d] for reversible processes was used. [b] At 25.0 ± 0.2 C and I = 0.5. [c] K = association constant. [d] Double distilled water. [e] Reversibility criteria, Rc = $2.303RT/nF$. [f] Rc = $2.303RT/\alpha nF$.

$$[M^{II}\cdot L_j] + 2e \leftrightarrows M^{II} + jL \ (M = Cd, Pb, \text{and } Zn) \quad (2)$$

Only in two cases, *viz.*, [$Pb^{II}\cdot$(**9**)] in buffer solution and [$Zn^{II}\cdot$(**9**)] in methanol, straight lines were obtained, but the reciprocal slope values were above the average obtained; i.e., the number of electrons consumed in the electrode process was smaller than 2 (n = 1.6). This indicates only a small over potential, much less than over 100 mV required for a two-electron irreversible diffusion-controlled process.

This phenomenon is well-known[23] to be due to a slow electrode process, taking place when the depolarizer (e.g., the

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metal complex) becomes able to slowly exchange electrons with the electrode, requiring a certain energy of activation. Nevertheless, in such circumstances of small overpotential, the logarithmic current−voltage expression is modified to $(\alpha nF/2.303RT)(E_{1/2} - E) = \log(i/i_d - i)$, where α is the charge transfer coefficient, regarded as the fraction of the applied potential, which may either assist or hinder the process. We analyzed the dependence of $\log(i/i_d - i)$ on the potential E for $[(\mathbf{9})\cdot Pb^{II}]$ (in buffer solution) and $[(\mathbf{9})\cdot Zn^{II}]$ (in MeOH) and obtained reversibility values of 37 and 43 mV, respectively (Table 4). These values were obtained at high, moderate, and low ligand concentrations. Given the $(2.303RT/\alpha nF)$ values and assuming that the charge transfer coefficient α remains constant, we could determine the stability constant ($\log K$) and stoichiometry (j) for these processes:

$$\Delta E_{1/2} = (2.303RT/\alpha nF)\log K + j(2.303RT/\alpha nF)\log[L] \quad (3)$$

Apparently, the complex's stability in methanol is significantly higher than in water, due to the latter's stronger solvation of the cations; indeed, in water at pH = 7, all ligands were partially protonated, and the number of available binding sites (N donor atoms) decreased, resulting in lower binding constants and in entirely different complex formation. This was particularly acute for ethanolamine (EA), which, already at pH = 7 turned to the ammonium form, was incapable of chelating cations. The lower binding constant (by 3 orders of magnitude) in the complex of **9** with Cd^{II} in water at pH 7 versus nonbuffered water (Table 4, DDW) confirmed this protonation effect on the binding affinity of the ligand toward metal ions. The EN ligand, however, appeared to "adjust itself" at pH = 7, by acting as a monodentate ligand, and the binding affinity toward cadmium ion is only slightly stronger.

The coordination number, n, in ML_n complexes of Cd^{II} is higher than in Pb^{II} analogous complexes in methanol (Table 4), mainly due to the smaller ionic radius of Cd^{II} and covalent nature of the coordinate bonds, which preclude comparison between association constants of Cd^{II} complexes with those of Pb^{II} ones and determination of selectivity between $[M\cdot L_{1-3}]$ complexes. Nevertheless, comparing between $[Cd^{II}\cdot EN]$ and $[Pb^{II}\cdot EN]$ complexes by polarography in methanol solutions reveals higher stability constants of the former, as opposed to the general convention that five-membered chelate rings have minimum strain energy with larger metal ions,[29] and that hard *N*-donor ligands are expected to bind strongly a good lone pair acceptor ($Pb^{II} > Cd^{II}$).[30] Also, $\log K$ of $[Cd^{II}\cdot(EN)_2]$ is slightly higher than $\log K$ of $[Cd^{II}\cdot(\mathbf{9})_2]$, notwithstanding the additional oxygen donors in **9** relative to EN, due perhaps to torsional rigidity in **9** and to steric strain in the $(\mathbf{9})_2$ arrangement relative to $(EN)_2$.

Altogether, it was rewarding to find that, already at the podand level, **9** exhibited, by any standards,[31] remarkable heavy metal ion, *viz.*, Cd^{II} and Pb^{II} binding affinity, as indicated by the large equilibrium constants measured by both normal (NPP) and differential (DPP) pulse polarography. Significantly, the $[Pb^{II}\cdot(\mathbf{9})]$ complex showed particularly strong binding, the dissociation of the complex being lower than 0.02% at 0.002 M concentration. Indeed, Lingane's method[22c,d] failed at these conditions, and only an evaluation of the lowest limit of the stability constant of **9** with Pb^{II} in methanol ($\log K \gg 10$) could be made (Table 4). In addition, Hancock et al.[32a] had pointed out that when equilibration of the metal ion with the ligand is slower than the rate of reduction of the complex at the mercury electrode, separate peaks are obtained for the free metal ion and its complex. Earlier,[2a] we observed two reversible half-wave potentials on the same polarogram, attributed to Pb^{II} (−0.70 V) and to the $[Pb^{II}\cdot(\mathbf{9})]$ complex (−0.550 V), and could hence determine the ligand to metal ratio by titration experiment.

Structure, Spectroscopy, and Bonding. The solid-state structure of $[Cd^{II}\cdot(\mathbf{9})]Br_2$ and $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ complexes provided valuable information about the binding interactions of these inclusion complexes. The single-crystal X-ray crystallographic data and refinement details of these complexes were reported earlier,[2a] and we proceed now discussing the structural parameters emphasizing their unique binding mode. Significant bond lengths (L, Å), bond angles (A, deg), and torsion angles (T, deg) are presented in Table 5, and a stereoview of the complexes is shown in Figure 1, illustrating their evident asymmetrical nature. Both complexes exhibit 2-hydroxymethyl-5-amino-1,3-diazane ligation, unprecedented but warranted by

Table 5. Selected Geometry Values of the $[Cd^{II}\cdot\mathbf{9}]Br_2$ and $[Pb^{II}\cdot\mathbf{9}](NO_3)_2$ Complexes: Bond Lengths (L, Å) and Bond and Torsion Angles (A deg, T deg)[a]

L	Cd	Pb
M−N1	2.474(4)	2.599(9)
M−N3	2.456(5)	2.563(9)
M−N5	2.398(5)	2.488(10)
M−O13	2.488(5)	2.690(9)
M−Br1	2.592(1)	
M−Br2	2.642(1)	
M−O16		2.706(7)
M−O17		2.862(9)
M−O21		3.002(10)
M−O22		3.208(10)
N1−C2	1.468(7)	1.504(13)
C2−N3	1.458(7)	1.481(13)
N1−C9	1.476(8)	1.468(16)
N5−C6	1.479(8)	1.478(12)
C6−N7	1.455(7)	1.453(15)
N5−C10	1.487(7)	1.444(14)
N7−C8	1.476(8)	1.451(15)
A		
N5−M−O13	138.7(2)	129.8(3)
N3−M−O13	69.7(1)	64.8(3)
N3−M−N5	74.6(2)	70.2(3)
N1−M−O13	70.2(1)	66.2(3)
N1−M−N5	72.9(2)	69.5(3)
N1−M−N3	55.9(1)	52.7(3)
Br1−M−O13	101.9(1)	
Br2−M−O13	94.9(1)	
O16−M−O13		92.1(3)
O17−M−O13		135.8(3)
Br1−M−Br2	102.6(1)	
T		
N1−C2−C11−O13	59.5(6)	56.4(14)
N3−C2−C11−O13	−54.7(6)	−52.7(14)
N3−C4−C10−N5	−66.5(6)	−66.8(11)
N5−C6−C12−O14	−51.0(6)	69.1(11)
N7−C6−C12−O14	−172.5(5)	−56.2(12)
N7−C8−C9−N1	−73.6(6)	−68.2(12)
N1−C9−C10−N5	68.6(5)	68.5(10)

[a]Bond lengths (L, Å) and bond and torsion angles (A deg, T deg). CSD refcodes: RUTXIN and RUTXOT.[34]

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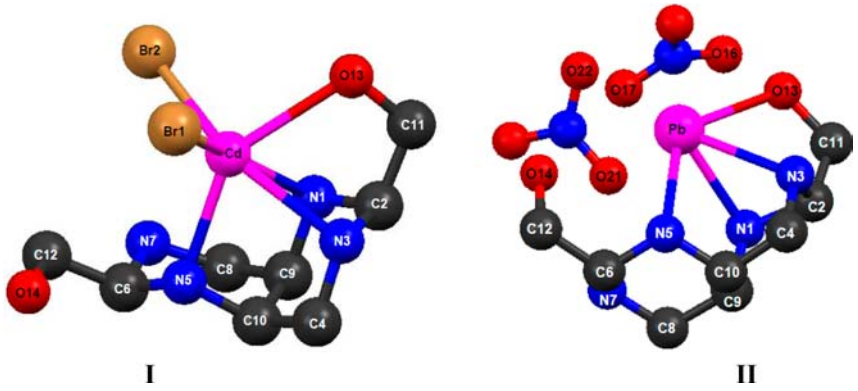

Figure 1. Stereoviews of the X-ray crystal structures $[Cd^{II}\cdot(\mathbf{9})]Br_2$ (**I**) and $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ (**II**). Hydrogen bonds were omitted from all structures for clarity.

Hancock's correlation[32b,33] of the metal ion size with the geometry of the chelate ring, in these cases, two five-membered (diazane) ones.

As expected from TAD molecules with their double N−C−N motives, which exhibit the well-known stereoelectronic *anomeric effect*,[2b,35] the latter is structurally well expressed in the N−C−N moieties of both complexes, *viz.*, the proton on N7 is axial, with N7 as donor and N5 as acceptor (with higher electron density), and consequently, C6−N7 is appreciably shorter than C6−N5 (ΔL = 0.024−0.025 Å). Similarly, the M^{II}−N5 bond is indeed shorter (stronger) than the other M^{II}−N1 and M^{II}−N3 bonds (in Cd^{II} complex ΔL = 0.0584−0.076 Å and in Pb^{II} complex ΔL = 0.075−0.111 Å). The apparent weaker coordination of N1 and N3 to the metal is due to the manifest absence of negative hyperconjugation in N1−C2−N3 (with diaxial coordination and both protons equatorial).

Cadmium Complex. In the $[Cd^{II}\cdot(\mathbf{9})]Br_2$ structure (Figure 1, **I**) the metal is six-coordinate, in a N_3OBr_2 distorted octahedron. Hence, one coordination hemisphere is filled by a tetradentate N_3O ligand, and the second is occupied by two bromide counterions in a *cis* configuration. Earlier crystallographic structural investigations have shown unhindered complexes of general formula $CdLX_2$ (L = N_3O-mixed donor ligands and X = Br, Cl) are always six-coordinate, with their structures consisting of discrete octahedral geometry.[36]

The strong binding propensity of the 5-amino-2-hydroxyethyl-1,3-diazane structure is apparently due to the combined cooperation between chelate and pendant donor group effects in the form of two M^{II}(N−C−C−N) and two M^{II}(O−C−C−N) five-membered ring arrangements, along with one M^{II}(N−C−N) four-membered ring fragment. The latter strained confinement, combined with the unencumbered binding of two bromides, causes the distortion of the octahedral structure. Thus, there are two types of N−Cd−N bond angles in the $[Cd^{II}\cdot(\mathbf{9})]Br_2$ complex: one is within the Cd^{II}[N(1)−C(2)−N(3)] four-member chelate ring, with an understandably small N(1)−Cd−N(3) bond angle (55.9°), while the second, Cd^{II}[N(1,3)−C(2)−N(5)], type adopts a conformation in which the N(3)−Cd−N(5) and N(1)−Cd−N(5) angles are nearly 75° (Figure 2, 74.6° and 72.9°, respectively). The latter type fits the observed N−Cd−N bond angles in three five-membered chelate rings of the recently reported $[Cd^{II}(EN)_3](ClO_4)_2$ crystal structure (75.1°, 74.0°, and 73.5°).[37]

On the basis of minimum ring strain energy for a five-membered ring involving EN, the ideal metal ion for coordination to EN thus has an M−N bond length of 2.5 Å

O-M-N = 69.7(1); 70.2(1)
ω = 59.5(6); 54.7(6)

N-M-N = 74.6(2); 72.9(2)
ω = 66.5(6); 68.6(6)

Figure 2. Bond and torsion (ω) angles of five-membered chelate rings in $[Cd^{II}\cdot(\mathbf{9})]Br_2$.

away creating a N−M−N bond angle of 69°.[33] The slightly larger N−Cd^{II}−N bond angles in the complex of $[Cd^{II}\cdot\mathbf{9}]Br_2$ are as a result of the anomeric effect that imposed relatively shorter Cd^{II}−N bond lengths. Two other five-membered chelate rings Cd^{II}[O−C−C−N] based on ethanolamine moieties feature O−Cd^{II}−N bond angles of similar magnitude (69.7° and 70.2°) to the ideal angle (69°). These observations can be explained in terms of bond distance between the metal cation and the O-donor atom (Table 5, 2.488 Å), which is close to the theoretical M−N bond length in five-membered ring chelate (2.5 Å). Prominently, the N−C−C−N and N−C−C−O torsion angles in the five-membered chelate rings are considerably different (Figure 2). This and the relatively small N−Cd−N bond angle (55.9°) along with the large Br−Cd−Br bond angle (102.6°) account for the deviation from ideal octahedral geometry.

NMR Studies. The ^1H and ^{13}C NMR spectra of **9** and $[Cd^{II}\cdot(\mathbf{9})]ClO_4$ in D_2O−CD_3OD (1:1) at room temperature were recorded, and their data are given in Table 6. The ^1H NMR spectrum of **9** exhibits only three signals in a ratio of 3:2:1 endorsing the C_2 symmetry of the ligand. The two double doublets at δ 3.05 and 2.95 were assigned to the $H_{4,8}$ equatorial and axial protons, respectively, on the basis of the proton chemical shift assignment of the parent *cis*-TAD (Scheme 1, X═N).[2b]

Likewise, the ^{13}C NMR spectrum supports the symmetrical structure by showing four signals for one set of equivalent C atoms. As expected from the exploratory experiments (*vide supra*), the ^1H NMR signals show clearly shielding effects as Cd^{II} approaches the binding sites of **9**, stronger on nitrogen than on oxygen, and the occurrence of only four signals in both ^1H and ^{13}C spectra reveals that the C_2 symmetrical structure in the complex is preserved. Moreover, the binding process induces a progressive splitting of the broad singlet at δ 3.57 ppm to three new chemical shift signals at δ 3.93, 3.74, and 3.65 assigned to the aminal ($H_{2,6}$) proton and two pendant arm

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Table 6. ^{1}H and ^{13}C NMR Chemical Shifts for Cadmium(II) Complexes with 9 in D_2O/CD_3OD [1:1] Solution (δ ppm)[a]

	position			
compd	2,6	CH_2OH[b]	4,8	9,10
^{1}H				
0.1 M **9** (free ligand)	3.57 [bs, 6H]		3.05, 2.95 [dd], ^{2}J = 14.5 Hz, ^{3}J = 2.0 Hz	2.76 [bs]
0.1 M **9**, 0.1 M $Cd(ClO_4)_2$	3.93 [bs]	3.74, 3.65 [dd], ^{2}J = 12.4 Hz, ^{3}J = 1.3 Hz	3.18, 3.09 [bd], ^{2}J = 13.5 Hz	3.27 [bs]
0.3 M **9**, 0.1 M $Cd(ClO_4)_2$	3.79 [bs]	3.67 [bs]	3.11 [bm]	3.11 [bm]
^{13}C				
0.1 M **9**	71.1	64.9	49.8	50.3
0.1 M **9**, 0.1 M $Cd(ClO_4)_2$	71.1	62.9	49.2	51.5
0.3 M **9**, 0.1 M $Cd(ClO_4)_2$	72.2	63.9	49.7	50.3

[a]Abbreviations in brackets indicate multiplicity, viz., b = broad, s = singlet, d = doublet, m = multiplet. [b]Exchangeable OH proton.

protons, respectively. On addition of **9** in excess, the shielding effect is reduced, in particular in both aminal ($H_{2,6}$) and angular ($H_{9,10}$) proton signals, implying that complexes of different stoichiometry than 1:1 are involved, which contain fewer binding sites per ligand unit. Similarly, ^{13}C NMR spectral data exhibit noticeable upfield shift of both the hydroxymethyl carbon and $C_{4,8}$. Following addition of **9** in excess, all ^{13}C signals are shifted downfield compared to the ^{13}C signals of the 1:1 complex, as expected from conformational changes, in particular in both $C_{9,10}$ the pendant arms, when ML is converted to either ML_2 or M_2L_3.[38]

All above led to a solution NMR study by ^{113}Cd NMR spectroscopy, ^{113}Cd being the highest natural abundance isotope of cadmium, suitable for NMR experiments.[39] It has received much attention as an NMR metallobioprobe,[40] in addition to many studies reported on coordination complexes[41] and on organocadmium species.[42] Previous studies on ^{113}Cd NMR demonstrated that chemical shifts strongly depend on the environment of the metal ion and, consequently, are sensitive to minor changes in the coordination sphere, the ligand donor atom type (e.g., N, O, etc.), the number of sites, and the geometry of the complex.[39,43−46]

Hence, we used ^{113}Cd NMR to probe Cd(II) complexes with the ligands **4** (R = H), **9**, **10**, and ethylenediamine, EN (Table 7). The latter served as a known reference compound for

Table 7. ^{113}Cd NMR Chemical Shifts (δ, ppm) for Cd(II) Complexes with TAD Derivatives and EN[a]

ligand/ratio	1:1	2:1	1:1:1
4 (R = H)		280	
9	41	98, 105, 145	
10	39	88	
EN	128	262	
9 + EN			214

[a]In all experiments, to a solution of 0.1 M $Cd(ClO_4)_2$ in CH_3OH/H_2O [1:1] was added either 0.1 M of each ligand (ratio 1:1) or 0.2 M (ratio 2:1) at 293 K.

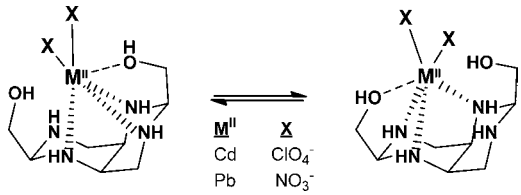
comparison with literature data.[43] These ^{113}Cd chemical shifts were referenced to external 1 M $Cd(ClO_4)_2$ aqueous solution. For comparison, the ^{113}Cd chemical shift of 0.1 M $Cd(ClO_4)_2$ in CH_3OH/H_2O [1:1] is −8.4 ppm. Different ^{113}Cd NMR chemical shifts were detected subsequent to the various Cd(II) species, and their assignments are given in Table 7.

As anticipated, the ^{113}Cd NMR chemical shift is deshielded as the ligand concentration was increased, viz., **9**, **10**, and EN, given that the deshielding of ^{113}Cd NMR signals increases in the order N > O, when the donor atoms changed and/or coordination number increase.[47] Consequently, oxygen atom donors of perchlorate groups coordinated to Cd^{II} tend to make the ^{113}Cd nucleus more shielded. Poorer electron donor (certainly perchlorate oxygen is one) will be replaced with either oxygen or nitrogen binding site following increment addition of the ligand.[48]

Interestingly, the ^{113}Cd NMR spectra of both [Cd^{II}·(**9**)] and [Cd^{II}·(**10**)] in CH_3OH/H_2O [1:1] solution at 293 K show one signal at δ 41 and 39 ppm, respectively, revealing that the two complexes adopt a six-coordinate structure characterized by an N_3O_3 (1:1 N/O ratio) environment. Indeed, according to X-ray structure determination, two monodentate anions (or one bidentate) are included in the coordination sphere of Cd^{II}. Certain chemical shift values are reported in the literature for Cd^{II} complexes with a 1:1 N/O ratio of donor atoms, namely, in the case of Cd(II)-cryptate complex (δ 46 ppm)[42] and of pyridine (or γ-picoline) base adducts of Cd(II)-β-ketonate complexes (δ 40.6 and 42.7 ppm, respectively).[49]

As mentioned above, increasing the ligand (**9**, **10**, and EN) to Cd^{II} ratio to 2:1 and up caused the ^{113}Cd signal at δ 41, 39, and 128 ppm, respectively, to disappear, and three new signals emerged: in the case of **9** at δ 98, 105, and 145 ppm, one signal at δ 88 ppm for **10**, and a signal at δ 262 ppm for EN (Table 7). The former case indicates an increasing number of ligand **9** around the cadmium cation. Even at excessively high ligand concentration all three ^{113}Cd signals are evident, probably due to a slow equilibrium state between these three species in solution. In fact, even the 1:1 complex of [Cd^{II}·(**9**)]·$(ClO_4)_2$ exhibits a broad ^{113}Cd signal, suggesting equilibrating sites.[46c] We attribute this to an intramolecular exchange between the equivalent sites in the two octahedral forms (Scheme 5), which

Scheme 5. Schematic Cd^{II}·**9** and Pb^{II}·**9** Complexes and Their Intramolecular Ligation Exchange in Solution



causes increased linewidths. The key features of ligand **9**, which make this behavior possible, are the 5-amino-1,3-diazane units, complemented by the adjacent hydroxymethyl pendant: altogether, two double *gauche*, $NC(CN)_2$ and $OC(CN)_2$ combinations. The fourth nitrogen in the TAD core and the second hydroxymethyl on it or, in other words, the C_2

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symmetry of the ligand **9**, enable the $[Cd^{II}\cdot(\mathbf{9})]$ complex to undergo the rapid intramolecular exchange process to a totally equivalent structure (Scheme 5).

Investigation at detailed correlation of solution ^{113}Cd NMR spectra with the coordination environment of Cd(II) complexes of ligands **9** and **10** included ^{113}Cd VT-NMR studies (Figure 3). Thus, while at room temperature (293 K) a

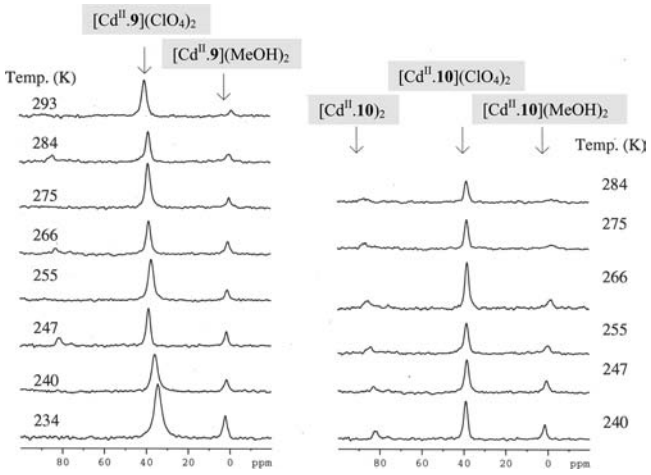

Figure 3. ^{113}Cd NMR spectra of 0.1 M $Cd(ClO_4)_2$ and 0.1 M **9** (left) and 0.1 M **10** (right) in H_2O/MeOH [1:1] solution at variable temperature.

single broad singlet was observed at δ 41 and 39 ppm, respectively (cf. Table 7); on lowering the temperature, additional resonance signals developed at δ 5 ppm in both experiments. In the Cd(II) complex of ligand **10**, an additional resonance appeared at δ 83 ppm, which is attributed to the $[Cd\cdot(\mathbf{10})_2]$ complex (cf. Table 7). These low temperature ^{113}Cd NMR data reflect ligand exchange at the metal center. Exchange is also suggested between the coordinated counterion and the solvent (methanol), and thus, the signal at δ 5 ppm is ascribed to the formation of both $[Cd^{II}\cdot(\mathbf{9})](MeOH)_2$ and $[Cd^{II}\cdot(\mathbf{10})](MeOH)_2$ complexes. Similar solvent ligand exchange was observed in the ^{113}Cd VT NMR study of Cd(II) complexes of human erythrocyte carbonic anhydrases.[50] Notably, no resonance of higher order complexes (e.g., $[Cd\cdot(\mathbf{9})_2]$) was observed even at low temperatures, although these were favored in methanol (cf. Table 4).

Using EN, a simple and classic N-donor ligand that is known for its five-membered ring chelate, the choice of this ligand was driven by the possible formation of individual $Cd^{II}EN_n$ (n = 1–3) either in water or DMSO; each complex exhibits a distinct resonance, distinguishable from the free Cd^{II} ion.[37] Accordingly, the ^{113}Cd chemical shift in Cd^{II} tris-EN complex in solution was identical to that of solid state ^{113}Cd NMR (δ 349 ppm), and the counterion was not involved in the octahedral geometry. In contrast, the bidentate counterion participates in the favored octahedral structure, as demonstrated by the counterion exchange experiments in mono- and bis-EN complexes. The ^{113}Cd chemical shifts in our complexation experiments with EN show similar chemical shift resonances; the mono-EN complex is observed at 128 ppm, slightly upfield in comparison to the reported one in water (δ 141 ppm), possibly due to the contribution of O-donor of methanol from the solvent mixture. The bis-EN complex is observed at 262 ppm, identical to the reported one, demonstrating that solvent is not involved in the complex. We were not able to observe the tris-EN complex even at higher Cd^{II}/EN ratio in H_2O/MeOH solution probably due to the poorer solubility of tris-EN complex in this solvent mixture. This was also confirmed by FAB-MS, indicating characteristic signals for $[ML(ClO_4)]^+$ (L = EN) at 273 m/z (40%), and $[ML_2(ClO_4)]^+$ at 333 m/z (100%).

When EN and **9** ligands (in equimolar concentrations) are mixed with $Cd(ClO_4)_2$, only one signal is observed in the ^{113}Cd NMR spectrum with a totally new chemical shift (δ 214 ppm). FAB-MS shows the appearance of a new complex type, namely MLL′ (L = **9** and L′ = EN) at 475 m/z (35%). The mass spectrum contains also signals of $[Cd^{II}\cdot(\mathbf{9})]$, but no evidence of $[Cd^{II}\cdot(\mathbf{EN})]$ formation. These results indicate that although **9** and EN bind to cadmium cation to the same extent (cf. Table 4), **9** still has the advantage of forming several chelate rings with Cd^{II} over one chelate ring in case of the $[Cd^{II}\cdot(EN)]$ complex. Moreover, good bidentate ligands, such as EN, may coordinate with the $[Cd^{II}\cdot(\mathbf{9})]$ complex sphere as a complementary complexant between the pendant arms.

The nature of mixed ligand complexes has received much attention lately, especially in the studies of antibiotics activity,[51] anticancer drugs,[52] and DNA binding.[53] From coordination point of view, mixed ligands are frequently used to enhance regioselective complexations. Thus, large (sometimes macrocyclic) ligands are assisted by the use of small molecules due to their ability to act as an additional complexing site.[54]

^1H and ^{13}C NMR were also utilized in geometry determination of the new complex as shown in Table 8.

Table 8. ^1H and ^{13}C NMR Data[a] of EN, 9, and Their Cd^{II} Complexes in D_2O/CD_3OD [1:1]

		position with L_2 = **9**			
	L_1 = EN, $-CH_2NH_2$	2,6	CH_2OH	4,8	9,10
L					
^1H	2.64 [s]	3.58 [bm]	3.58 [bm]	3.01 [bdd]	2.76 [bs]
^{13}C	44.3	71.1	64.9	49.8	50.3
CdL					
^1H	2.79 [s]	3.93 [bs]	3.68 [bdd]	3.18; 3.08 [bd]	3.27 [bs]
^{13}C	40.9	71.1	62.9	49.2	50.3
CdL_1L_2					
^1H	2.80 [s]	3.91 [bs]	3.71 [bs]	3.20; 3.12 [bd]	3.24 [bs]
^{13}C	40.8	71.9	63.1	49.4	51.4

[a]Multiplicities: s = singlet, d = doublet, q = quintet, sp = septet, and m = multiplet.

Although the chemical shift differences are too small to consider a clear geometry preference, one might notice that the ^{13}C chemical shifts of the mixed ligand complex are shifted downfield relative to the $[Cd^{II}\cdot(\mathbf{9})]$ (1:1) complex, just as the ML complex transformed into ML_2 complex (M = Cd^{II}; L = **9**) at high L concentrations (Table 6). This means that the conformational geometries adopted in ML_2 and ML_1L_2 are similar.

Lead Complex. Turning to $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ (Figure 1, **II**), its structure is essentially similar to the structure observed for $[Cd^{II}\cdot(\mathbf{9})]Br_2$, especially the unique 2-hydroxymethyl-5-amino-1,3-diazane ligation mode, cf. Figure 4 and Table 5. The lead cation is located noncentrosymmetrically with respect to

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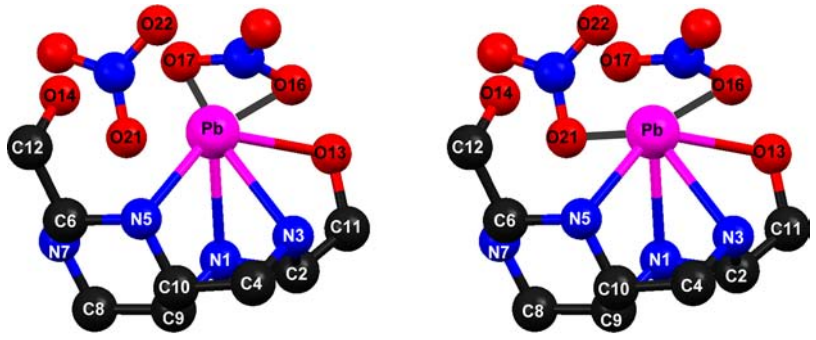

Figure 4. Possible bonding schemes (**IIA** and **IIB**) in $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$.

the six potential donor atoms (N_4O_2) of **9**. The major association of the cation is with the adjacent TAD core donor atoms N(1), N(3), and N(5). The Pb^{II}–N(5) distance of 2.488 Å is at the short end of the range observed for N-macrocyclic complexes of this cation,[55a,d–f,56,57] and is the shortest bond to Pb(II) in this structure.

Two types of Pb^{II}–O interactions are discerned in $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$: three oxygen atoms (one from **9** and two from bidentate nitrate ion) are bonded to Pb^{II} ion at distances 2.690, 2.706, and 2.862 Å, and two more oxygen atoms of the second nitrate ion exist at distances of 3.002 and 3.208 Å. The former three Pb^{II}–O bond lengths are comparable with those found in lead nitrate (2.7482(06) and 2.8688(06) Å)[58] and in macroheterocyclic lead complexes (2.7–2.9 Å).[56]

Interestingly, the bond lengths between the cation and the nitrate anion oxygen atoms display, for each bidentate nitrate ion, one short bond (cf. Table 5; Pb–O(16) and Pb^{II}–O(21)) and one long bond (cf. Table 5; Pb–O(17) and Pb^{II}–O(22)). These observations are typical and in line with those observed in *cis* unsymmetrical bidentate coordination.[56] The sum of the ionic radius of Pb^{2+} with coordination number eight and that of O^{2-} with coordination number two is 2.64 Å.[57] Thus, the three shorter Pb^{II}–O bond lengths are probably best described as predominantly ionic with only very little covalent bonding. Hence, one might be tempted to attribute those shortest Pb^{II}–O distances, viz. Pb^{II}–O(16) = 2.706(7) Å and Pb^{II}–O(17) = 2.862(9) Å, to a bidentate NO_3^-ligand in $[Pb^{II}\cdot(\mathbf{9})(NO_3)](NO_3)$ form (Figure 4, **IIA**), rather than to accept the unconditioned $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ one (Figure 4, **IIB**), but we leave this to posterior consideration. Another explanation for the overall coordination number of the complex is offered: the lead center in **9** attains a coordination number of 6 (three short Pb^{II}–N and Pb^{II}–O interactions, respectively) or 8 (6 + 2) if the two long Pb^{II}–O distances are also taken into consideration. Similar "dual" behavior was observed in the crystal structure of $[Pb^{II}\cdot(\mathbf{L})](NO_3)_2$ (**L** = 1,4,7-triazacyclononane).[55c]

A second point of interest in the context of the coordination number is the invocation of the so-called "inert-pair effect".[59] The lone pair of electrons ($6s^2$ in divalent lead) can cause a nonspherical charge distribution around the Pb(II) cation; i.e., the disposition of ligands around the cation results in an identifiable void.[59c] This "gap" in the coordination sphere has been recognized as an evidence for stereochemically active lone pair of electrons.[60] A close inspection of the structure of $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ (Figure 4, Table 5) reveals that there is an apparent vacant site between the oxygen donors, since the O(13)–Pb^{II}–O(17) bond angle seems nearest to the location of the lone pair: its value is in the vicinity of 136° and is larger than any other non-*trans*-angle (Figure 5). Likewise, the Pb^{II}–

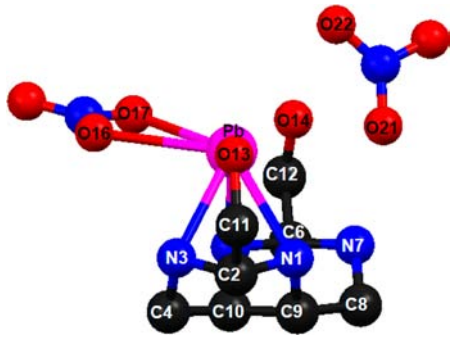

Figure 5. Side view of $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ complex (90° rotation along *b* axis) showing that disposition of the ligand and counterions is directed throughout only part of an encompassing globe (hemidirected geometry).

O(17), Pb^{II}–O(16), and Pb^{II}–O(13) distances are the shortest ones among the six available oxygen donor atoms in the coordination sphere of Pb^{II}. Thus, considering the Pb^{II} center in the plane of the three oxygen donors O(13), O(16), and O(17), the putative lone valence-electron pair points perpendicular above the plane (Figure 5). Moreover, the observation that the two longest Pb^{II}–O(21) and Pb^{II}–O(22) bonds, which would be most affected by the presence of the lone pair, occur on the orthogonal side of the Pb^{II} center, while the bonds most remote from the proposed position of the lone pair are shorter than the adjacent.[61]

Its position is further indicated by the short Pb^{II}–N bonds on the opposite side of Pb^{II}, away from the proposed site of the lone pair; i.e., Pb^{II}–N(5), Pb^{II}–N(3), and Pb^{II}–N(1) bond lengths are 2.488, 2.563, and 2.599 Å, respectively (Table 5). This matches Hancock's reported results for Pb^{II}–N bond lengths in Pb(II) complexes active lone pairs, in the range 2.37–2.56 Å, whereas for inactive lone pairs, the Pb^{II}–N bond lengths fall in the range 2.62–2.88 Å.[62] We conclude that $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$, with an average Pb^{II}–N bond length of 2.55 Å, has an active lone valence-electron pair and that the coordination number around the lead(II) cation is 6. To be sure, complexes with coordination number of 7 or less have been suggested as indicators of stereochemical active lone pair.[55d,61,62]

Up to this point the presence of stereochemically active lone pair has been inferred from the appearance in the X-ray

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structure of a "hole" in the coordination sphere; however, the presence of stereochemically either active or nonactive lone pair may also be inferred using NMR (*vide infra*).

^{207}Pb NMR. The excellent receptivity, high natural abundance (22.6%), and large chemical shift range (~16 000 ppm) of the ^{207}Pb isotope facilitates NMR study.[63] Although ^{207}Pb NMR has been extensively used for the study of organolead(IV) compounds, relatively few studies reported on the solution Pb(II) complexes in probing the stereochemically active/inactive Pb(II) lone pair.[64] Here we report the ^{207}Pb NMR study to support the evidence of an existing stereochemically active lone pair in the $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ complex since relatively high field resonances are indicative of high coordination numbers and stereochemically inactive lone pairs.[65]

A ^{207}Pb NMR study of the complex species of **9** with $Pb(NO_3)_2$ is shown in Figure 6. At 294 K the 75.27 MHz ^{207}Pb NMR spectra of 1 M $Pb(NO_3)_2$ in H_2O (as external reference) display a resonance at −2961 ppm ($w_{1/2}$ = 25 Hz). In a MeOH−H_2O [1:1] mixture, 0.1 M $Pb(NO_3)_2$ exhibits a broader resonance at −2868 ppm ($w_{1/2}$ = 55 Hz), consistent with solvent exchange processes.[64] On addition of up to 1 mol equiv of ligand **9**, a much broader resonance formed (Figure 6), at −900 ppm ($w_{1/2}$= 640 Hz), attributed to $[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$ in a fast exchange process with the counterion.[66]

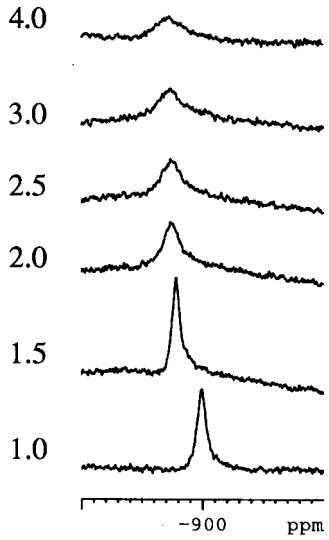

Figure 6. ^{207}Pb NMR spectra of 0.1 M $Pb(NO_3)_2$ following addition of **9** (up to 4 equiv) in H_2O−MeOH [1:1] solution at 294 K.

On increasing the **9**/Pb^{II} ratio, a small upfield shift but considerable further broadening of the resonance occurred, until constancy at a 2:1 ratio and up (−874 ppm; $w_{1/2}$ = 1290 Hz), consistent with a dynamically stable $[Pb^{II}\cdot(\mathbf{9})_2](NO_3)_2$ complex. From comparison with existing relevant complexes (Table 9),[67] it appears that, in both $[Pb^{II}\cdot(\mathbf{9})](NO_2)_2$ and $[Pb^{II}\cdot(\mathbf{4})_2](NO_2)_2$, the lead(II) lone pair is stereochemically active.

Regarding MS, FAB MS proved to be a valuable tool to infer the binding of lead(II) to **9** and to the peripheral ligands (viz. NO_3^- and ClO_4^-). Mainly two peaks were observed in the spectrum of the lead(II) complex and assigned with the help of calculated versus measured isotope patterns of Pb^{II}−L: $[Pb^{II}\cdot(\mathbf{9})-H^+]^+$ *m/z* 409 (100%), $[Pb^{II}\cdot(\mathbf{9})-ClO_4^-]^+$ *m/z* 509 (85%). As pointed out previously,[68] the observed species distribution in the matrix basically reflects solution chemistry. Notably, no $[ML_2-H^+]^+$ or $[ML_2-(ClO_4)^-]^+$ were observed, and this is also an indication for the strong binding mode of Pb^{II} (cf. Table 5) with an active lone pair coordination. Furthermore, the effect of counterion in stabilization of the monopositive charge was established; viz., when $Pb(NO_3)_2$ was used instead of $Pb(ClO_4)_2$, only the $[ML-H]^{+1}$ entity was observed, revealing that, at least under FAB conditions, the perchlorate is more stable.

Finally, the high binding propensity of lead was emphasized in a metal exchange selectivity test, in which addition of a stoichiometric amount of $Pb(NO_3)_2$ to 0.1 M solution of $[Cd^{II}\cdot(\mathbf{9})]$ [1:1] complex gave rise to drastic changes in ^{113}Cd NMR (Figure 7). Thus, the original ^{113}Cd signal of the $Cd^{II}\cdot(\mathbf{9})$ complex is dramatically shifted upfield, revealing that the cadmium ion is no longer bound to the ligand.

This metal-ion exchange was also proven by FAB-MS on addition of $Pb(ClO_4)_2$, resulting in the appearance of two new molecular ion peaks, $[Pb^{II}\cdot(\mathbf{9})-H]^+$ (409 *m/z*) and $[Pb^{II}\cdot(\mathbf{9})\text{-}(ClO_4^-)]^+$ (509 *m/z*). This complete metal exchange clearly indicates that in $[Pb^{II}\cdot(\mathbf{9})]$ binding affinity is much stronger than in the cadmium complex one. Both NMR and MS data confirm the relative magnitude of equilibrium constants as observed by polarography (cf. Table 4).

Table 9. ^{207}Pb NMR Chemical Shifts (δ, ppm) and Line Widths

complex type[a]	^{207}Pb (ppm)	Pb $w_{1/2}$ (Hz)	stereochemically lone pair	source	coordination type
$[Pb^{II}\cdot(bbh)]_2$	−732	N/A	active	ref 64a[b]	N_2O_2/N_2O_3
$[Pb^{II}\cdot(H_2daps)](H_2O)_2$	−648	N/A	active	ref 64b[b]	N_3O_3
$[Pb^{II}\cdot(Hdaps)(CH_3CO_2^-)]$	−490	N/A	active	ref 64b[b]	N_2O_4
$[Pb^{II}\cdot(H_2DPTsz\text{-}Me]$	−304	N/A	active	ref 64c[b]	N_3S_2
$[Pb^{II}\cdot(\mathbf{4})_2](NO_3)_2$ (R=H)	−796	900	active	this study[c]	N_4O_2
$[Pb^{II}\cdot(\mathbf{9})](NO_3)_2$	−900	640	active	this study[c]	N_3O_3
$[Pb^{II}\cdot(H_2B(pz)_2)_2]Cl_2$	−139	150	active	ref 67[d]	N_4
$[Pb^{II}\cdot(B(pz)_4)_2]Cl_2$	−534	200	active	ref 67[d]	N_4
$[Pb^{II}\cdot(HB(pz)_3)_2]Cl_2$	−895	600	active	ref 67[d]	N_6
$[Pb^{II}\cdot(HB(3,5\text{-}Me_2pz)_3)_2]Cl_2$	−1481	300	inactive	ref 67[d]	N_6

[a]Abbreviations follow: bbh, benzil, bis(benzoylhydrazone); dapd, 2,6-bis(1-salicyloylhydrazonoethyl)pyridine; DPTsz-Me, bis(4-*N*-methylthiosemicarbazone)-2,6-diacetylpyridine; B(pz), pyrazolyl borate. [b]Data in DMSO-d_6. [c]Data in H_2O/MeOH [1:1] at 294 K and 75.27 MHz. [d]Data in $CDCl_3$ at 224 K.

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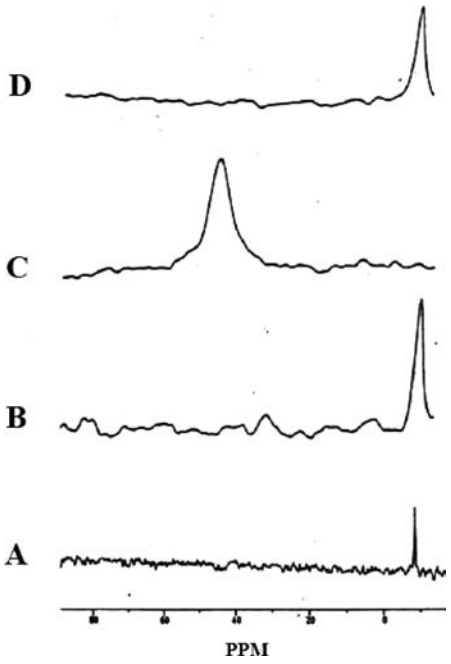

Figure 7. Metal ion exchange in [Cd^{II}·(**9**)] complex followed by addition of equimolar $Pb(NO_3)_2$ [all spectra were recorded in H_2O/MeOH 1:1 solution and reported with respect to external 1 M $Cd(ClO_4)_2$ in H_2O: (A) 0.1 M $Cd(ClO_4)_2$; (B) mixture of 0.1 M $Cd(ClO_4)_2$ and $Pb(NO_3)_2$; (C) 0.1 M [Cd^{II}·**9**]$(NO_3)_2$; (D) mixture of 0.1 M [Cd^{II}·**9**]$(NO_3)_2$ and 0.1 M $Pb(NO_3)_2$].

■ CONCLUSIONS

An in-depth study of the complexation of TAD (**4**, R═H) and bis-hydroxy-TAD derivatives (**9** and **10**) with heavy metal ions (i.e., Cd(II), Pb(II)) in polar protic media revealed strong binding within a unique 2-hydroxymethyl-5-amino-1,3-diazane ligation mode, as made evident by both ^{1}H NMR and X-ray analysis of the complexes. In addition, X-ray analysis reveals that the counterions associated with the metal cations also have considerable effect on the formation of the complexes. These observations were corroborated by the heavy nuclei VT NMR study. The close agreement between the results obtained by polarography and ^{113}Cd or ^{207}Pb NMR is remarkable as it gives a clear indication of the stabilities of these complexes, as proven in NMR competition experiments performed for ^{113}Cd and for, the strongest one, Pb^{II}·(**9**) in methanol. In addition to that, a thorough and insightful study of the active pair issue in these Pb^{II} complexes has been performed, stressing the power of the ^{207}Pb NMR tool for such studies. Furthermore, these results open the way to synthesis and study of exciting new ligands within this and similar classes of heterocyclic macrocycles and their complexes.

■ EXPERIMENTAL SECTION

General. Reactions were carried out in dry solvents under argon and monitored by TLC on aluminum sheets silica gel 60 F_{254}, (layer thickness 0.2 mm), GC, or ^{1}H NMR. Chromatographic purification of products was accomplished using column chromatography on silica gels (60, particle size 0.040−0.063 mm) or alumina (90 active basic, particle size 0.063−0.2 mm). Melting points were determined on capillary melting point apparatus and uncorrected. Elemental analyses were performed by investigation of C, H, and N. HRMS values were measured in a double focusing, triple sector mass analyzer. Mass spectra were measured in EI, CI, or FAB ionization mode. The NMR spectra were obtained at 200 or 360 MHz (^{1}H) and 50 or 75 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS or otherwise as reported. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale: $CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm; D_2O/CD_3OD (with internal CD_3OH), δ_H = 3.30 ppm, δ_C = 49 ppm. 1D selective NOE experiments (on resonance irradiation) were used to confirm the NMR peak assignmements. Solution heavy nuclei (^{113}Cd, ^{207}Pb) NMR experiments were performed at 79.87 and 75.27 MHz, respectively, with a multinuclear broad-band probe. Tubes of 10 mm diameter were used throughout. Standard acquisition parameters were as follows: (1) spectral width 32 kHz (400 ppm); (2) pulse delay, 1.5 s; (3) data points, 4 K; (4) pulse width, 8 and 24 μs respectively; (5) collected number of scans, 1600. ^{113}Cd chemical shifts are referenced to an externally aqueous solution of 1 M $Cd(ClO_4)_2$ at 293 K. ^{207}Pb chemical shifts are referenced to an externally aqueous solution of 1 M $Pb(NO_3)_2$ at 294 ± 1 K (−2961 ppm).

IR Measurements. Spectra were recorded in KBr pellets.

Polarography. Methanol (HPLC grade) and doubly distilled deionized water (DDW) were used for the preparation of the solutions of the ligands (0.02, 0.2, and 2 M) and solutions of lead nitrate and cadmium bromide (2.5 mM), as well as of sodium perchlorate (0.5 M), as supporting electrolyte. The pH of all aqueous solution was kept at a value of about 7.0, with 0.1 M 3-[*N*-morpholino]-propanesulfonic acid (MOPS), hemisodium salt. The polarographic measurements were carried out at 25 ± 0.2° C, equipped with a dropping mercury electrode (d.m.e.) in a three electrode arrangement. A Pt wire with a considerably larger surface area than that of the d.m.e. was used as the auxiliary electrode and Ag/AgCl/KCl 1.0 M as reference electrode. The capillary diameter was 8 μm, and mercury height was 60 cm. The instrumental parameters for normal pulse polarography (NPP) and differential pulse polarography (DPP) were as follows: (1) pulse width, 50 ms; (2) pulse amplitude, 50 mV; (3) scan rate, 2 mV s^{-1}; and (4) constant drop time, 0.5 s. In all experiments the concentrations of the metal ions were kept constant (0.1 mM) while the ligand concentration was varied (0.1−100 mM). Solutions were purged with argon for 10 min and maintained under argon during the measurements.

threo-1,2,3,4-Tetraaminobutane (**3**) was prepared as previously described,[3a] and *cis*-1,3,5,7-tetraazadecaline (TAD, **4** R═H) was prepared as reported.[2b]

General Procedure for the Preparation of 2,6-Diaryl-*cis*-TAD (*o*-,*m*-,*p*-6′) (Aryl = *o*-, *m*-, and *p*-Nitrophenyl). A solution of monosubstituted aryl aldehyde in methanol was added dropwise to a stirred methanolic solution of **1** (0.5 mol equiv) at room temperature (rt) under argon. The reaction was rapid, and after its completion (according to TLC or ^{1}H NMR) the solvent was removed under reduced pressure. H_2O was added, and the suspension obtained was extracted with $CHCl_3$. The organic layer was separated, washed with H_2O, and dried over $CaCl_2$, and the solvent was removed under reduced pressure. The residue was purified by either column chromatography or crystallization.

*(rac)-2,6-Bis(o-nitrophenyl)-cis-1,3,5,7-TAD (**o-6′**).* Compound **1** (0.175 g. 1.5 mmol), *o*-nitrobenzaldehyde (0.46 g, 3 mmol), and MeOH (40 mL) made up the reaction mixture. Compound ***o*-6′** was obtained as white solid (0.55 g, 80%) after column chromatography (silica gel, DCM/MeOH 95:5). Mp 67−69 °C (sealed tube, moisture sensitive). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.87 (dd, ^3J = 7.8, ^4J = 1.2 Hz, $2H_{aryl}$), 7.69 (dd, ^2J = 7.8, ^4J = 1.2 Hz, $2H_{aryl}$), 7.66 (dd, ^2J = 7.8, ^4J = 1.2 Hz, $2H_{aryl}$), 7.45 (dd, ^3J=7.8, ^4J = 1.2 Hz, $2H_{aryl}$), 5.08 (s, 2H, $H_{2,6}$), 3.22 (dd, ^2J = 13.0, ^3J = 1.9 Hz, 2H, $H_{4,8ax}$), 3.12 (dd, ^2J = 13.0, ^3J = 1.1 Hz, 2H, $H_{4,8eq}$), 2.95 ppm (bs, 2H, $H_{9,10}$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 149.5, 135.3, 132.6, 128.7, 128.5, 123.9, 70.7, 51.5, 51.3 ppm. IR (KBr pellet): 1526, 1384 cm^{-1}. MS (EI) *m*/*z*: calcd for $C_{18}H_{20}N_6O_4$ 384; found 192 [M^+/2]. HRMS (FAB) *m*/*z*: calcd for $C_{18}H_{21}N_6O_4$ 385.1624, found 385.1623 [MH^+].

*(rac)-2,6-Bis(m-nitrophenyl)-cis-1,3,5,7-TAD (**m-6′**).* Compound **1** (0.175 g. 1.5 mmol), *m*-nitrobenzaldehyde (0.46 g, 3 mmol), MeOH (40 mL) made up the reaction mixture. After solvent removal under reduced pressure, the crude product is moisture sensitive, and attempts to crystallize it failed. Compound ***m*-6′** was obtained as a yellow oil

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(0.55 g, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.44 (t, ^4J = 1.9 Hz, $2H_{aryl}$), 8.15 (dt, ^3J = 8.2, ^4J = 1.9 Hz, $2H_{aryl}$), 7.94 (t, ^3J = 8.2, ^4J = 1.9 Hz, $2H_{aryl}$), 7.54 (t, ^3J = 8.2 Hz, $2H_{aryl}$), 4.82 (s, 2H, $H_{2,6}$), 3.28 (bs, 4H, $H_{4,8}$), 3.02 ppm (bs, 2H, $H_{9,10}$). ^{13}C NMR (50.3, $CDCl_3$): δ 148.2, 144.2, 133.0, 129.4, 123.1, 121.7, 73.1, 51.3, 51.0 ppm. MS (FAB) m/z: calcd for $C_{18}H_{20}N_6O_4$ 384; found 385 [MH^+]. HRMS (FAB) m/z: calcd for $C_{18}H_{21}N_6O_4$ for 385.1624, found 385.1628 [MH^+].

*(rac)-2,6-Bis(p-nitrophenyl)-cis-1,3,5,7-TAD (**p-6′**).* Compound **1** (0.175 g. 1.5 mmol), *p*-nitrobenzaldehyde (0.46 g, 3 mmol), and MeOH (40 mL) made up this reaction mixture. Compound ***p-6′*** was obtained as a white solid (0.55 g, 85%) after column chromatography (silica gel, CH_2Cl_2–NEt_3–MeOH, 95:2:3). Mp: 147–151 °C (in sealed tube, moisture sensitive). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.19 (d, ^3J = 8.6 Hz, $2H_{aryl}$), 7.75 (d, ^3J = 8.6 Hz, $2H_{aryl}$), 4.81 (s, 2H, $H_{2,6}$), 3.31 (dd, ^2J = 12.7, ^3J = 1.9 Hz, 2H, $H_{4,8ax}$), 3.25 (dd, ^2J = 12.7, ^3J = 1.1 Hz, 2H, $H_{4,8eq}$), 3.02 ppm (bs, 2H, $H_{9,10}$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 149, 147.5, 127.6, 123.5, 73, 51.3, 50.9 ppm. IR (KBr pellet): 1518.8, 1347.4 cm^{-1}. MS (EI) m/z: calcd for $C_{18}H_{20}N_6O_4$ 384; found 192 [$M^+/2$]. HRMS (FAB) m/z: calcd for $C_{18}H_{21}N_6O_4$ 385.1624, found 385.1626 [MH^+].

*Hexahydro-3,4-bis(o-nitrophenyl)-7-N-o-nitrobenzylidene-2,3a,5-triazaindan (**8**).* This was synthesized with compound **1** (0.175 g, 1.5 mmol) and *o*-nitrobenzaldehyde (0.68 g, 4.5 mmol), or, alternatively, by using ***o-6′*** as starting material and adding 1 equiv of aldehyde at rt. Compound **8** was obtained from methanol as orange solid (0.7 g, 90%). Mp: 118–120 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.69 (s, 1H, Schiff-base proton), 8.10–7.35 (m, $12H_{aryl}$), 5.51 (s, 1H, H_3), 5.27 (s, 1H, H_4), 3.89 (dd, ^2J = 12.4, ^3J = 4.6 Hz, $1H_1$), 3.86 (dd, ^2J = 12.4, ^3J = 6.4 Hz, $1H_1$), 3.70 (m, H_{7a}), 3.35 (m, H_7), 2.97 (dd, ^2J = 11.8, ^3J = 2.3 Hz, H_{6eq}), 2.84 ppm (dd, ^2J = 11.8, ^3J = 6.4 Hz, H_{6ax}). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 158.8, 149.9, 148.9, 136.3, 135.9, 130.6, 133.4, 132.8, 132.3, 130.3, 129.7, 129.4, 129.0, 128.4, 124.6, 124.4, 124.3, 81.2, 78.5, 69.6, 64.9, 63, 48.5 ppm. IR (KBr pellet): 1610, 1526, 1384 cm^{-1}. MS (CI) m/z: calcd for $C_{25}H_{23}N_7O_6$ 517, found 518 [MH^+]. HRMS (FAB) m/z: calcd for $C_{25}H_{24}N_7O_6$ 518.1788, found 518.1814 [MH^+].

*threo-1,2,3,4-Tetrakis(o-nitrobenzylideneimino)-butane (**5′**).* An ethanolic solution of *o*-nitrobenzaldehyde in excess was added dropwise at rt under inert atmosphere to a stirred methanolic solution of **1**. Product **5′** precipitated out from the solution as a deep orange powder in quantitative yield without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.76 and 8.72 (s, 4H, Schiff-base protons), 8.13–7.40 (unresolved peaks, 16H), 4.39 (bd, ^2J = 11.7, 2H, H_1), 4.23 (bd, ^3J = 7.5 Hz, 2H, $H_{2,3}$), 4.01 ppm (dd, ^2J = 11.7, ^3J = 7.5 Hz, 2H, H_4).

*threo-1,2,3,4-Tetrakis(o-aminobenzylideneimino)-butane (**5a**).* 2-Aminobenzaldehyde (0.2 g, 1.6 mmol) in ethanol (20 mL) and **1** (0.118 g, 1 mmol) in ethanol (20 mL) made up the reaction mixture. During the addition the solution turned deep yellow. After removal of the solvent under reduced pressure, product **5a** was obtained quantitatively as a yellow solid without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.38 (s, 4H, Schiff-base protons), 7.18 (m, 8H, H-4′, H-6′), 6.65 (m, 8H, H-3′, H-5′), 6.85 (bs, 8H, NH_2), 2.98 (bs, 4H, $H_{1,4}$), 2.86 ppm (bs, 2H, $H_{2,3}$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 165.5, 148.4, 133.5, 131, 128.7, 116, 115.5, 55.8, 46.2 ppm.

*threo-1,2,3,4-Tetrakis(salicylideneimino)-butane (**5b**).* Salicylaldehyde (0.58 g, 4.7 mmol) in methanol (30 mL) and **1** (0.35 g, 2,4 mmol) in methanol (30 mL) made up the reaction mixture. $CHCl_3$ (100 mL) was added, and then methanol and water-soluble materials were washed out repeatedly with H_2O. The organic layer was separated, and solvent was removed under reduced pressure. The residual yellow solid was recrystallized from *i*PrOH/benzene 4:1 to obtain yellow needles of **5b** (0.37 g, 15%). Mp: 165–6° C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 13.2 (s, 2H, OH), 13.0 (s, 2H, OH), 8.40 (s, 2H, Schiff-base protons), 8.29 (s, 2H, Schiff-base protons), 7.34 and 7.32 (2t, ^3J = 8 Hz, 4H, H-4′), 7.20 and 7.17 (2d, ^3J = 8 Hz, 4H, H-6′), 7.01 and 6.93 (2d, ^3J = 8 Hz, 4H, H-5′), 6.85 (bt, ^3J = 8 Hz, 4H, H-3′), 3.98 (ddd, ^2J = 13.3, ^3J = 10.9, ^3J = 6.3 Hz, 4H, $H_{1,4}$), 3.78 ppm (dd, ^3J = 10.9, ^3J = 6.3 Hz, 2H, $H_{2,3}$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 167.5, 161.2, 160.8, 132.9, 132.7, 131.9, 131.7, 118.9, 118.4, 118.3, 117.2, 116.9, 71.0, 62.0 ppm. MS (EI) m/z: calcd for $C_{32}H_{30}N_4O_4$ 534, found 534 [M^+]. Anal. Calcd for $C_{32}H_{30}N_4O_4$: C, 71.89; H, 5.66; N, 10.48. Found: C, 71.90; H, 5.78; N, 10.36.

General Procedure for the Reaction of Substituted Benzaldehydes (*m*-CN, *p*-NHAc, and *o*-CO_2H) with 1. A solution of substituted benzaldehyde in methanol was added dropwise to a solution of **1** in methanol at ambient temperature under argon atmosphere. After addition completed, the reaction mixture was stirred overnight, and then $CHCl_3$ (100 mL) was added. MeOH and water-soluble materials were washed out repeatedly with water, then the organic layer was dried with Na_2CO_3 and filtered, and solvent was removed under reduced pressure to leave a residual solid.

*(rac)-2,6-Bis(m-cyanophenyl)-cis-1,3,5,7-TAD (**6a**).* *m*-Cyanobenzaldehyde (0.28 g, 2.5 mmol) in methanol (20 mL) and **1** (0.141 g 1.2 mmol) in methanol (30 mL) made up the reaction mixture. The residual yellow solid was recrystallized from acetonitrile, to give yellow needles of **6a** (0.4 g, 95%). Mp: 160–2° C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.91 (s, 2H, H-2′), 7.86 (d, ^3J = 7.8 Hz, 2H, H-4′), 7.59 (bd, ^3J = 7.6 Hz, 2H, H-6′), 7.48 (t, ^3J = 7.7 Hz, 2H, H-5′), 4.73 (s, 2H, $H_{2,6}$), 3.27 (bdd, ^2J = 13.0, ^3J = 1.8 Hz, 2H, $H_{4,8eq}$), 3.20 (bdd, ^2J = 13.0 ^3J = 1.0 Hz, 2H, $H_{4,8ax}$), 2.99 ppm (s, 2H, $H_{9,10}$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 143.3, 131.6, 131.1, 130.3, 129.1, 118.6, 112, 72.9, 51.1, 50.8 ppm. MS (FAB) m/z: calcd for $C_{20}H_{20}N_6$: 344.4, found 345 [MH^+].

*(rac)-2,6-Bis(p-acetamidophenyl)-cis-1,3,5,7-TAD (**6b**).* *p*-Acetamidobenzaldehyde (0.326 g, 4 mmol) in methanol (20 mL) with **1** (0.236 g, 2 mmol) in methanol (30 mL) made up the reaction mixture. The residual orange solid was identified as compound **6b** (0.73 g, 1.8 mmol) in 90% yield with less than 5% impurities according to ^{1}H NMR. ^{1}H NMR (200 MHz, CD_3OD): δ 7.58 (d, ^3J = 8.7 Hz, 4H, H-3′), 7.50 (d, ^3J = 8.7 Hz, 4H, H-2′), 4.56 (s. 2H, $H_{2,6}$), 3.20 (d, ^2J = 13.4 Hz, 2H, $H_{4,8ax}$), 3.09 (d, ^2J = 13.4 Hz, 2H, $H_{4,8ax}$), 2.90 (s, 2H, $H_{9,10}$), 2.10 ppm (s, 3H). ^{13}C NMR (50.3 MHz, CD_3OD): δ 171.6, 139.9, 138.4, 128.3, 120.9, 74.89, 51.9, 51.5, 23.9 ppm. MS (FAB) m/z: calcd for $C_{22}H_{27}N_6O_2$ 408, found 409 [MH^+]. HRMS (FAB) m/z: calcd for $C_{22}H_{28}N_6O_2$ 409.2352, found 409.2340 [MH^+].

*(rac)-2,6-Bis(o-benz-1,5-amido)-cis-1,3,5,7-TAD (**7**).* Phthalaldehyde (0.86 g, 5.7 mmol) in methanol (25 mL) and **1** (0.338 g, 2.9 mmol) in methanol (25 mL) made up the reaction mixture. The residual yellowish solid was treated with charcoal in hot ethanol, and after filtration **7** was crystallized as white powder (0.66 g, 60%). Mp: 240° C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (dd, ^3J = 7.1, ^4J = 1 Hz, 2H, H-3′), 7.53 (m, 4H, H-6′, H-5′), 7.45 (bd, ^3J = 7.1 Hz, 2H, H-4′), 5.20 (d, ^3J = 9.8 Hz, 2H, $H_{2,6}$), 4.51 (d, ^2J = 13.9 Hz, 2H, $H_{4,8eq}$), 3.57 (d, ^2J = 13.9, ^3J = 3.6 Hz, 2H, $H_{4,8ax}$), 3.35 (bs, 2H, $H_{9,10}$), 1.85 ppm (bt, ^3J = 9.8 Hz, 2H, NH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 166, 141.8, 132.3, 131.8, 129.5, 123.7, 123.1, 70.7, 50.2, 43.8 ppm. IR ($CHCl_3$): 1690.1 cm^{-1}. MS (FAB) m/z: calcd for $C_{20}H_{18}N_4O_2$ 346, found 347 [MH^+]. Anal. Calcd for $C_{20}H_{18}N_4O_2 \cdot 1/2CH_3OH$: C, 67.94; H, 5.56; N, 15.46. Found: C, 67.52; H, 5.12; N, 15.24.

Preparation of 2,6-Dialkyl-TAD. *(rac)-2,6-Bis(hydroxymethyl)-cis-1,3,5,7-TAD (**9**).* A solution of glycolaldehyde (dimer) (1.2 g, 10 mmol) in ethanol (6 mL) was added to a solution of (*rac*)-1,2,3,4-tetraaminobutane (1.22 g, 10 mmol) in ethanol (24 mL) at rt and stirred for 30 min while the product precipitated as a white powder. The precipitate was collected and washed with ethanol/acetone 1:1 mixture before drying in vacuo. After recrystallization from ethanol, **9** was obtained as a white solid (1.8 g, 90%). Mp: 151–153 °C (dec). ^{1}H NMR (200 MHz, D_2O, TMS salt): δ 3.57 (m, 6H, $4H_\alpha$ + $2H_{2,6}$), 3.05 (dd, ^2J = 14.0, ^3J = 2.4 Hz, 2H, $H_{4,8eq}$), 2.95 (dd, ^2J = 14.0, ^3J = 0.9 Hz, 2H, $H_{4,8ax}$), 2.77 ppm (bs, 2H, $H_{9,10}$). ^{13}C NMR (50.3 MHz, D_2O, TMS salt): δ 72.4, 66.3, 51.5, 51.0 ppm. IR (KBr): 3300–3000, 2900, 1496 cm^{-1}. MS (CI) m/z: 203 [MH^+]. Anal. Calcd for $C_8H_{18}N_4O_2$: C, 47.51; H, 8.97; N, 27.71. Found: C, 47.81; H, 9.11; N, 27.74.

*(rac)-2,6-Bis(α,α′-dimethyl-β-hydroxyethyl)-cis-1,3,5,7-TAD (**10**).* A solution of 2,2-dimethyl-3-hydroxy-propanaldehyde (dimer) (0.35 g, 3.4 mmol) in ethanol (10 mL) was added slowly over 20 min at rt under argon, to a solution of **1** (0.2 g, 1.7 mmol) in ethanol (20 mL), and the mixture was stirred at rt overnight. After solvent removal under reduced pressure, the crude was dissolved in $CHCl_3$ and

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extracted with aqueous sat. K_2CO_3. The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated. The oily product was solidified upon addition of benzene or diethyl ether. Recrystallization from benzene afforded **10** as white crystals (0.3 g, 60%). Mp: 111−113 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 3.55 (d, ^2J = 10.81 Hz, 2H, $2H_{\beta}$), 3.47 (d, ^2J = 10.8 Hz, 2H, $2H_{\beta'}$), 3.10 (s, 2H, $H_{2,6}$), 2.49 (dd, ^2J = 12.8, ^3J = 1.1 Hz 2H, $H_{4,8eq}$), 2.37 (dd, ^2J = 12.8, ^3J = 1.9 Hz, 2H, $H_{4,8ax}$), 2.05 (bs, 2H, $H_{9,10}$), 0.88 (s, 3H), 0.75 ppm (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 79.1, 72.4, 51.1, 51.0, 37.8, 20.8, 19.5 ppm. MS (FAB) *m/z*: 287.3 [MH^+]. HRMS *m/z*: calcd for $C_{14}H_{30}N_4O_2$ 287.2447, found 287.2447 [MH^+].

*(rac)-2,6-Bis(hydroxymethyl)-cis-1,3,5,7-TAD Cadmium Bromide Complex [Cd^{II}.(**9**)]Br_2.* A solution of $CdBr_2$ (70 mg, 0.25 mmol) in hot (50 °C) MeOH (10 mL) was added dropwise to a hot (50 °C) solution of **9** (52 mg, 0.25 mmol) in MeOH (10 mL). The mixture was refluxed for 10 min and then allowed to stand for several days at rt until a white precipitation was obtained. After recrystallization from H_2O/EtOH, 1:1 colorless crystals were obtained (52 mg, 43%). Full characterization of the complex is given in the Results and Discussion section.

*(rac)-2,6-Bis(hydroxymethyl)-cis-1,3,5,7-TAD Lead Nitrate Complex [Pb^{II}.(**9**)]$(NO_3)_2$.* A solution of $Pb(NO_3)_2$ (185 mg, 0.55 mmol) in hot (50 °C) MeOH (25 mL) was added dropwise to a hot (50 °C) solution of **9** (120 mg, 0.6 mmol) in MeOH (10 mL). The mixture was refluxed for 10 min and then allowed to stand for several days at rt until a white precipitate was obtained. After recrystallization from H_2O/EtOH, 1:1 colorless crystals were obtained (183 mg, 60%). Full characterization of the complex is given in the Results and Discussion section.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Proton and carbon NMR spectra of compounds of **5b**, ***o*-6′**, **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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