Schiff-Base Podates − X-ray, NMR and Ab Initio Molecular-Orbital Studies of the Cadmium(II) Complexes of Linear and Three-Armed Podands in Solution and Solid State

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Cadmium(II) complexes of two Schiff bases, 1,3-di(pyridine-2-carboxaldimino)propane ($C_{15}H_{16}N_4$, **L1**)[1] and tris[4-(2′-pyridyl)-3-aza-3-butenyl]amine ($C_{24}H_{27}N_7$, **L2**)[2] are described. An efficient route utilising molecular sieves for the synthesis of Schiff bases is presented. The ligands **L1** and **L2** can be described as linear and three-armed podands, respectively, **L1** being conformationally flexible and **L2** preorganised. Cadmium perchlorate in methanol with **L1** yields a crystalline complex $[Cd(\mathbf{L1})_2](ClO_4)_2$ (**1**), the structure of which was determined by X-ray structure analysis. The complex **1** has an unusual nonsymmetrical 8-coordinated helical structure and crystallizes in an acentric space group (*Cc*, no. 9) as a pure enantiomer due to spontaneous resolution. Solution studies of **1** in $CHCl_3$/DMSO (10:1) and pure DMSO were performed using ^1H-, ^{13}C-, ^{113}Cd-NMR and ^1H,^{15}N z-GS HMBC spectroscopy and they suggest a reorientation of **1** into the more symmetrical 4-coordinate complex due to the flexible nature of **L1**. The preorganised, potentially tetra-, hexa- or heptadentate, three-armed podand **L2** and its in situ complexation with the Cd^{2+} cation were investigated by ^1H-, ^{13}C-, ^{113}Cd-NMR and ^1H,^{15}N z-GS HMBC spectroscopy. The results support the formation of a highly symmetrical helical 6-coordinate podate $[Cd\mathbf{L2}](NO_3)_2$ (**2**). The structure of **2** has also been verified by ab initio HF-MO calculations using a standard 3-21G* basis set (Lan2DZ for Cd).

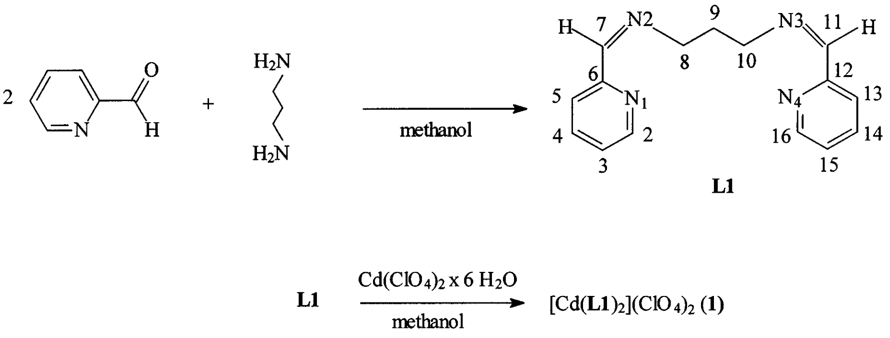
There is a growing interest in finding alternative approaches for the design of new inexpensive and easy-to-prepare ligand/podand systems. Hannon and coworkers have described a simple and inexpensive way to prepare imine-based rigid ligands that can form a triple-helicate structure with proper metal ions.[3a] Schiff-base complexes are considered to be among the most important stereochemical models in main-group and transition-metal coordination chemistry due to their preparative accessibility and structural variety.[4] The Schiff-base ligands and podands are not so well studied as their macrocyclic and macrobicyclic counterparts. In particular, the macrocyclic Schiff bases have been synthesized, as their metal complexes, through the [1+1] or [2+2] condensation of proper bis-amines and bis-aldehydes, using metal ions as templates.[5] In the absence of templating metal ions the reactions give poor yields and oligomeric/polymeric products. On the other hand, by using metal ions, it is often very difficult or impossible to remove the template from the macrocycle. Schiff-base helical structures are still rare[3a] and only a few examples exist for similar Schiff-base cryptates[3b]. Earlier we reported the synthesis and some metal complexes of the podand **L1**[1]. **L1** has a short flexible spacer between the two metal-binding sites, thus giving a tweezer-like bite to a single transition-metal ion. As an alternative approach to prepare Schiff-base compounds we used activated molecular sieves to increase yields in the nontemplated synthesis for a known podand **L2**[2]. **L2** offers a chemically similar complexation site, but now preorganised for *endohedral* 4-, 6- or 7-coordination. We selected the Cd^{2+} ion as a probe for a study of the solution complexation, since it has very versatile coordination behaviour and ^{113}Cd NMR has proved to be an exellent tool to monitor complex formation.[6] In this work we report the preparation of Cd^{II} complex from **L1** (Scheme 1) and the definitive characterization of the complex in the solid state by X-ray diffraction together with the synthesis of three-armed podand **L2** derived from tris(2-aminoethyl)-amine (TREN) and 2-pyridylcarbaldehyde and its in situ complexation with Cd^{2+} (Scheme 2). The Cd^{II} complexes **1** and **2** were investigated by ^1H-, ^{13}C-, ^{113}Cd-NMR and 2-D (two-dimensional) ^1H,^{15}N z-GS HMBC (z-gradient selected heteronuclear multiple-bond coherence) spectroscopy and the complex **2** also by an ab initio HF-MO calculation.

Results and Discussion

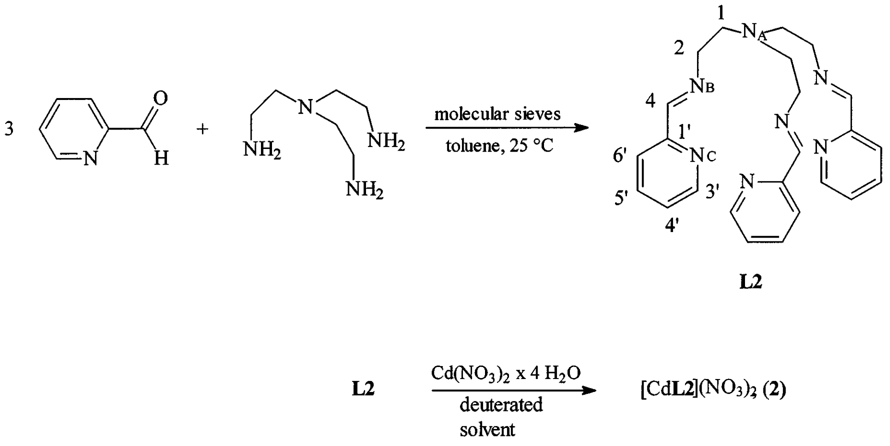
Although **L1** itself is a liquid its complexation with Cd^{II} perchlorate in methanol produced crystals suitable for X-ray diffraction study (Table 1 in Experimental Section). The

1434−1948/98/1010−1555 $ 17.50+.50/0

Scheme 1



Scheme 2

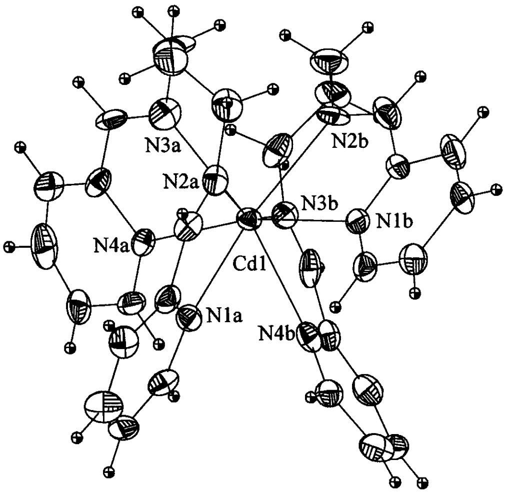


molecular structure of Cd^{II} complex **1** is displayed in Figure 1. The complex **1** is formed by coordination of two **L1** podands into a single cadmium ion. Due to its flexible nature **L1** acts as a pseudo-macrocyclic tetradentate ligand, thus resulting in a sandwich-type of 8-coordinated 1:2 complex.

Similar 8-coordination for Cd^{II} has been observed in some macrocyclic complexes.[7] The observed bond lengths and angles are consistent with the literature.[8][9] Selected bond lengths and angles for complex **1** of the Cd^{2+} ion are presented in Figure 1. To our great surprise complex **1** crystallized in an acentric space group and a detailed inspection of the structure revealed a helical arrangement of **L1** [in pseudo-macrocyclic conformation, the nonbonded intramolecular contact distances between the *ortho*-H atoms (H2, H16) are 223 pm (**L1**A) and 246 pm (**L1**B)] around the Cd^{II} ion. In some cases crystallization from a racemic solution of helical molecules can induce spontaneous resolution of the enantiomers and a mixture of enantiomerically pure crystals can be obtained[10]. The helical arrangement of the ligands results from the sterical factors around the Cd^{II} ion. The covalent radius of Cd^{II} ion is too small to bind all eight spatially neighbouring N atoms in a symmetrical cubic coordination, thus creating a twist of approximately 64° between the lower and upper ligand (Figure 2).

The four N atoms in a single **L1** ligand form a nearly symmetrical square plane (torsion angles for N1a−N2a−N3a−N4a and N1b−N2b−N3b−N4b are −4.63 and −3.69°, respectively) with almost equal nonbonded contact distances between the N atoms (N1a···N2a = 270.9 pm, N2a···N3a = 287.2 pm, N3a···N4a = 272.4 pm and N1a···N4a = 324.2 pm; N1b···N2b = 277.4 pm, N2b···N3b = 280.3 pm, N3b···N4b = 273.6 and N1b···N4b = 328.2 pm). The conformation of **L1** in the complex **1** is very close to an aza-crown conformation with all N atom lone pairs pointing in the same direction. The least-squares planes for the pyridine−imine (N1, C2−C7, N2 and N3, C11−C16, N4) parts show that they are nearly planar and the angles between the planes within the coordinated **L1** are quite similar: (N1a → N2a) and (N3a → N4a) 86.02°; (N1b → N2b) and (N3b → N4b) 75.80° The packing of the molecules in the unit cell along the *b* axis is shown in Figure 3. The weak π-stacking interactions between the two adjacent and co-planar pyridine rings along the *c* axis stabilise the packing. The distance between the co-planar pyridine rings is 416 pm.

Figure 1. The molecular structure of compound **1** [DIAMOND drawing with 20% (size reduced to improve clarity) probability ellipsoids (all non-hydrogen atoms), the uncoordinated perchlorate anions have been omitted for clarity][a]



[a] Selected bond lengths [pm] and angles [°]: Cd1−N1a (−N1b) 256.3(14) [251.8(18)], Cd1−N2a (−N2b) 247.7(17) [251.8(14)], Cd1−N3a (−N3b) 250.9(20) [250.9(20)], Cd1−N4a (−N4b) 246.9(15) [259.5(19)]; N4a−Cd1−N3b 71.6(6), N4a−Cd1−N1b 169.0(2), N3b−Cd1−N2a 161.6(3), N4a−Cd1−N3a 65.9(6), N3b−Cd1−N3a 95.7(6), N2a−Cd1−N3a 70.3(6), N3b−Cd1−N1b 109.8(5), N3a−Cd1−N1b 124.0(6), N4a−Cd1−N2b 122.5(5), N1b−Cd1−N2b 66.9(5), N1b−Cd1−N1a 91.5(5), N3b−Cd1−N1a 32.0(6), N1a−Cd1−N4b 77.6(2), N2b−Cd1−N1a 156.0(5), N2a−Cd1−N4b 131.4(6), N4a−Cd1−N1a 80.2(5), N4a−Cd1−N4b 91.2(5).

In order to obtain some information about the structure of the metal complex **1** in solution we also carried out ^{113}Cd-NMR and 2-D ^{1}H,^{15}N z-GS HMBC measurements in [D$_6$]DMSO. The metal complex shows only one strong ^{113}Cd signal at $\delta = 84.4$ measured from external 0.1 M aqueous Cd(ClO$_4$)$_2$ ($\delta = 0.0$). This result can be regarded as good evidence for the reorientation of the unsymmetrical complex **1** into a more symmetrical tetracoordinate complex. This result is also in good agreement with the value for the tetracoordinate Cd^{2+} complex ($\delta = 95$) reported by Munataka et al.[6b]

The ^{15}N chemical shift of the imine nitrogen atoms changes from $\delta = -35.8$ for the free ligand to $\delta = -62.2$ for the cadmium complex **1**. The signal of the pyridine nitrogen atoms at $\delta = -62.6$ of the free ligand, is not visible in the ^{1}H,^{15}N z-GS HMBC correlation map of the cadmium complex of **L1** in solution, although the delay for evolution of long-range couplings was increased to 200 ms. The ^{15}N-NMR chemical shifts of the ligand itself are in agreement with those reported for (*Z*)-*N*-benzylidenecyclohexylamine ($\delta = -36.4$[11]) and 2-methylpyridine ($\delta = -62.6$[12]). The absence of the ^{1}H,^{15}N z-GS HMBC correlation can be due to (i) too small a scalar coupling constant $J(^{1}\mathrm{H},^{15}\mathrm{N})$ to allow magnetization transfer between proton and ^{15}N or (ii) a dynamic process taking place inside the complex at room temperature.

We have also investigated the complexation properties of tris[4-(2′-pyridyl)-3-aza-3-butenyl]amine (**L2**) in solution

Table 1. Crystal data, data collection and structure refinement for compound **1**

Crystal data	
Formula	$C_{30}H_{32}CdCl_2N_8O_8$
M_r	815.94
Crystal system	Monoclinic
Space group	*Cc* (No. 9)
Wavelength, Mo-K_α [Å]	0.71073
Crystal size [mm]	0.4 × 0.4 × 0.3
a [pm]	1809.3(4)
b [pm]	1065.7(3)
c [pm]	1753.1(5)
β [°]	95.85(2)
V [nm^3]	3.3627(2)
D$_c$ [g cm^{-1}]	1.612
Z	4
F(000)	1656
μ (Mo-K_α) [mm^{-1}]	0.870
Data collection	
T [K]	293(2)
Scan mode	ω/2θ
hkl range	h 0 → 21
	k 0 → 12
	l −20 → 20
θ$_{\mathrm{min/max}}$ [°]	2.22/24.97
Measured reflections	3068
Unique reflections	3068
Refls. used for refinement	2570
Absorption correction	ψ scans
T$_{\mathrm{min}}$/T$_{\mathrm{max}}$	0.84/0.99
Refinement	
Refinement method on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3068/44/392
H atoms (found/calcd.)	0/32
Final *R* values [$I > 2\sigma(I)$]	
$R1$[a]	0.0475
$wR2$[b]	0.1285
(shift/error)$_{\mathrm{max}}$	< 0.001
Goodness-of-fit on F^2 (*S*)	1.079
ρ$_{\mathrm{fin}}$(max/min) [e Å^{-3}]	0.673/−1.224

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)]\}^{1/2}$; $w = 1/[\delta^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0946$; $b = 8.58$. – $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

Figure 2. A view of the coordination sphere showing the twist between the lower and upper ligand (the coordinating bonds are presented as dotted bars and the non-bonded intramolecular distances as thick solid bars)

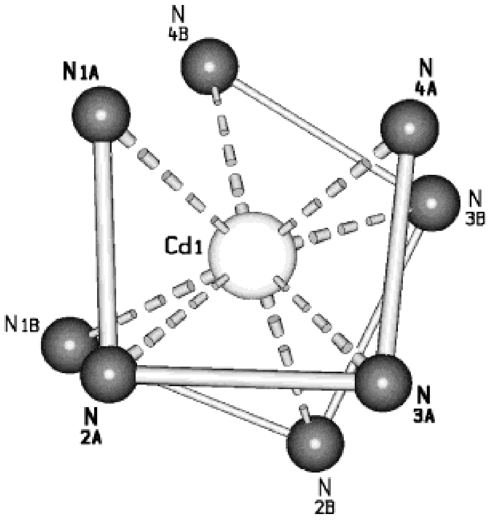
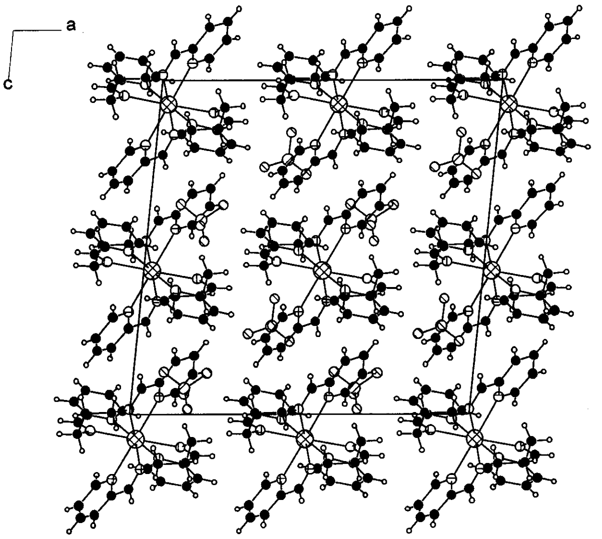


Figure 3. The packing of the molecules in the unit cell along the *b* axis



with Cd^{2+} using ^{1}H-, ^{13}C-, ^{113}Cd-NMR and 2-D $^{1}H,^{15}N$ z-GS HMBC spectroscopy. The measurements show that Cd^{2+} [added as $Cd(NO_3)_2 \cdot 4\ H_2O$] is efficiently complexed with the ligand **L2** forming tris[4-(2′-pyridyl)-3-aza-3-butenyl]aminecadmium(II) (**2**).

The metal complex **2** exhibits a strong ^{113}Cd signal at $\delta = 188.1$ in $CDCl_3$/[D_6]DMSO (10:1). From the fact that only one ^{113}Cd signal is observed it can be concluded that the potentially heptadentate Schiff-base ligand **L2** provides a highly symmetrical time-averaged complexation site for the Cd^{2+} cation. Furthermore, the more deshielded chemical shift value of **2** in comparison with **1** suggests that the coordination number must be larger in **2** than in **1**, as shown by Munataka et al.[6b]

A comparison of the $^{1}H,^{15}N$ z-GS HMBC correlation map of the free ligand **L2** with that of the cadmium complex **2** reveals that both pyridyl- and Schiff-base nitrogen atoms coordinate towards the cadmium cation. Due to the interaction with the metal centre the ^{15}N-NMR chemical shifts are moved upfield by approximately 50 ppm for each N atom compared with the free ligand **L2**. In [D_6]DMSO the ^{15}N-NMR chemical shift of the Schiff-base nitrogen atoms changes from $\delta = -38.9$ of **L2** to $\delta = -90.0$ in **2**. The pyridine nitrogen atoms show a shift from $\delta = -62.2$ to $\delta = -113.0$, respectively. The $^{1}H,^{15}N$ z-GS HMBC correlation map does not show any cross peak at room temperature due to the tertiary nitrogen atom N_A.

From the X-ray studies of related tris[4-(2′-pyridyl)-3-aza-3-butenyl]aminemetal complexes[2] it is already known that the bridging tertiary nitrogen atom N_A should also be coordinating. This assumption is further supported by the present ab initio calculation carried out on tris[4-(2′-pyridyl)-3-aza-3-butenyl]aminecadmium(II) (**2**) with a full geometry optimization at the HF/3-21G* (using Lan2DZ

Table 2. Calculated Cartesian atomic coordinates of the optimized standard orientation for the cation [Cd**L2**]$^{2+}$ in [Cd**L2**]$(NO_3)_2$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd(1)	0.327679	0.115479	−0.116882	H(1AA)	4.242137	−0.409747	0.616059
N(A)	2.989909	0.359778	−0.871631	H(1BA)	4.594015	1.252063	0.215507
N(BA)	1.767749	0.124783	1.705724	H(1AB)	4.422504	−1.106293	−1.487278
N(BB)	1.114459	−1.706196	−1.320791	H(1BB)	3.172969	−0.741547	−2.652850
N(BC)	0.907513	2.353453	−0.654099	H(1AC)	2.433796	1.235742	−2.673551
N(CA)	−0.456477	−1.470165	1.649774	H(1BC)	3.965292	1.838415	−2.064705
N(CB)	−1.380929	−0.683573	−1.744201	H(2AA)	3.578743	0.914095	2.483553
N(CC)	−1.419530	1.666177	0.660750	H(2BA)	2.612870	1.997155	1.495694
C(1A)	3.788146	0.540514	0.370504	H(2AB)	2.676744	−2.254262	−0.064183
C(1B)	3.367161	−0.884064	−1.599658	H(2BB)	2.789114	−2.967091	−1.674338
C(1C)	2.961904	1.532508	−1.778203	H(2AC)	2.147590	3.507315	−1.936604
C(2A)	2.959017	0.981227	1.595700	H(2BC)	2.816624	3.153870	−0.359261
C(2B)	2.526131	−2.074039	−1.118607	H(4A)	2.151676	−0.617145	3.580905
C(2C)	2.244584	2.739249	−1.178054	H(4B)	0.685271	−3.135606	−2.729425
C(4A)	1.518982	−0.590757	2.707267	H(4C)	0.223119	4.287073	−0.616247
C(4B)	0.369533	−2.281908	−2.150254	H(3′A)	−2.103666	−2.257197	0.720052
C(4C)	0.054743	3.243325	−0.399196	H(3′B)	−2.852297	0.710329	−1.444561
C(1′A)	0.331912	−1.472820	2.731171	H(3′C)	−2.626556	0.344378	1.657186
C(1′B)	−0.996225	−1.782350	−2.408261	H(4′A)	−2.684997	−3.765472	2.593520
C(1′C)	−1.218263	2.932485	0.278310	H(4′B)	−4.420500	−0.296887	−3.062499
C(3′A)	−1.509052	−2.281728	1.608649	H(4′C)	−4.339934	2.030504	2.229239
C(3′B)	−2.584515	−0.170967	−1.983798	H(5′A)	−1.246286	−3.759834	4.613101
C(3′C)	−2.515077	1.360925	1.350639	H(5′B)	−3.725300	−2.343116	−4.278651
C(4′A)	−1.830568	−3.125481	2.660123	H(5′C)	−3.997017	4.372728	1.489814
C(4′B)	−3.462284	−0.740765	−2.892955	H(6′A)	0.724458	−2.261354	4.669779
C(4′C)	−3.472215	2.310958	1.670299	H(6′B)	−1.475936	−3.284162	−3.837361
C(5′A)	−1.026964	−3.121522	3.782083	H(6′C)	−1.936577	4.936403	0.235822
C(5′B)	−3.072291	−1.877534	−3.569435				
C(5′C)	−3.277275	3.614069	1.260539				
C(6′A)	0.077533	−2.280765	3.817006				
C(6′B)	−1.812595	−2.407909	−3.322603				
C(6′C)	−2.124876	3.931822	0.554219				

Table 3. Selected bond lengths [Å] and bond angles [°] and some TAP structural parameters for the cation [Cd**L2**]$^{2+}$ in [Cd**L2**](NO$_3$)$_2$ (**2**)

Cd(1)−N(A)	2.778	C(2B)−N(BB)	1.473	C(3′A)−C(4′A)	1.386
Cd(1)−N(BA)	2.323	C(2C)−N(BC)	1.487	C(3′B)−C(4′B)	1.386
Cd(1)−N(BB)	2.321	N(BA)−C(4A)	1.256	C(3′C)−C(4′C)	1.386
Cd(1)−N(BC)	2.373	N(BB)−C(4B)	1.255	C(4′A)−C(5′A)	1.380
Cd(1)−N(CA)	2.500	N(BC)−C(4C)	1.259	C(4′B)−C(5′B)	1.379
Cd(1)−N(CB)	2.491	C(4A)−C(1′A)	1.479	C(4′C)−C(5′C)	1.380
Cd(1)−N(CC)	2.462	C(4B)−C(1′B)	1.477	C(5′A)−C(6′A)	1.389
N(A)−C(1A)	1.488	C(4C)−C(1′C)	1.475	C(5′B)−C(6′B)	1.389
N(A)−C(1B)	1.490	C(1′A)−N(CA)	1.338	C(5′C)−C(6′C)	1.388
N(A)−C(1C)	1.483	C(1′B)−N(CB)	1.340	C(5′C)−C(6′C)	1.388
C(1A)−C(2A)	1.544	C(1′C)−N(CC)	1.338	C(6′A)−C(1′A)	1.377
C(1B)−C(2B)	1.535	N(CA)−C(3′A)	1.330	C(6′B)−C(1′B)	1.376
C(1C)−C(2C)	1.527	N(CB)−C(3′B)	1.330	C(6′C)−C(1′C)	1.377
C(2A)−N(BA)	1.471	N(CC)−C(3′C)	1.330		

N(BA)−Cd(1)−N(BB)	101.5	C(4A)−N(BA)−Cd(1)	120.0
N(BA)−Cd(1)−N(BC)	91.28	C(4B)−N(BB)−Cd(1)	120.1
N(BA)−Cd(1)−N(CA)	69.05	C(4C)−N(BC)−Cd(1)	117.1
N(BA)−Cd(1)−N(CB)	159.9	C(1′A)−N(CA)−Cd(1)	112.8
N(BA)−Cd(1)−N(CC)	100.9	C(1′B)−N(CB)−Cd(1)	112.9
N(BB)−Cd(1)−N(BC)	122.7	C(1′C)−N(CC)−Cd(1)	113.5
N(BB)−Cd(1)−N(CA)	88.57	C(3′A)−N(CA)−Cd(1)	127.8
N(BB)−Cd(1)−N(CB)	69.02	C(3′B)−N(CB)−Cd(1)	127.9
N(BB)−Cd(1)−N(CC)	154.0	C(3′C)−N(CC)−Cd(1)	127.1
N(BC)−Cd(1)−N(CA)	146.6	C(1A)−C(2A)−N(BA)	109.2
N(BC)−Cd(1)−N(CB)	108.8	C(1B)−C(2B)−N(BB)	106.8
N(BB)−Cd(1)−N(CC)	69.57	C(1C)−C(2C)−N(BC)	110.8
N(CA)−Cd(1)−N(CB)	92.47	C(1A)−N(A)−C(1B)	111.9
N(CA)−Cd(1)−N(CC)	87.35	C(1A)−N(A)−C(1C)	115.1
N(CB)−Cd(1)−N(CC)	85.50	C(1B)−N(A)−C(1C)	111.5
C(2A)−N(BA)−Cd(1)	116.5	N(A)−C(1A)−C(2A)	114.2
C(2B)−N(BB)−Cd(1)	116.8	N(A)−C(1B)−C(2B)	110.8
N(2C)−N(BC)−Cd(1)	123.0	N(A)−C(1C)−C(2C)	113.2

Coordination polyhedron model values[a]	[Cd**L2**]$^{2+}$ (this work)	[Zn**L2**]$^{2+}$ in [Zn**L2**](BF$_4$)$_2$[b]
twist angle ϕ [°]	47	45.9
M−N$_A$ [pm]	277.8	301.3
M−N$_6$ [pm]	2.344	2.180
a	3.36	3.29
c	3.29	3.14
a/*c*	1.02	1.05
"bite" *b*	2.79	2.64

[a] For the definition of the model, see ref.[2a]. − [b] See ref.[2a].

basis set for Cd) level of theory. Calculated Cartesian atomic coordinates of **2** are collected in Table 2.

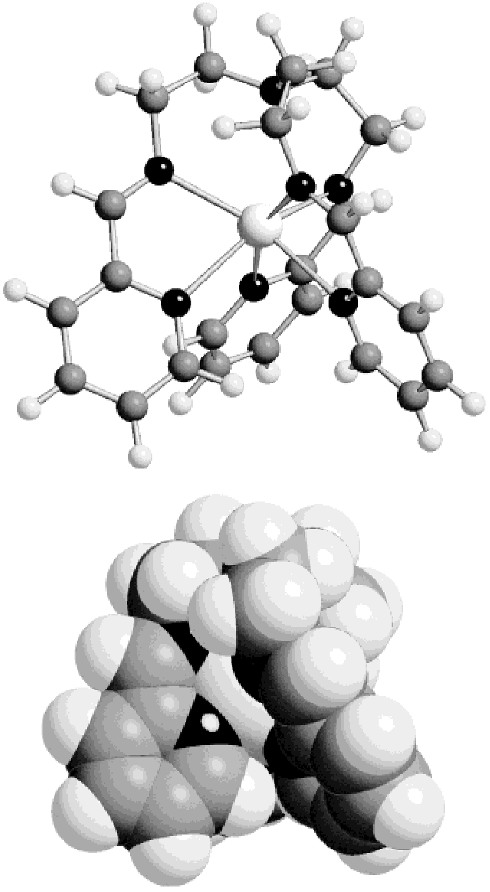
The calculated Cd^{2+} ($4d^{10}$) complex **2** and the analogous Zn^{2+} ($3d^{10}$) complex[2a] have a similar distorted trigonal antiprism (TAP) 6-coordinated structure, as might be expected. Selected bond lengths and bond angles of **2**, together with some TAP structural model parameters,[2a] are given in Table 3.

The six Cd−N distances are calculated to be between 232 pm and 250 pm as shown in Table 3 and are in agreement with the experimental range from 246.9 pm to 259.5 pm found for complex **1** (see Figure 1). The size of the coordination polyhedron in **2**, given by M−N$_6$ (the weighted mean of all M−N bond length, M−N$_A$ not included)[2a] is calculated to be 241.2 pm (weighted by $\delta = 2.0$ pm for each bond length). The model parameters are in fair agreement when the larger size of Cd^{II} ion compared to Zn^{II} ion is taken into account. The distance between the bridgehead nitrogen atom N$_A$ and the metal centre is calculated as 278 pm. This distance is long for an actual bond but is clearly less than 295 pm which is the sum of the covalent radius of Cd (141 pm) and the van der Waals radius of N (154 pm),[13] indicating a moderate non-bonding interaction. It is also clearly shorter than found in the Zn analogue, see Table 3. Consequently, the calculated structure of **2** allows more flexibility in that part of complex where N$_A$ is located than for the other nitrogen atoms coordinated to Cd^{2+}. These results also can explain the fact that in ^{1}H,^{15}N z-GS HMBC experiments, nitrogen atom N$_A$ did not give any cross peak. An ab initio optimized structure of the cation [Cd**L2**]$^{2+}$ is shown in Figure 4.

Such an indicated dynamic process, involving the protons at C2 close to the bridgehead nitrogen atom N$_A$ is indeed observed and can easily be studied by ^{1}H NMR.

At 303 K the ^{1}H-NMR spectrum of **2** in CDCl$_3$/[D$_6$]DMSO (10:1) shows one broad singlet for the methylene protons of C2 at $\delta = 3.51$. This signal broadens even further when the sample is cooled down to 287 K. Further cooling leads to a splitting of this singlet into two separate signals with a multiplet splitting. At 253 K the dynamics of the diastereotopic protons 2-H and 2′-H are frozen out completely and then their separation is 86.6 Hz. Using now

Figure 4. An ab initio optimized structure and a van der Waals representation of the cation [Cd**L2**]$^{2+}$



the Guttowsky−Holm equation[14] modified by Green[15] the activation barrier of the proton topomerization can be calculated as $\Delta G^{\neq}(287\ K) = 56.1 \pm 2.1$ kJ/mol. In contrast to above, the ^{1}H-NMR signals of the aromatic protons do not show significant temperature dependency. This finding also points to a well-defined geometry of the complexation site with strong binding interactions between the Cd^{2+}cation and the pyridine and Schiff-base nitrogen atoms.

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Experimental Section

General: Metal salts, 2-pyridylcarbaldehyde and 1,3-diaminopropane were purchased from Merck, tris(2-aminoethyl)amine from Aldrich, powdered molecular sieves (3 Å) from Acros and used as received without further purification. Condensation reactions with molecular sieves were carried out under N_2, using a modified Schlenk technique. NMR spectra were recorded with either a Bruker Avance DRX 500 or a Bruker Avance DPX 250 FT NMR spectrometer. The ^{113}Cd-NMR chemical shift scale was fixed to the signal of a 1-mm diameter capillary tube containing 0.1 M aqueous or ethanolic (in low temperature runs) solutions of $Cd(ClO_4)_2$ inserted coaxially inside the 5-mm NMR tube as an external standard ($\delta = 0.0$). External neat nitromethane was used for the calibration in the case of ^{15}N-NMR experiments. The mass spectrum of **L1** was run with a VG AutoSpec HRMS spectrometer and the HRMS measurement of **L2** was recorded at 70 eV with a MAT 312 Finnigan mass spectrometer. IR spectra of **L2** were recorded with a Nicolet 5DXC FT-IR spectrometer, using KBr pellets.

Crystal-Structure Determinations: A specimen of suitable quality and size of compound **1** was mounted on top of a glass fibre and used for measurements of precise cell constants and intensity data collection with an Enraf Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å]. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for compound **1**, where the data was corrected for decay (−1.4%). Lp correction was applied and intensity data were corrected for absorption effects (max $T = 0.99$, min $T = 0.84$). The atomic scattering factors and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography.[16] The structure was solved by direct methods (SHELXS-86[17]) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93[18]). All non-hydrogen atoms were refined anisotropically. Geometrical restraints were used to prevent anomalous bond lengths for the perchlorate anions. Calculations were performed with the hydrogen atoms in their idealized calculated positions (C−H distance 0.93 Å for aromatic CH and 0.97 Å for CH_2) and allowed to ride on their corresponding carbon atoms with fixed isotropic temperature factors ($U_{\mathrm{iso(fix)}} = 1.2 \times U_{\mathrm{eq}}$ of the attached C atom). Further information on crystal data, data collection and structure refinement are summarized in Table 1. Selected interatomic distances and angles are shown in the caption to Figure 1. The plots were generated with the program DIAMOND[19] and SCHAKAL92[20]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101258. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk].

Ab Initio Molecular-Orbital Calculations: A full optimization of the structure of tris[4-(2′-pyridyl)-3-aza-3-butenyl]aminecadmium-(II) (**2**) was performed at the ab initio HF level of theory using gradient techniques with the Gaussian 94 set of programs.[21] The effective core potential (ECP) standard basis set Lan2DZ[22] was utilized for cadmium. The full-electron standard basis set 3-21G* [23] was used for all other atoms. A starting MM$^+$ structure for the ab initio calculations was optimized using the HyperChem 4.5 program.[24]

1,3-Bis(pyridine-2-carboxaldimino)propane (**L1**): We have earlier reported the synthesis of **L1**.[1] The structure of **L1** was further characterized by elemental analysis, ^{1}H/^{13}C NMR, ^{1}H,^{13}C HMQC and ^{1}H,X (X = ^{13}C,^{15}N) HMBC as well as mass spectrometry. All attempts to crystallize **L1** failed. − ^{1}H NMR (CD_3OD, 250.13 MHz, 303 K): δ = 2.15 (m, 9-H), 3.80 (m, 8-H, 10-H), 7.46 (t, 3-H), 7.88 (d, 4-H), 8.00 (m, 5-H), 8.41 (s, 7-H, 11-H), 8.59 (m, 2-H). − ^{13}C NMR (CD_3OD, 62.90 MHz, 303 K): δ = 32.5 (C-9), 59.8 (C-8, C-10), 122.8 (C-5), 126.6 (C-3), 138.6 (C-4), 150.2 (C-2), 155.1 (C-6), 163.5 (C-7, C-11). − ^{1}H,^{15}N z-GS HMBC

([D$_6$]DMSO, 250.13 MHz/25.35 MHz, 303 K): δ = −35.8/7.46 (N-4/3-H), −62.6/8.41 (N-3/7-H and 11-H). − MS (75 eV); *m/z* (%): 252 [M$^+$]. − $C_{15}H_{16}N_4$ (252.32): calcd. C 71.40, H 6.39, N 22.20; found C 68.82, H 6.32, N 21.49. Owing to the difficulties in purifying **L1**, satisfactory elemental analysis could not be obtained.

Bis{1,3-bis(pyridine-2-carboxaldimino)propane}cadmium(II) Perchlorate {[Cd(**L1**$_2$)](ClO$_4$)$_2$ (**1**)}: To 2.00 mmol of **L1** in 10 ml of methanol was added dropwise methanolic Cd(ClO$_4$)$_2$·6 H$_2$O (1.00 mmol in 10 ml of MeOH) until precipitation was observed. The solution was allowed to stand overnight during which time yellowish crystals of the complex formed. Yield 54%. The crystals were separated by filtration and washed with acetone and a suitable crystal was selected for the X-ray diffraction study.− ^{1}H NMR ([D$_6$]DMSO, 250.13 MHz, 303 K): δ = 1.86 (m, 9-H), 3.73 (m, 8-H, 10-H), 7.68 (m, 3-H), 7.91 (m, 5-H), 8.11 (m, 4-H), 8.57 (s, 7-H, 11-H), 8.75 (m, 2-H). − ^{13}C NMR ([D$_6$]DMSO, 125.75 MHz, 303 K): δ = 31.8 (C-9), 57.8 (C-8, C-10), 125.6 (C-5), 127.4 (C-3), 139.4 (C-4), 149.5 (C-6), 149.9 (C-2), 161.2 (C-7, C-11). − $^{1\ \mathrm{H},13}$C z-GS HMQC ([D$_6$]DMSO, 250.13 MHz/62.90 MHz, 303 K): δ = 125.6/7.91 (C-5, 5-H), 127.4/7.68 (C-3, 3-H), 139.4/7.91 (C-4, 5-H), 139.4/8.11 (C-4, 4-H), 149.9/8.75 (C-2, 2-H), 161.2/8.57 (C-7, C-11, 7-H, 11-H). − ^{1}H,^{15}N z-GS HMBC ([D$_6$]DMSO, 250.13 MHz/25.35 MHz, 303 K): δ = −62.2/8.57 (N-3/7-H and 11-H). − ^{113}Cd NMR {[D$_6$]DMSO, 110.94 MHz, 348 K, calibration with 0.1 M aqueous Cd(ClO$_4$)$_2$}: δ = 84.4.

Tris[4-(2′-pyridyl)-3-aza-3-butenyl]amine (**L2**): 10.0 g of molecular sieves (3 Å, powdered) was thoroughly activated at 500°C in vacuo (oil pump). After addition of 90 ml of toluene, 0.51 ml (500 mg, 3.42 mmol) of tris(2-aminoethyl)amine and 0.98 ml (1.10 g, 10.3 mmol) of 2-pyridylcarbaldehyde, the resulting suspension was stirred under nitrogen at room temperature (23°C) for 12 h. The molecular sieves were then removed by filtration. After evaporation of the solvent, the slightly yellowish oil was dried under vacuum (oil pump). The yield of **L2** was 1.23 g (87%). − IR (NaCl): $\tilde{\nu}$ = 3053 (m) cm^{-1}, 3007 (m), 2940 (vs), 2906 (vs), 2886 (vs), 2850 (vs), 1648 (vs), 1587 (vs), 1567 (vs), 1468 (vs), 1436 (vs), 1352 (m), 1292 (m), 1146 (m), 1066 (s), 1045 (s), 992 (s), 773 (vs), 754 (s), 617 (m). − ^{1}H NMR (CDCl$_3$, 500.13 MHz, 303 K): δ = 2.97 (t, ^3J = 6.8 Hz, 6 H, 1-H), 3.75 (t, ^3J = 6.8 Hz, 6 H, 2-H), 7.22 (m, 3 H, 4′-H), 7.64 (m, 3 H, 5′-H), 7.87 (m, 3 H, 6′-H), 8.30 (s, 3 H, 4-H), 8.56 (m, 3 H, 3′-H). − ^{1}H NMR(CD$_3$CN, 500.13 MHz, 303 K): δ = 2.93 (t, ^3J = 6.5 Hz, 6 H, 1-H), 3.72 (dt, ^3J = 6.5 Hz, ^4J = 1.3 Hz, 6 H, 2-H), 7.32 (m, 3 H, 4′-H), 7.72 (m, 3 H, 5′-H), 7.89 (m, 3 H, 6′-H), 8.28 (s, 3 H, 4-H), 8.56 (m, 3 H, 3′-H). − ^{1}H NMR ([D$_6$]DMSO, 250.13 MHz, 303 K): δ = 2.88 (t, ^3J = 6.3 Hz, 6 H, 1-H), 3.69 (t, ^3J = 6.3 Hz, 6 H, 2-H), 7.36 (m, 3 H, 4′-H), 7.73 (m, 3 H, 5′-H), 7.86 (m, 3 H, 6′-H), 8.30 (s, 3 H, 4-H), 8.56 (m, 3 H, 3′-H) . − ^{13}C NMR (CDCl$_3$, 125.75 MHz, 303 K): δ = 55.3 (C-1), 59.8 (C-2), 121.2 (C-6′), 124.5 (C-4′), 136.4 (C-5′), 149.3 (C-3′), 154.5 (C-1′), 162.2 (C-4). − ^{13}C NMR (CD$_3$CN, 125.75 MHz, 303 K): δ = 56.1 (C-1), 60.5 (C-2), 121.4 (C-6′), 125.6 (C-4′), 137.5 (C-5′), 150.3 (C-3′), 155.8 (C-1′), 163.5 (C-4) . − ^{1}H,^{13}C HMQC (CD$_3$CN, 500.13/125.75 MHz, 303 K): δ = 56.1/2.93 (C-1, 1-H), 60.5/3.72 (C-2, 2-H), 121.4/7.89 (C-6′, 6′-H), 125.6/7.32 (C-4′, 4′-H), 137.5/7.72 (C-5′, 5′-H), 150.3/8.56 (C-3′, 3′-H), 163.5/8.28 (C-4, 4-H). − ^{1}H,^{13}C HMBC (CDCl$_3$, 500.13 MHz/125.75MHz, 303 K): δ = 55.3/3.75 (C-1/2-H), 59.8/2.97 (C-2/1-H), 59.8/8.30 (C-2/4-H), 121.2/7.22 (C-6′/4′-H), 121.2/8.30 (C-6′/4-H), 124.5/7.87 (C-4′/6′-H), 136.4/8.56 (C-5′/3′-H), 149.3/7.22 (C-3′/4′-H), 149.3/7.64 (C-3′/5′-H), 154.5/7.64 (C-1′/5′-H), 154.5/8.30 (C-1′/4-H), 154.5/8.56 (C-1′/3′-H), 162.2/3.75 (C-4/2-H). − ^{1}H,^{15}N z-GS HMBC (CDCl$_3$, 25.35 MHz/250.13 MHz, 303 K): δ = −42.0/2.97 (N$_B$/1-H), −42.0/8.30 (N$_B$/4-H), −66.8/7.22 (N$_C$/4′-H), −347.0/3.75 (N$_A$/2-H). − ^{1}H,^{15}N z-GS HMBC ([D$_6$]DMSO, 25.35 MHz/250.13 MHz, 303 K): δ = −38.9/2.88 (N$_B$/1-H), −38.9/8.30 (N$_B$/4-H), −62.2/7.36 (N$_C$/4′-H), −62.2/7.73 (N$_C$/5′-H), −62.2/8.56 (N$_C$/3′-H), −347.1/3.69 (N$_A$/2-H). − HR MS (75 eV) ($C_{24}H_{27}N_7$): calcd. 413.23279, found 413.23191.

In Situ Preparation of Tris[4-(2′-pyridyl)-3-aza-3-butenyl]aminecadmium(II) Nitrate {[Cd**L2**](NO$_3$)$_2$ (**2**)}: 31 mg (74.5 μmol) of tris[4-(2′-pyridyl)-3-aza-3-butenyl]amine (**L2**) was dissolved in 0.5 ml of CDCl$_3$. The solution was mixed with a portion of 8.0 mg (25.9 μmol) of Cd(NO$_3$)$_2$·4H$_2$O. To this mixture [D$_6$]DMSO was added dropwise until the precipitate was dissolved. The ^{1}H-NMR chemical-shift changes unambiguously revealing the complex formation between Cd^{2+}cation and **L2**, the molar ratio **2**/**L2** being 1:3 at this stage. After another addition of 15.0 mg (48.6 μmol) of the Cd salt the Schiff base **2** was completely complexed with Cd^{2+} cation. The same procedure was also carried out in pure [D$_6$]DMSO. − ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO = 10:1, 500.13 MHz, 303 K): δ = 2.70 (m, 6 H, 1-H), 2.79 (br. s, 8 H, H$_2$O), 3.51 (br. s, 6 H, 2-H and 2-H′), 7.29 (m, 6 H, 3′-H and 4′-H), 7.68 (m, 3 H, 6′-H), 7.80 (m, 3 H, 5′-H), 8.58 (s, 3 H, 4-H). − ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO = 10:1, 500.13 MHz, 253 K): δ = 2.65 (m, 6 H, 1-H), 3.27 (br. s, 8 H, H$_2$O), 3.38 (m, 3 H, 2-H or 2-H′), 3.55 (m, 3 H, 2-H′ or 2-H), 7.25 (m, 6 H, 3′-H and 4′-H), 7.67 (m, 3 H, 6′-H), 7.79 (m, 3 H, 5′-H), 8.56 (s, 3 H, 4-H). − ^{1}H NMR([D$_6$]DMSO, 250.13 MHz, 303 K): δ = 3.01 (br. s, 6 H, 1-H), 3.77 (br. s, 8 H, H$_2$O), 3.83 (br. s, 6 H, 2-H), 7.72 (m, 6 H, 3′-H and 4′-H), 8.08 (m, 3 H, 6′-H), 8.28 (m, 3 H, 5′-H), 8.94 (s, 3 H, 4-H) . − Variable-temperature ^{1}H NMR: $\Delta G^{\neq}(T_C) = R\cdot T_C \ln [(R\cdot T_C\cdot 21/2)/(2\pi\cdot N_A\cdot h\cdot\Delta\nu)]$, $\Delta G^{\neq}$(287 K) = 56.1 kJ mol^{-1} ± 2.1 kJ mol^{-1}, T_C = 287 K (coalescense temperature), $\Delta\nu$ (253 K) = 86.6 Hz [difference of the baseline-separated signals of the observed protons (dynamics frozen out)], R = 8.3144 J K^{-1} mol^{-1} (gas constant), N$_A$ = 6.0220 × 10^{23} mol^{-1} (Avogadro′s number), h = 6.6262 × 10^{-34} J s (Planck constant). − ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO = 10:1, 125.75 MHz, 303 K): δ = 53.9 (C-1), 54.2 (C-2), 128.5 (C-3′ or C-4′), 129.0 (C-6′), 140.4 (C-5′), 146.3 (C-1′), 148.3 (C-4′ or C-3′), 162.2 (C-4). − ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO = 10:1, 125.75 MHz, 253 K): δ = 53.3 (C-1), 53.9 (C-2), 128.0 (C-3′ or C-4′), 128.4 (C-6′), 140.3 (C-5′), 145.8 (C-1′), 148.0 (C-4′ or C-3′), 161.8 (C-4). − ^{1}H,13C HMQC (CDCl$_3$/[D$_6$]DMSO = 10:1, 500.13 MHz/125.75MHz, 303 K): δ = 53.9/2.70 (C-1/1-H), 54.2/3.51 (C-2/2-H), 128.5/7.29 (C-4′andC-3′/4′-H and 3′-H), 129.0/7.68 (C-6′/6′-H), 140.4/7.80 (C-5′/5′-H), 148.3/7.29 (C-3′ and C-4′/3′-H and 4′-H), 162.2/8.58 (C-4/4-H). − ^{1}H,^{13}C z-GS HMBC (CDCl$_3$/[D$_6$]DMSO = 10:1, 250.13 MHz/62.90MHz, 303 K): δ = 54.2/8.58 (C-2/4-H), 128.5/7.29 (C-3′ and C-4′/4′-H and 3′-H), 128.5/7.68 (C-3′ and C-4′/6′-H), 128.5/7.80 (C-3′ and C-4′/5′-H), 129.0/8.58 (C-6′/4-H), 140.4/7.29 (C-5′/3′-H and 4′-H), 146.3/7.29 (C-1′/3′-H and 4′-H), 146.3/7.68 (C-1′/6′-H), 146.3/7.80 (C-1′/5′-H), 146.3/8.58 (C-1′/4-H), 148.3/7.80 (C-3′/5′-H), 162.2/7.68 (C-4/6′-H). − ^{1}H,^{15}N z-GS HMBC (CDCl$_3$/[D$_6$]DMSO = 10:1, 250.13 MHz/25.35 MHz, 303 K): δ = −91.6/2.70 (N$_B$/1-H), −91.6/8.58 (N$_B$/4-H), −113.7/7.29 (N$_C$/3′-H and 4′-H),-113.7/7.68 (N$_C$/6′-H), −113.7/7.80 (N$_C$/5′-H), −113.7/8.58 (N$_C$/4-H). Cross peaks for the nitrogen atom N$_A$ could not be detected at 303 K. − ^{1}H,^{15}N z-GS HMBC ([D$_6$]DMSO, 25.35 MHz/250.13 MHz, 303 K): δ = −90.0/8.94 (N$_B$/4-H), −113.0/7.72 (N$_C$/3′-H and 4′-H), −113.0/8.94 (N$_C$/4-H). Cross peaks for the nitrogen atom N$_A$ could not be detected at 303 K. − ^{113}Cd NMR {CDCl$_3$/[D$_6$]DMSO = 10:1, 110.94 MHz, 303 K, calibration with ethanolic 0.1 M Cd(ClO$_4$)$_2$}: δ = 227.0. − ^{113}Cd NMR {CDCl$_3$/[D$_6$]DMSO = 10:1, 110.94 MHz, 303 K, calibration with aqueous 0.1 M Cd(ClO$_4$)$_2$}: δ = 188.1.

[1] A. Jäntti, K. Rissanen and J. Valkonen, *Acta Chem. Scand.*, in press.

[2] [2a] R. M. Kirchner, C. Mealli, M. Bailey, N. Howe, L. P. Torre, L. J. Wilson, L. C. Andrews, N. J. Rose, E. C. Lingafelter, *Coord. Chem. Rev.* **1987**, *77*, 89–163. [2b] J. A. Thomas, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **1991**, *184*, 99–105. [2c] L. J. Wilson, N. J. Rose, *J. Am. Chem. Soc.* **1968**, *90*, 6041–6045.

[3] [3a] M. J. Hannon,C. J. Painting, A. Jackson, J. Hamblin and W. Errington, *J. Chem. Soc., Chem. Commun.* **1997**, 1807–1808. [3b] J. de Mendoza, E. Mesa, J.-C. Rodriquez-Ubis, P. Vazguez, F. Vögtle, P.-M. Windscheif, K. Rissanen, J.-M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem. Int. Ed. Eng.* **1991**, 1331–1333.

[4] A. D. Garnovskii, A. L. Nivorozhkin and V. I. Minkin, *Coord. Chem. Rev.* **1993**, *126*, 1–69.

[5] S. M. Nelson, *Pure Appl. Chem.* **1980**, *52*, 2461–2476.

[6] [6a] J. Ratilainen, K. Airola, E. Kolehmainen and K. Rissanen, *Chem. Ber.* **1997**, 1353–1359. [6b] M. Munataka, S. Kitagawa and F. Yagi, *Inorg. Chem.* **1986**, *25*, 964–970.

[7] M. G. B. Drew, J. de O. Cabral, M. F. Cabral, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.* **1979**, 1033–1035.

[8] J. M. Epstein, J. C. Dewan, D. L. Kepert and A. H. White, *J. Chem. Soc., Dalton Trans.* **1974**, 1949–1954.

[9] K. R. Adam, S. Donnelly, A. J. Leong, L. F. Lindoy, B. J. McCool, A. Bashall, M. R. Dent, M. McPartlin, D. E. Fenton and P. A. Tasker, *J. Chem. Soc., Dalton Trans.* **1990**, 1635–1643.

[10] H. Sleiman, P. Baxter, J.-M. Lehn, K. Airola and K. Rissanen, *Inorg. Chem.* **1997**, 4734–4742.

[11] P. W. Westerman, R. E. Botto and J. D. Roberts, *J. Org. Chem.* **1978**, *43*, 2590–2596.

[12] R. E. Botto and J. D. Roberts, *J. Org. Chem.* **1977**, *42*, 2247–2249.

[13] J. Emsley, *The Elements*, Clarendon Press, Oxford, Great Britain, **1989**.

[14] H. Friebolin, *Ein-und zweidimensionale NMR-Spektroskopie*, Verlag Chemie, Weinheim, **1988**.

[15] M. L. H. Green, L.-L. Wong, A. Sella, *Organometallics* **1992**, *11*, 2660–2668.

[16] *International Tables for X-Ray Crystallography*, vol IV, The Kynoch Press, Birmingham, England, **1974**.

[17] G. M. Sheldrick, *Acta Cryst.* **1990,** *A46*, 467–473.

[18] G. M. Sheldrick, *SHELXL-93, A Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

[19] G. Bergerhoff, *DIAMOND, Visual Crystal Structure Information System*, version 1.0.4, Bonn, Germany, **1995**.

[20] E. Keller, *SCHAKAL92, A FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models*, University of Freiburg, Freiburg, Germany, **1992**.

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, *Gaussian 94, Revision B3*, Gaussian Inc., Pittsburgh, PA, **1995**.

[22] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.

[23] K. D. Dobbs and W. J. Hehre, *J. Comp. Chem.* **1987**, *8*, 880–893.

[24] *HyperChem, Release 4.5*, Hypercube, Inc., Gainesville, **1995**.

[98093]