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Synthesis and Characterisation of Dinuclear Nickel(II) and Cadmium(II) Complexes of *N*-Alkylated Derivatives of Hexaazadithiophenolate Macrocycles

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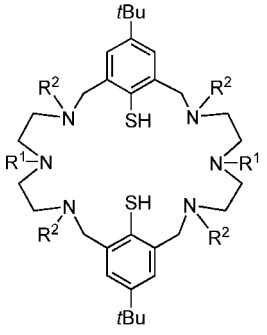
The effect of *N*-alkylation on the ligating properties of the Robson-type 24-membered hexaazadithiophenolate macrocycle H_2L^1 [13,27-bis(*tert*-butyl)-3,6,9,17,20,23-hexaazatricyclo[23.3.1^{11,15}]triaconta-1(28),11,13,15(30),25,26-hexaene-29,30-dithiol] has been examined. Two new derivatives (H_2L^3 and H_2L^4) of H_2L^1 have been prepared. H_2L^3 is a dimethylated derivative of H_2L^1 and H_2L^4 is a tetraethylated derivative of H_2L^3. A series of complexes of the type $[(L^R)M^{II}_2(\mu\text{-}Cl)]^+$ [R = 1, M = Cd (**10**), R = 3, M = Ni (**8**), M = Cd (**12**), R = 4, M = Ni (**9**), M = Cd (**13**)] have been prepared and structurally characterised. The X-ray crystal structure determination of these dioctahedral complexes with an $N_3M(S)_2(\mu\text{-}Cl)MN_3$ core structure has revealed two conformations of the supporting ligands. In **8**, **9**, **10** and **12** the ligands adopt a folded C_s-symmetric conformation of type A whereas in the cadmium complex **13** the alternative C_{2v}-symmetric "bowl-shaped" conformation (type B) is present. A structural comparison has allowed us to determine the factors that determine the ligand conformations. It has been established that the ligand conformations adopted depend not only on the co-ligand but also on the metal ion radius and the *N*-alkylation grade.

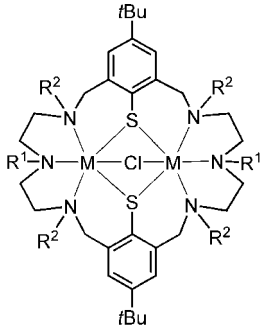
Introduction

Macrocyclic ligands containing 14 or more ring atoms are known to have a rather flexible structure, and it is often observed that such ligands can adopt several different conformations.[1,2] Typical examples are the N_4 macrocycle cyclam and its countless *N*-alkylated derivatives,[3] which can have planar (*trans*) or folded (*cis*) conformations in octahedral complexes.[4–6] It is well-known that the physical and chemical properties of macrocyclic complexes are highly dependent on the conformations of the supporting ligands. This is of importance for a number of applications, since often only one of several possible conformational isomers exhibits the desired property.[7] Thus, in macrocyclic chemistry it is of importance to establish the factors that are responsible for the stabilisation/destabilisation of the various structural forms.

We recently reported the synthesis of the hexaazadithiophenolate macrocycle H_2L^1 and its permethylated derivative



H_2L^1 ($R^1 = R^2 = H$)
H_2L^2 ($R^1 = R^2 = CH_3$)
H_2L^3 ($R^1 = CH_3$, $R^2 = H$)
H_2L^4 ($R^1 = CH_3$, $R^2 = CH_2CH_3$)



6, $[(L^1)Ni_2(\mu\text{-}Cl)]^+$ **10**, $[(L^1)Cd_2(\mu\text{-}Cl)]^+$
7, $[(L^2)Ni_2(\mu\text{-}Cl)]^+$ **11**, $[(L^2)Cd_2(\mu\text{-}Cl)]^+$
8, $[(L^3)Ni_2(\mu\text{-}Cl)]^+$ **12**, $[(L^3)Cd_2(\mu\text{-}Cl)]^+$
9, $[(L^4)Ni_2(\mu\text{-}Cl)]^+$ **13**, $[(L^4)Cd_2(\mu\text{-}Cl)]^+$

Scheme 1. Ligands and complexes studied in this work.

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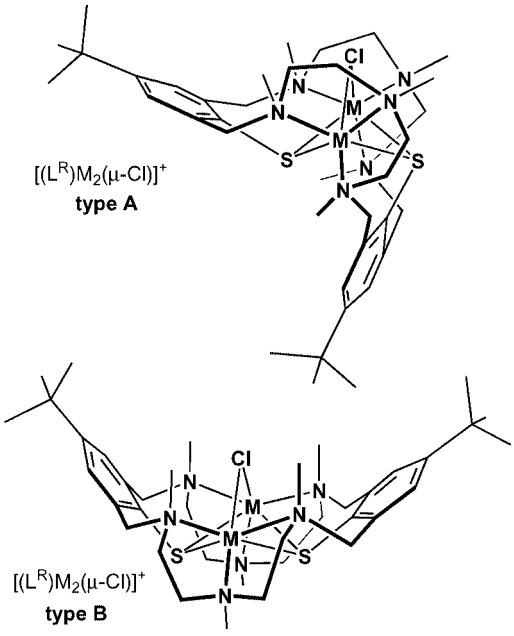
H_2L^2 (Scheme 1)[8] and their use in the preparation of dinuclear transition metal complexes for regioselective substrate transformations.[9,10]

Examination of the structures of the chlorido-bridged $[(L^R)M^{II}_2(\mu\text{-Cl})]^+$ complexes has revealed that the octadentate ligands most often adopt a folded C_s-symmetric conformation of type A (e.g. complexes **6** and **7**, see Scheme 2).[11,12] Very recently, however, the alternative C_{2v}-symmetric "bowl-shaped" conformation of type B was detected for the chlorido-bridged cadmium complex **11**.[13] These findings encouraged us to look for the factors that determine these ligand conformations.



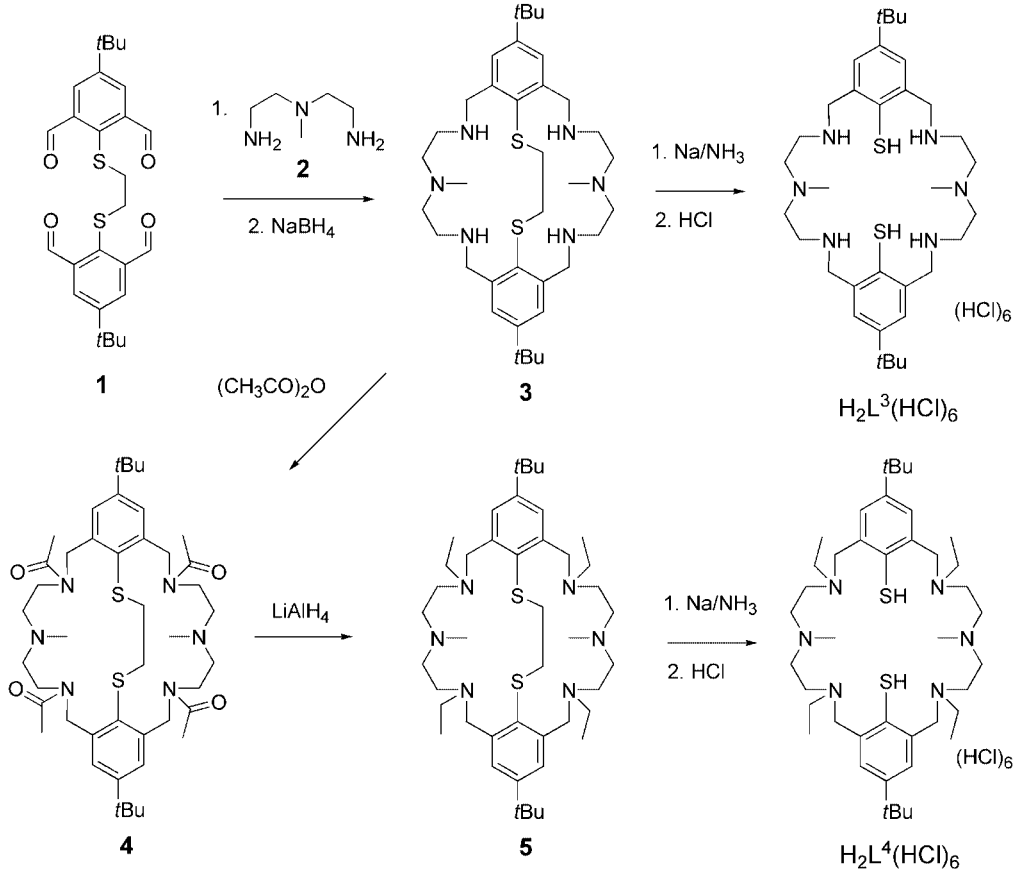
Scheme 2. Schematic representation of the two ligand conformations of the octadentate macrocycles $(L^R)^{2-}$ observed in the chlorido-bridged $[(L^R)M_2(\mu\text{-Cl})]^+$ complexes **6**, **7** and **11**.[11,13]

In this study we describe the synthesis and characterisation of a series of chlorido-bridged Ni and Cd complexes of the type $[(L^R)M_2(\mu\text{-Cl})]^+$ supported by 24-membered hexaazadithiophenolate ligands $(L^R)^{2-}$ with different *N*-alkylation grades and patterns (see Scheme 1 for ligand abbreviations). We have obtained single crystals of the complexes **8**, **9**, **10**, **12** and **13** suitable for X-ray structure determinations, which has allowed us to study the ligating properties of the supporting ligands as a function of the *N*-alkylation grade. The solution-state structures of the cadmium complexes **10**–**13** derived from NMR studies and the solid-state structure of one proligand are also presented.

Results and Discussion

Ligand Synthesis

The synthetic route to the new ligands H_2L^3 and H_2L^4 is outlined in Scheme 3. The bicyclic macrocycle **3** was prepared by a [2 + 1] condensation reaction between tetraaldehyde **1**[14] and bis(aminoethyl)methylamine (**2**) in an etha-



Scheme 3. Synthesis of the ligands H_2L^3 and H_2L^4.

nol/dichloromethane mixed solvent system, followed by reduction of the intermediate imine functions with $NaBH_4$. To prevent the formation of higher condensation products the cyclisation reaction was performed under high dilution conditions. Thus, proligand **3** was obtained in nearly quantitative yield upon workup. Subsequent deprotection of the thioether functions was achieved in the usual way,[14] with sodium in liquid ammonia followed by acidic workup. The second ligand system was prepared according to a protocol used for the alkylation of triazacyclononane[15] and cyclam.[16] Acylation of the four benzylic nitrogen donors of **3** was accomplished with acetic anhydride. The subsequent $LiAlH_4$ reduction of the resulting tetraamide **4** furnished the tetraethylated macrobicycle **5** in good yield. The final deprotection of the masked thiophenolate functions with sodium in liquid ammonia followed by acidic workup gave H_2L^4 as its hexahydrochloride salt. These new ligands were obtained in good overall yields without the need for metal templates. All new compounds were characterised by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy (see Exp. Sect.), and compound **5** also by X-ray crystallography. The hydrochloride salts of the ligands H_2L^3 and H_2L^4 could not be obtained in analytically pure form. Nevertheless, they were of sufficient purity for metal complex syntheses.

Synthesis of Complexes

A series of chlorido-bridged nickel(II) and cadmium(II) complexes of the type $[(L^R)M_2(\mu\text{-}Cl)]^+$ were prepared in order to systematically investigate the effect of *N*-alkylation on metal ion complexation and metal complex structures. The synthesised complexes and their labels are collected in Scheme 1. Of these, $[(L^1)Ni_2(\mu\text{-}Cl)]^+$ (**6**),[11] $[(L^2)Ni_2(\mu\text{-}Cl)]^+$ (**7**)[17] and $[(L^2)Cd_2(\mu\text{-}Cl)]^+$ (**11**)[13] have been reported previously. The complexation reactions of the macrocycles with $NiCl_2{\cdot}6H_2O$ (or $CdCl_2{\cdot}H_2O$) in the presence of triethylamine proceeded smoothly and yielded yellow or colourless solutions of the respective $[(L^R)M_2(\mu\text{-}Cl)]^+$ monocations, which could be readily isolated as their crystalline perchlorate or tetraphenylborate salts. The new compounds gave satisfactory elemental analyses and were characterised by spectroscopic methods (IR, UV/Vis, ^1H and ^{13}C NMR spectroscopy) and compounds **8**$[BPh_4]$, **9**$[BPh_4]$, **10**$[BPh_4]$, **12**$[BPh_4]$ and **13**$[BPh_4]$ also by X-ray structure analysis.

Spectroscopic Characterisation: IR and UV/Vis Spectroscopy

The infrared spectra of all compounds display the bands expected for the macrocyclic ligands and counterions, but are not informative with respect to the conformations of the supporting ligands. The electronic absorption spectra of the nickel complexes were recorded in the range 300–1600 nm in acetonitrile solution. Selected spectroscopic data are reported in Table 1. The data for complexes **6** and **7** have been reported previously and are included for comparative purposes.[11] The spectra of the nickel complexes are similar but not identical. Each compound displays three weak absorption bands above 500 nm. The absorption band in the range 620–670 nm can be attributed to the ν_2 transition $[^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)]$ of an octahedral nickel(II) (d^8) ion. The bands between 900 and 1100 nm can be assigned to the ν_1 transition $[^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)]$, which is split presumably due to lower symmetry. The slight differences in the positions of the d–d transitions indicate that each complex retains its integrity in solution. This is also supported by the NMR spectroscopic data for the cadmium complexes **10**, **12** and **13** described below.

Table 1. Synthesised complexes, their labels, structure type and selected UV/Vis data.

Complex	Structure type	λ_{max} [nm] (ε [$M^{-1}\,cm^{-1}$])[a]	Ref.
6 $[(L^1)Ni_2(\mu\text{-}Cl)]^+$	A	625 (58), 894 (54), 941 (56)	[11]
7 $[(L^2)Ni_2(\mu\text{-}Cl)]^+$	A	658 (41), 920 (59), 1002 (80)	[11]
8 $[(L^3)Ni_2(\mu\text{-}Cl)]^+$	A	623 (76), 902 (63), 960 (68)	this work
9 $[(L^4)Ni_2(\mu\text{-}Cl)]^+$	A	675 (31), 928 (62), 1013 (82)	this work
10 $[(L^1)Cd_2(\mu\text{-}Cl)]^+$	A		this work
11 $[(L^2)Cd_2(\mu\text{-}Cl)]^+$	B		[13]
12 $[(L^3)Cd_2(\mu\text{-}Cl)]^+$	A		this work
13 $[(L^4)Cd_2(\mu\text{-}Cl)]^+$	B		this work

[a] The UV/Vis spectra were recorded for the perchlorate salts. Spectra were recorded in CH_3CN solution at 295 K for solutions with a concentration of about 1.0×10^{-3} M for **6** and **7** and 1.9×10^{-3} M for complex **8**.

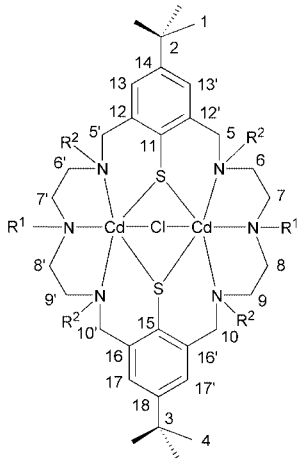
NMR Spectroscopy

Selected ^1H and ^{13}C NMR spectroscopic data for the cadmium complexes **10**, **12** and **13** are presented in Table 2. The data for complex **11** have been reported previously and are included for comparative purposes.[13] The ^1H NMR spectra of the dicadmium complexes **10** and **12** are different from those of **11** and **13**. For example, the signals for the aromatic protons and the *tert*-butyl protons are split into two singlets. Similarly, the ^{13}C NMR spectra of **10** and **12** display eight signals for the aromatic carbon atoms labelled C^{11}–C^{18}, whereas only four signals are seen for the respective atoms in **11** and **13**. These data are indicative of a ligand conformation of type A for **10** and **12** and of type B for **11** and **13**. Thus, in contrast to the nickel complexes above, the ligand conformations in the $[(L^R)Cd_2(\mu\text{-}Cl)]^+$ complexes clearly depend on the *N*-alkylation grade. This conclusion is also borne out by the single-crystal X-ray structure determinations of **10**, **12** and **13** described below.

X-ray Crystallography

The X-ray crystal structures of the proligand **5** and the complexes **8**$[BPh_4]{\cdot}3EtOH$, **9**$[BPh_4]{\cdot}5MeCN$, **10**$[BPh_4]{\cdot}5MeOH$, **12**$[BPh_4]{\cdot}2MeCN$ and $\{$**13**$[BPh_4]{\cdot}3.5MeCN\}_2$ were determined in order to establish the geometries about the metal ions and the bonding modes of the supporting ligands.

Table 2. Selected ^1H and ^{13}C NMR spectroscopic data for complexes **10**–**13**.[a]



$(L^1)^{2-}$, R^1 = H, R^2 = H
$(L^2)^{2-}$, R^1 = CH_3, R^2 = CH_3
$(L^3)^{2-}$, R^1 = CH_3, R^2 = H
$(L^4)^{2-}$, R^1 = CH_3, R^2 = Et

	10[ClO_4]	**11**[ClO_4]	**12**[ClO_4]	**13**[ClO_4]
^1H NMR[a]				
$C^{13,13',17,17'}H$	7.34 s	7.20 s	7.17 s	7.28 s
	7.16 s		7.32 s	
R^1	–	2.84 s (CH_3)	2.65 s (CH_3)	2.83 s (CH_3)
R^2	–	2.33 s (CH_3)	–	1.12 t (CH_2CH_3)[b]
C^1H_3, C^4H_3	1.26	1.26 s	1.25 s	1.27 s
	1.32		1.29 s	
^{13}C NMR[c]				
$C^{14,18}$	145.1	147.1	148.21	146.78
	145.0		147.96	
$C^{11,15}$	139.1	141.8	140.24	142.13
	138.2		138.45	
$C^{12,12',16,16'}$	137.4	135.8	139.46	136.29
	137.3		138.95	
$C^{13,13',17,17'}$	127.8	131.0	129.01	130.18
	127.5		129.28	
$C^{5-10,5'-10'}$	56.0, 55.2	63.8	60.37, 58.17	58.13
	54.2, 49.2	60.8	58.06, 56.20	56.65
	48.9, 47.4	58.0	55.19, 50.68	55.74
R^1	–	50.1 (CH_3)	49.48 (CH_3)	50.30 (CH_3)
R^2	–	46.0 (CH_3)	–	6.63 (CH_2), 50.00 (CH_3)
$C^{2,3}$	33.8	34.7	34.84	34.70
	33.7		34.93	
$C^{1,4}$	31.3	31.6	31.61	31.50
	31.2		31.74	

[a] Spectra were recorded in CD_3CN (**11**–**13**) or CD_3OD (**10**) solution at 295 K. [b] The resonances for the methylene protons of the ethyl substituents are obscured by the resonances of the ethylene groups. [c] Spectra were recorded in CD_3CN (**11**–**13**) or [D_6]DMSO (**10**) solution at 295 K.

Compound 5

The molecular structure of the proligand **5** is shown in Figure 1. The thioether adopts a highly folded conformation that is typical for such large macrocycles.[18] The two phenyl rings are not really coplanar to each other, the dihedral angle being 30.9°. The ethyl substituents bonded to N(3) and N(3′) point into the central cavity, partly filling the void between the phenyl rings. The distance between their centroids amounts to 6.216 Å. There are no unusual features as far as bond lengths and angles are concerned. The C–S sulfur bond lengths involving the sp^2-hybridized carbon atoms (C1, C1′) [1.786(2) Å] are shorter than the ones involving the sp^3-hybridized carbon atoms [1.820 Å] C22 and C22′. Virtually the same distances are seen in the permethylated derivative.[19]

[(L^3)Ni^{II}_2(μ-Cl)][BPh_4]·3EtOH (8[BPh_4]·3EtOH) and [(L^4)Ni^{II}_2(μ-Cl)][BPh_4]·5MeCN (9[BPh_4]·5MeCN)

The crystal-structure determinations of the two title compounds reveal the presence of dioctahedral complex

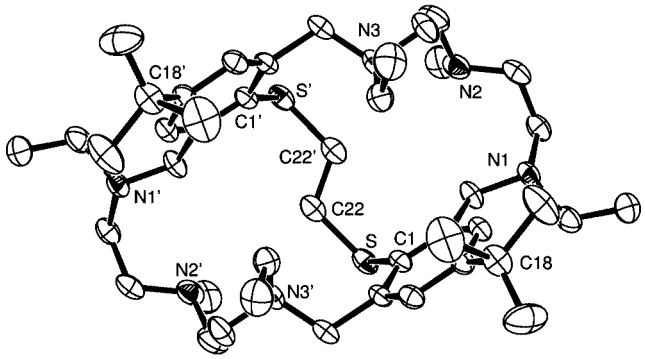
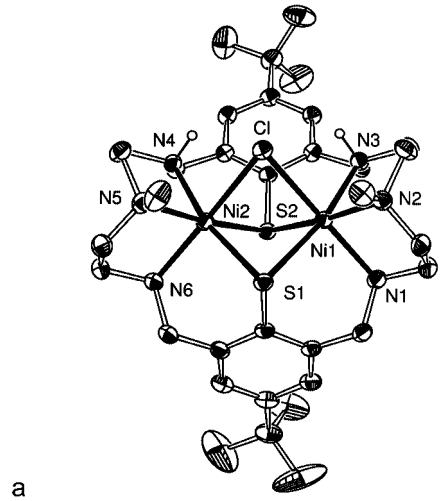
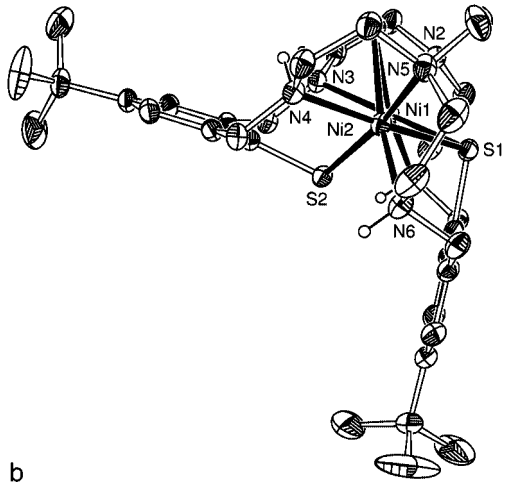


Figure 1. Molecular structure of compound **5** with atomic numbering for key atoms. Hydrogen atoms have been omitted for clarity. Symmetry codes used to generate equivalent atoms: $-x$, $+y$, $0.5 - z$ ($'$).



a



b

Figure 2. Two perspective views of the molecular structure of **8** with atomic numbering for key atoms (30% probability thermal ellipsoids). Hydrogen atoms (except those bonded to N atoms) have been omitted for clarity.

cations, tetraphenylborate anions and ethanol or acetonitrile molecules of solvent of crystallisation. ORTEP plots of **8** and **9** are displayed in Figures 2 and 3, respectively. The atomic numbering scheme for the central $N_3Ni(\mu\text{-}S)_2(\mu\text{-}Cl)NiN_3$ core in **8** is used throughout to facilitate structural comparisons. Selected bond lengths and angles are listed in Tables 3 and 4. The corresponding values for $[(L^1)Ni_2(\mu\text{-}Cl)]^+$ (**6**) and $[(L^2)Ni_2(\mu\text{-}Cl)]^+$ (**7**) are included for comparative purposes.

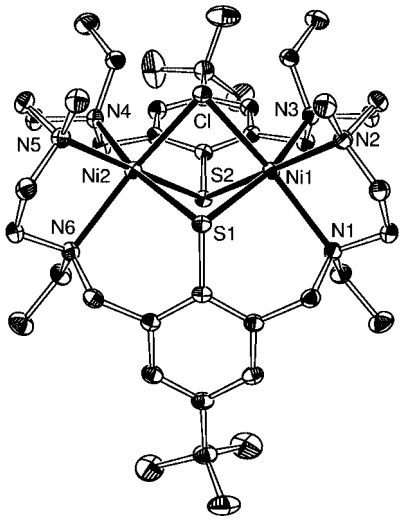


Figure 3. Molecular structure of **9** with atomic numbering for key atoms (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

The structures of the chlorido-bridged dinickel(II) complexes **8** and **9** are very similar and, with the exception of the *N*-alkyl substituents, almost superimposable with those of **6** and **7**.[11] The structure of **8** is representative for all complexes. As can be seen from Figure 2, the supporting ligand adopts a saddle-shaped, C_s-symmetric conformation that is reminiscent of the "partial-cone" conformation of calixarenes.[20] The metal ions are in a strongly distorted octahedral N_3S_2Cl environment, being coordinated by two sulfur and three facially oriented nitrogen atoms of the macrocycle and a symmetrically bridging chloride ion to give an $N_3Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}Cl)Ni^{II}N_3$ core. The distortions from the ideal octahedral geometry are manifested in the *cis* and *trans* L–M–L bond angles, which deviate by as much as 18.2° from their ideal values (see Table 4). The diethylenetriamine units coordinate facially with one larger and two smaller N–M–N bond angles. This is commonly observed in complexes with this tridentate unit.[21]

As can be seen in Table 3, the metal–ligand bond lengths in **6**–**9** clearly depend on the type of nitrogen donor atoms. Thus, upon conversion of the six secondary amines in **6** to tertiary amine functions in **9**, the average M–N bond length increases by about 0.15 Å. This, in turn, results in a large decrease in the M–Cl bond lengths by about 0.25 Å. In other words, the larger the number of tertiary amine donors the shorter the distance between the metal ions and the co-ligand. Similar effects have been reported for nickel complexes of other azamacrocycles and their peralkylated deriv-

Table 3. Selected bond lengths [Å] in complexes **6**–**13**.

	6	**7**[b]	**8**	**9**	**10**	**11**	**12**	**13**[b]
M(1)–Cl	2.639(2)	2.433(2) [2.516(2)]	2.512(1)	2.4870(4)	2.728(2)	2.682(1)	2.747(3)	2.676(1) [2.703(1)]
M(1)–N(1)	2.078(6)	2.352(5) [2.349(5)]	2.129(3)	2.383(1)	2.411(5)	2.453(3)	2.351(6)	2.456(4) [2.410(3)]
M(1)–N(2)	2.103(7)	2.173(5) [2.173(5)]	2.167(3)	2.163(1)	2.354(5)	2.424(3)	2.460(7)	2.399(3) [2.395(3)]
M(1)–N(3)	2.085(6)	2.181(5) [2.167(5)]	2.083(3)	2.232(1)	2.386(5)	2.410(4)	2.388(7)	2.444(3) [2.508(3)]
M(1)–S(1)	2.418(2)	2.471(2) [2.475(2)]	2.453(1)	2.4843(4)	2.699(2)	2.653(1)	2.660(2)	2.709(1) [2.685(1)]
M(1)–S(2)	2.419(2)	2.405(2) [2.407(2)]	2.420(1)	2.3750(4)	2.637(2)	2.699(2)	2.656(2)	2.653(1) [2.693(1)]
M(2)–Cl	2.602(2)	2.450(2) [2.455(2)]	2.535(1)	2.4885(4)	2.674(3)	2.723(1)	2.793(3)	2.645(2) [2.648(1)]
M(2)–N(4)	2.099(7)	2.171(5) [2.222(5)]	2.081(3)	2.188(1)	2.368(5)	2.441(3)	2.353(6)	2.442(3) [2.464(3)]
M(2)–N(5)	2.141(7)	2.175(6) [2.172(5)]	2.161(3)	2.165(1)	2.372(6)	2.388(3)	2.440(7)	2.399(3) [2.399(3)]
M(2)–N(6)	2.134(7)	2.380(6) [2.357(5)]	2.141(3)	2.411(1)	2.447(6)	2.409(3)	2.401(8)	2.474(3) [2.473(3)]
M(2)–S(1)	2.423(2)	2.498(2) [2.483(2)]	2.458(1)	2.4968(4)	2.682(2)	2.696(1)	2.611(2)	2.663(1) [2.656(1)]
M(2)–S(2)	2.405(2)	2.423(2) [2.371(2)]	2.423(1)	2.3940(4)	2.664(2)	2.659(1)	2.662(2)	2.698(1) [2.713(1)]
M–N[a]	2.107(7)	2.239(6) [2.240(5)]	2.127(3)	2.257(1)	2.390(5)	2.421(4)	2.399(7)	2.436(4) [2.442(3)]
M–Cl[a]	2.621(2)	2.442(2) [2.486(2)]	2.524(1)	2.4878(4)	2.701(3)	2.703(1)	2.770(3)	2.661(1) [2.676(1)]
M–S[a]	2.416(2)	2.449(2) [2.434(2)]	2.439(1)	2.4375(4)	2.671(2)	2.677(1)	2.647(2)	2.681(1) [2.687(1)]
M···M	3.098(2)	3.184(2) [3.217(2)]	3.074(1)	3.2400(4)	3.2666(17)	3.3584(9)	3.267(1)	3.3550(8) [3.3387(8)]

[a] Average values. [b] There are two crystallographically independent molecules A and B in the asymmetric unit. Values in square brackets refer to molecule B.

Table 4. Selected bond angles [°] in complexes **6**–**13**.

	6	**7**[c]	**8**	**9**	**10**	**12**		**11**	**13**[c]
N(1)–M(1)–N(2)	82.7(3)	78.9(2) [78.6(2)]	83.17(12)	78.55(5)	75.9(2)	76.3(3)	N(1)–M(1)–N(2)	75.2(1)	75.4(1) [76.0(1)]
N(1)–M(1)–N(3)	101.6(3)	100.2(2) [100.6(2)]	97.97(12)	102.09(5)	100.0(2)	89.0(2)	N(1)–M(1)–N(3)	99.4(1)	102.8(1) [102.1(1)]
N(2)–M(1)–N(3)	82.4(3)	83.2(2) [82.6(2)]	83.07(11)	82.94(5)	76.2(2)	73.5(3)	N(2)–M(1)–N(3)	76.5(1)	76.4(1) [75.1(1)]
N(4)–M(2)–N(5)	81.6(3)	82.4(2) [82.5(2)]	83.21(11)	82.92(5)	76.1(2)	73.5(2)	N(4)–M(2)–N(5)	76.0(1)	75.5(1) [76.1(1)]
N(4)–M(2)–N(6)	101.7(3)	101.8(2) [100.7(2)]	98.83(12)	100.97(5)	99.9(2)	107.9(2)	N(4)–M(2)–N(6)	99.8(1)	103.6(1) [101.4(1)]
N(5)–M(2)–N(6)	82.7(3)	79.5(2) [78.4(2)]	82.40(12)	78.77(5)	75.4(2)	75.6(3)	N(5)–M(2)–N(6)	76.8(1)	75.2(1) [76.0(1)]
N–M–N[a]	*88.8(3)*	*87.7(2) [87.2(2)]*	*88.11(12)*	*87.6(5)*	*83.9(2)*	*82.6(3)*		*84.0(1)*	*84.8(1) [84.5(1)]*
Dev[b]	*8.9(3)*	*9.7(2) [9.9(2)]*	*7.49(12)*	*9.99(5)*	*12.7(2)*	*13.37(3)*		*12.5(1)*	*14.0(1) [14.3]*
N(1)–M(1)–S(1)	95.0(2)	90.8(1) [90.4(1)]	91.80(9)	89.95(3)	87.0(1)	87.2(2)	N(1)–M(1)–S(1)	87.52(9)	86.29(9) [87.24(8)]
N(2)–M(1)–S(1)	105.8(2)	105.2(1) [107.2(1)]	104.45(9)	107.57(4)	111.9(2)	109.5(2)	N(2)–M(1)–S(1)	102.53(9)	103.29(9) [98.70(8)]
N(1)–M(1)–S(2)	96.2(2)	99.9(1) [101.1(1)]	98.13(9)	100.94(4)	97.9(1)	113.2(2)	N(2)–M(1)–S(2)	100.59(9)	102.1(1) [104.67(9)]
N(3)–M(1)–S(2)	88.2(2)	91.4(1) [91.4(1)]	89.39(8)	90.52(4)	86.4(1)	85.0(2)	N(3)–M(1)–S(2)	87.81(9)	86.99(9) [86.11(8)]
N(4)–M(2)–S(2)	87.7(2)	91.0(1) [91.9(2)]	88.83(8)	90.69(4)	86.1(1)	87.1(2)	N(4)–M(2)–S(2)	88.12(9)	85.16(8) [87.73(8)]
N(5)–M(2)–S(1)	106.4(2)	106.9(2) [106.8(2)]	104.92(9)	107.82(4)	112.4(1)	107.1(2)	N(5)–M(2)–S(1)	101.04(9)	102.45(9) [99.78(8)]
N(6)–M(2)–S(1)	92.8(2)	88.7(2) [90.5(1)]	92.59(9)	89.53(4)	87.2(1)	87.3(2)	N(6)–M(2)–S(1)	87.12(9)	86.99(8) [85.66(8)]
N(6)–M(2)–S(2)	98.6(2)	101.7(2) [98.7(1)]	99.53(9)	101.69(3)	100.1(2)	103.8(2)	N(5)–M(2)–S(2)	104.0(1)	100.46(9) [99.58(9)]
N–M–S[a]	*96.3(2)*	*97.0(2) [97.3(2)]*	*96.21(9)*	*97.34(4)*	*96.1(1)*	*97.5(2)*		*94.84(9)*	*94.22(9) [93.68(8)]*
Dev[b]	*7.4(2)*	*7.3(2) [7.3(2)]*	*6.65(9)*	*7.47(4)*	*6.95(1)*	*10.9(2)*		*7.20(9)*	*7.86(9) [7.00(9)]*
Cl–M(1)–N(2)	92.6(2)	94.2(1) [95.7(2)]	91.03(9)	95.20(4)	99.2(2)	90.1(2)	Cl–M(1)–N(1)	99.97(9)	98.3(1) [95.52(8)]
Cl–M(1)–N(3)	83.6(2)	92.0(1) [93.8(2)]	85.82(9)	92.99(4)	93.2(1)	104.7(2)	Cl–M(1)–N(3)	96.2(1)	97.25(8) [102.03(8)]
Cl–M(2)–N(4)	85.7(2)	93.6(2) [92.5(2)]	84.91(9)	94.95(4)	92.2(1)	84.1(2)	Cl–M(2)–N(4)	100.4(1)	97.34(9) [97.21(8)]
Cl–M(2)–N(5)	89.6(2)	93.2(2) [95.9(2)]	91.01(9)	94.70(4)	96.7(1)	100.1(2)	Cl–M(2)–N(6)	94.41(9)	100.4(1) [100.64(9)]

Table 4. *(continued)*.

	6	7[c]	8	9	10	12		11	13[c]
Cl–M–N[a]	*87.9(2)*	*93.3(2) [94.5(2)]*	*88.19(9)*	*94.46(4)*	*95.3(1)*	*94.8(2)*		*97.8(1)*	*98.3(1) [98.85(8)]*
Dev[b]	*3.4(2)*	*3.3(2) [4.5(2)]*	*2.83(9)*	*4.46(4)*	*5.3(1)*	*7.7(2)*		*7.8(1)*	*8.3(1) [8.85(8)]*
Cl–M(1)–S(1)	80.39(7)	78.26(6) [76.53(6)]	85.20(4)	76.48(1)	80.97(6)	80.21(8)	Cl–M(1)–S(1)	85.54(4)	84.41(4) [85.91(4)]
Cl–M(1)–S(2)	89.45(7)	88.29(6) [86.32(6)]	88.22(5)	87.16(2)	91.50(6)	86.49(7)	Cl–M(1)–S(2)	85.46(5)	85.71(4) [84.49(3)]
Cl–M(2)–S(1)	81.05(8)	77.42(7) [77.52(6)]	84.60(4)	76.23(1)	82.26(6)	80.21(8)	Cl–M(2)–S(1)	83.90(5)	85.93(4) [87.62(4)]
Cl–M(2)–S(2)	90.64(7)	87.47(6) [88.51(6)]	87.63(4)	86.71(1)	92.11(6)	85.45(7)	Cl–M(2)–S(2)	85.43(5)	85.43(4) [85.17(3)]
Cl–M–S[a]	*85.38(7)*	*82.94(6) [82.22(6)]*	*86.41(4)*	*81.65(1)*	*86.71(6)*	*83.09(8)*		*85.08(5)*	*85.37(4) [85.79(4)]*
Dev[b]	*4.94(7)*	*7.14(6) [7.78(6)]*	*3.59(4)*	*8.36(1)*	*5.10(6)*	*6.91(8)*		*4.92(5)*	*4.67(4) [4.21(4)]*
S(1)–M(1)–S(2)	84.03(8)	80.48(6) [79.01(6)]	82.96(4)	79.23(1)	86.30(7)	92.67(7)	S(1)–M(1)–S(2)	84.97(4)	83.67(4) [84.39(5)]
S(1)–M(2)–S(2)	84.22(8)	79.58(6) [79.54(6)]	82.79(4)	78.63(1)	86.09(5)	93.68(7)	S(1)–M(2)–S(2)	84.90(5)	83.69(4) [84.55(5)]
S–M–S[a]	*84.13(8)*	*80.03(6) [79.29(6)]*	*82.88(4)*	*78.93(1)*	*86.19(6)*	*93.18(7)*		*84.94(5)*	*83.68(4) [84.47(5)]*
Dev[b]	*5.87(8)*	*9.97(6) [10.73]*	*7.12(4)*	*11.07(1)*	*3.81(6)*	*3.18(7)*		*5.06(5)*	*6.32(4) [5.53(5)]*
Cl–M(1)–N(1)	172.4(2)	165.2(1) [163.6(1)]	172.61(9)	162.72(4)	164.2(1)	157.2(2)	Cl–M(1)–N(2)	170.23(9)	169.5(1) [170.04(9)]
N(2)–M(1)–S(2)	170.1(2)	174.2(1) [173.8(1)]	172.47(8)	173.14(4)	160.0(2)	156.7(2)	N(1)–M(1)–S(2)	170.37(9)	168.79(9) [171.61(8)]
N(3)–M(1)–S(1)	162.3(2)	167.4(1) [166.7(1)]	168.37(8)	165.55(4)	170.5(1)	174.4(2)	N(3)–M(1)–S(1)	172.41(9)	170.37(8) [166.98(8)]
Cl–M(2)–N(6)	168.4(2)	161.8(2) [164.7(2)]	171.94(9)	161.83(4)	163.3(2)	165.0(2)	Cl–M(2)–N(5)	169.60(9)	170.17(9) [171.52(9)]
N(4)–M(2)–S(1)	164.4(2)	167.2(2) [166.9(2)]	166.83(8)	166.40(4)	170.2(1)	164.1(2)	N(4)–M(2)–S(1)	171.51(9)	168.09(8) [170.53(7)]
N(5)–M(2)–S(2)	169.3(2)	173.5(2) [173.0(2)]	172.01(8)	173.55(4)	160.4(1)	159.1(2)	N(6)–M(2)–S(2)	172.00(8)	168.65(8) [168.40(8)]
X–M–Y[a]	*167.8(2)*	*168.2(2) [168.1(2)]*	*170.71(9)*	*167.20(4)*	*164.8(1)*	*162.8(2)*		*171.02(9)*	*169.26(9) [169.85(9)]*
Dev[b]	*12.2(2)*	*11.8(2) [11.9(2)]*	*9.29(9)*	*12.80(4)*	*15.2(1)*	*17.2(2)*		*8.98(9)*	*10.74(9) [10.15(9)]*
M(1)–S(1)–M(2)	79.55(7)	79.70(6) [80.90(6)]	77.50(4)	81.16(1)	74.75(5)	76.60(6)	M(1)–S(1)–M(2)	77.78(4)	77.29(4) [77.37(4)]
M(1)–S(2)–M(2)	79.90(7)	82.51(6) [84.63(6)]	78.78(4)	85.60(1)	76.07(5)	75.81(6)	M(1)–S(2)–M(2)	77.63(4)	77.66(3) [76.28(4)]
M–S–M[a]	*79.73(7)*	*81.11(6) [82.77(6)]*	*78.14(4)*	*83.38(1)*	*75.41(5)*	*76.21(6)*		*77.71(4)*	*77.48(4) [76.83(4)]*
Dev[b]	*10.27(7)*	*8.89(6) [7.23(6)]*	*11.86(4)*	*6.62(1)*	*14.59(5)*	*13.79(6)*		*12.29(4)*	*12.52(4) [13.17(4)]*
M(1)–Cl–M(2)	72.46(6)	81.38(6) [80.66(6)]	75.03(4)	81.27(1)	74.41(5)	72.27(6)	M(1)–Cl–M(2)	76.83(4)	78.18(4) [77.20(3)]

[a] *Average values.* [b] *Average deviations* from the ideal 90° or 180° L–M–L bond angles of a perfect octahedron. [c] There are two crystallogrphically independent molecules in the asymmetric unit. Values in square brackets refer to molecule B.

atives.[22] The dependence of the bond angles on the type of N donors is not so pronounced. The most visible changes across the series include the M–Cl–M bond angles, which increase by around 10° upon going from **6** to **9**. In summary, all N_6S_2 macrocycles support the formation of dinuclear nickel complexes of type A. As we will show below, a completely different situation is seen in the case of the cadmium complexes **10**–**13**.

Description of the Crystal Structures of [(L¹)Cd$^{II}_2$(μ-Cl)][BPh$_4$]·5MeOH (10[BPh$_4$]·5MeOH) and [(L³)-Cd$^{II}_2$(μ-Cl)][BPh$_4$]·2MeCN (12[BPh$_4$]·2MeCN)

The crystal structure determinations of the two title compounds revealed the presence of dioctahedral complex cations, tetraphenylborate anions and methanol or acetonitrile molecules of solvent of crystallisation. ORTEP plots of **10**

and **12** are displayed in Figures 4 and 5, respectively. Selected bond lengths and angles are collected in Tables 3 and 4. The structure of the $[(L^2)Cd_2^{II}(\mu\text{-}Cl)]^+$ complex **11** has been reported previously,[13] and its metrical parameters are also given for comparison. The conformation adopted by the supporting ligands in **10** and **12** is that of type A. For reasons that are still unclear, however, the configuration at N(3) in **12** is opposite to that found in **10** and in the nickel complexes above. Each cadmium atom is coordinated by two S and three N atoms from the supporting ligand and a bridging chloride in a severely distorted octahedral fashion. The distortions from the ideal octahedral geometry are somewhat more pronounced than in the nickel complexes above and in the cadmium complexes of type B described below, which is probably a consequence of the larger ionic radius of cadmium(II) (Cd^{II}: 1.06 Å; Ni^{II}: 0.83 Å).[23] The average Cd–N bond lengths of 2.390(5) (**10**) and 2.399(7) Å (**12**) are normal for six-coordinate cadmium complexes with amine donors.[24,25] The same holds for the average Cd–S [2.671(2) and 2.647(2) Å][26] and Cd–Cl distances [2.701(3) and 2.770(1) Å].[27–29] As expected, the Cd–N(secondary amine) distances in **10** and **12** are shorter (by about 0.04 Å) than the corresponding Cd–N(tertiary amine) bonds in **11** and **13**. The same trend was observed in the series of nickel complexes above.

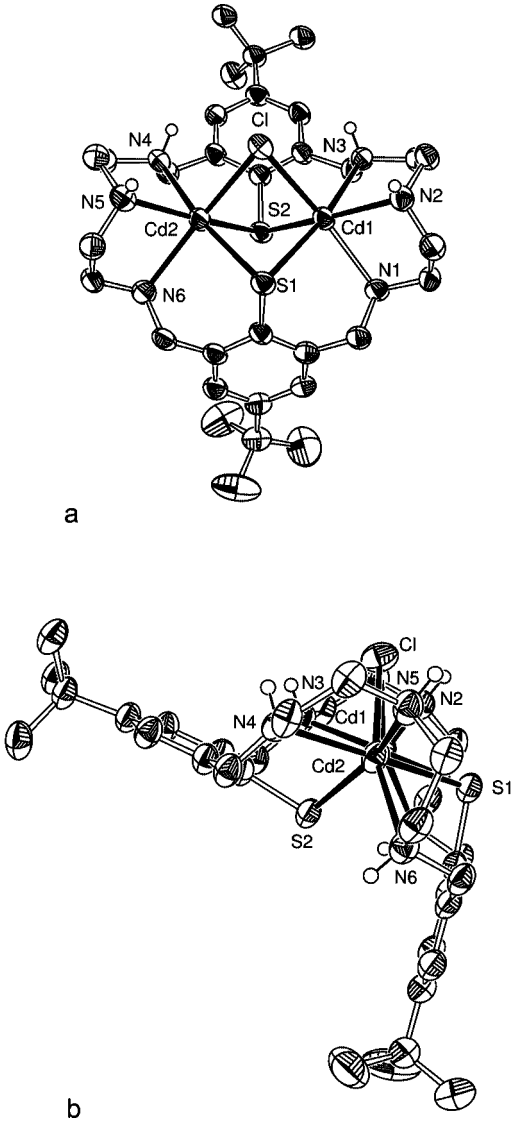


Figure 4. Two perspective views of the molecular structure of **10** with atomic numbering for key atoms (30% probability thermal ellipsoids). Hydrogen atoms (except those bonded to N atoms) have been omitted for clarity.

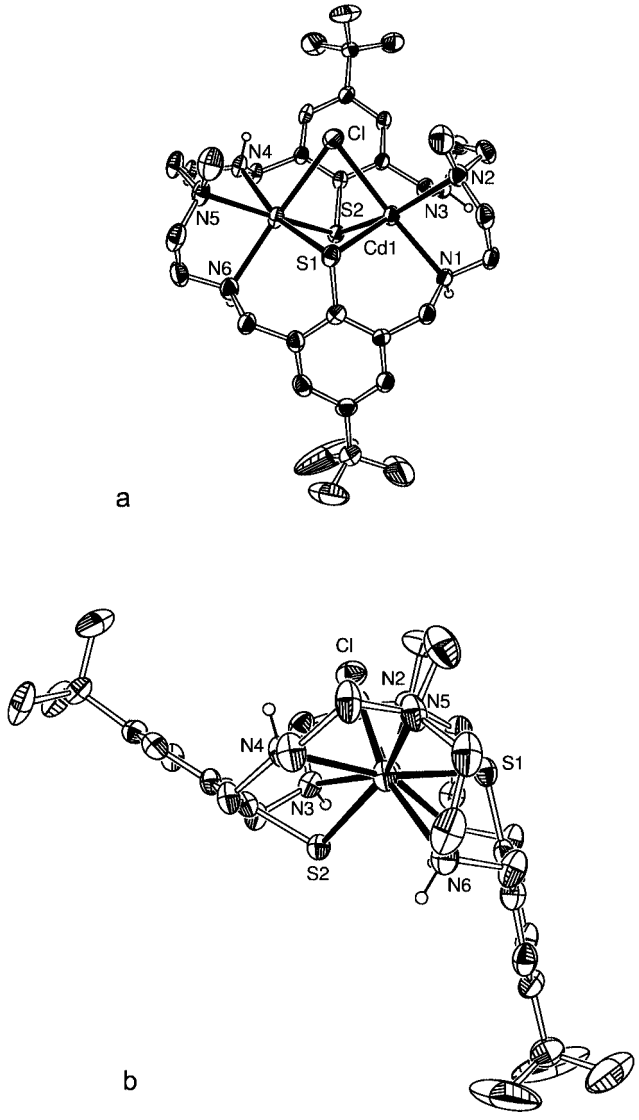


Figure 5. Two perspective views of the molecular structure of **12** with atomic numbering for key atoms (30% probability thermal ellipsoids). Hydrogen atoms (except those bonded to N atoms) have been omitted for clarity.

Description of the Crystal Structure of {[(L^4)Cd$^{II}_2$(μ-Cl)][BPh$_4$]·3.5MeCN}$_2$ {13[BPh$_4$]·3.5MeCN}$_2$

Crystals of the title complex grown from a mixed acetonitrile/ethanol solution are monoclinic with space group $P2_1/n$. The asymmetric unit contains two crystallographically independent molecules. A perspective view of the structure of molecule A is displayed in Figure 6. The structure of molecule B is identical to that of molecule A and is

not considered further. The $[(L^4)Cd_2(\mu\text{-}Cl)]^+$ complex **13** is isostructural with the $[(L^2)Cd_2(\mu\text{-}Cl)]^+$ cation **11**, with the macrocycle having a type-B conformation. There are no unusual features as far as bond lengths and angles are concerned. The average Cd–(μ-Cl) [2.661(1) Å], Cd–N [2.436(4) Å] and Cd–S [2.681(1) Å] bond lengths are very similar to the corresponding values in **11**. As in **11**, the two metal ions are coordinated in a distorted octahedral fashion by the two *fac*-$N_3(\mu\text{-}S)_2$ donor sets of the doubly deprotonated macrocycle and the bridging chloride. The diethylene triamine units are facially coordinated, with one larger and two smaller N–M–N bond angles. The same situation is observed in **11** and other complexes with this tridentate unit.[21] Likewise, the M–N bond lengths involving the four benzylic nitrogen donors are invariably longer (by around 0.1 Å) than the ones comprising the central nitrogen atoms of the linking diethylenetriamine units. This is also normal for complexes of this ligand system. The most salient feature of the structure of **13** is that $(L^4)^{2-}$ adopts a bowl-shaped, C_{2v}-symmetric conformation, an effect that may be traced to the more optimal L–Cd–L bond angles. In fact, it can be readily seen from Table 4 that there is a consistent decrease in the deviations of the *cis*- and *trans*-L–Cd–L bond angles upon going from **12** to **13** (or from **10** to **11**). Thus, for the present $[(L^R)M_2(\mu\text{-}Cl)]^+$ complexes the conformation adopted depends not only on the *N*-alkylation grade but also on the metal ion radius.

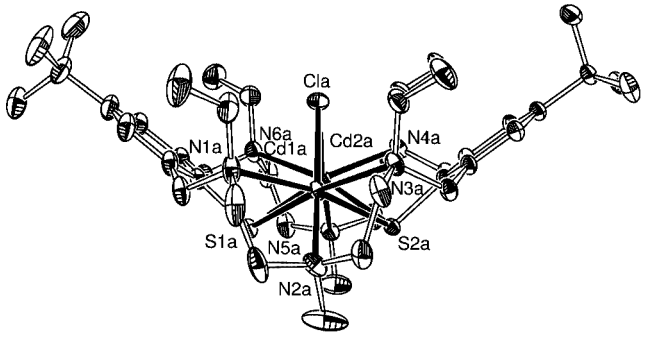


Figure 6. Molecular structure of **13** with atomic numbering for key atoms (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Conclusions

The main findings of this investigation are as follows: a) *N*-alkylated variants of H_2L^1 with different *N*-alkylation grades and patterns can be readily prepared by a [2 + 1] condensation reaction of tetraaldehyde **1** with bis(aminoethyl)methylamine followed by acylation and reduction of the resultant hexaamine dithioether compound **3**. b) All ligand systems are effective dinucleating ligands that support the formation of dioctahedral $[(L^R)M_2(\mu\text{-}Cl)]^+$ cations (M = Ni^{II} and Cd^{II}). c) The macrocycles adopt either a saddle-shaped (type A) or a bowl-shaped (type B) conformation. d) The actual conformation adopted depends not only on the type of co-ligand,[30] but also on the metal ion radius and the *N*-alkylation grade. Two trends are apparent for the present $[(L^R)M_2(\mu\text{-}Cl)]^+$ cations. In the case of small metal ions such as Ni^{II}, the conformation is always that of type A, irrespective of the *N*-alkylation grade, whereas for the larger Cd^{II} ion a clear correlation exists between the *N*-alkylation grade and the macrocycle conformation. Here, the higher the *N*-alkylation grade the more preferred the conformation of type B. e) Finally, it has also been demonstrated that the complexes exist as single isomers in solution. Computational studies are underway to determine the energy differences between the two complex conformations.

Experimental Section

Materials and Methods: Compounds **1** and H_2L^1 were prepared as described in the literature.[14] The syntheses of the metal complexes were carried out under a protective atmosphere of argon. Melting points were determined in open glass capillaries and are uncorrected. NMR spectra were recorded with a Bruker Avance DPX-200 spectrometer or a Bruker Avance DRX 400 spectrometer at 298 K. Chemical shifts are referred to solvent signals. Infrared spectra were recorded with a Bruker Vector 22 FT-IR spectrometer and electronic absorption spectra with a Jasco V-570 UV/VIS/NIR spectrometer. Elemental analyses were recorded with a VARIO EL-elemental analyzer. ESI-FTICR mass spectra were recorded with a Bruker Apex II instrument using dilute CH_2Cl_2/MeOH solutions.

CAUTION! *Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.*

Preparation of Compound 3: Solutions of 1,2-bis(4-*tert*-butyl-2,6-diformylphenylthio)ethane (**1**; 3.00 g, 6.37 mmol) in dichloromethane (100 mL) and bis(aminoethyl)methylamine (**2**; 1.51 g, 12.9 mmol) in ethanol (100 mL) were added simultaneously over a period of 3 h to a mixture of dichloromethane (300 mL) and ethanol (300 mL). After complete addition, the reaction mixture was stirred at room temperature for 18 h. The dichloromethane was removed under reduced pressure and a solution of sodium borohydride (1.21 g, 32.0 mmol) in ethanol (50 mL) was added. After stirring at room temperature for 2 h, the reaction mixture was acidified to pH 1 with conc. hydrochloric acid and the resulting colourless suspension was evaporated to dryness. The residue was taken up in aqueous potassium hydroxide (3 M, 80 mL) and extracted with dichloromethane (4 × 100 mL). The combined organic fractions were dried with magnesium sulfate. Evaporation of the solvent gave **3** (3.96 g, 97%) as a colourless, foamy solid. M.p. 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 [s, 18 H, ArC(CH_3)$_3$], 2.31 (s, 6 H, NCH_3), 2.69 (m, 8 H, NCH_2 CH_2N), 2.93 (m, 8 H, NCH_2CH_2N), 3.07 [s, 4 H, (ArSCH_2)$_2$], 3.99 (s, 8 H, ArCH_2N), 7.49 ppm (s, 4 H, Ar*H*). ^{13}C{^{1}H}NMR (50 MHz, $CDCl_3$): δ = 30.2 [C(CH_3)$_3$], 33.6 [*C*(CH_3)$_3$], 34.9 (SCH_2), 40.7 (NCH_3), 46.6 (ArCH_2N), 52.7 (NCH_2CH_2N), 56.7 (NCH_2CH_2N), 125.7 (C^{Ar}H), 127.9 (C^{Ar}S), 143.2 ($C^{Ar}CH_2$N), 150.9 ppm ($C^{Ar}t$Bu). IR (KBr): $\tilde{\nu}$ = 3425 (w), 3307 (w), 3049 (vw), 2952 (vs), 2902 (s), 2867 (s), 2801 (s), 2370 (w), 2273 (vw), 1641 (vw), 1630 (vw), 1596 (w), 1564 (vw), 1554 (vw), 1534 (vw), 1512 (vw), 1459 (s), 1393 (w), 1362 (m), 1330 (w), 1293 (w), 1262 (m), 1223 (m), 1203 (m), 1119 (s), 1045 (s), 926 (vw), 884 (w), 800 (m), 744 (w), 653 (vw), 631 cm^{-1} (vw). $C_{36}H_{60}N_6S_2{\cdot}H_2O$ (641.03 + 18.02): calcd. C 65.61, H 9.48, N 12.75, S 9.73; found C 65.40, H 9.28, N 12.39, S 10.52.

Preparation of Compound 4: A solution of **3** (3.40 g, 5.30 mmol) in acetic anhydride (150 mL) was stirred at 50 °C for 6 h. After re-

moval of the solvent under reduced pressure, the residue was taken up in aqueous potassium hydroxide solution (3 M, 100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were dried with magnesium sulfate and the solvents evaporated to dryness. The residue was taken up in methanol and purified by flash chromatography on silica gel using a methanol/water (9:1) mixture as eluting solvent. Drying in vacuo gave **4** (3.56 g, 83%) as a colourless solid. M.p. 116 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, 373 K): δ = 1.21 [s, 18 H, C(C*H*$_3$)$_3$], 2.31 (s, 6 H, NC*H*$_3$), 2.49–2.65 (m, 8 H, NC*H*$_2$CH$_2$N), 2.91 (s, 4 H, ArSC*H*$_2$), 3.03 (s, 12 H, COC*H*$_3$), 3.34 [m, 8 H, CH$_3$N(CH$_2$C*H*$_2$N)$_2$], 4.73 (s, 8 H, ArC*H*$_2$N), 6.99 ppm (s, 4 H, Ar*H*). IR (KBr): $\tilde{\nu}$ = 3442 (w), 2963 (s), 2868 (w), 2796 (w), 1649 [vs, ν(CO)], 1559 (vw), 1467 (s), 1413 (s), 1362 (m), 1298 (w), 1261 (m), 1231 (m), 1149 (m), 1083 (w), 1024 (m), 976 (w), 940 (w), 873 (vw), 801 (w), 730 (w), 698 (vw), 660 (vw), 602 (w), 572 (vw), 535 (vw), 463 cm^{-1} (vw). $C_{44}H_{68}N_6O_4S_2$·H_2O (809.18 + 18.02): calcd. C 63.89, H 8.53, N 10.16, S 7.75; found C 63.77, H 8.28, N 9.88, S 7.52.

Preparation of Compound 5: A solution of **4** (620 mg, 0.766 mmol) in tetrahydrofuran (40 mL) was added dropwise to a suspension of lithium aluminium hydride (429 mg, 11.3 mmol) in tetrahydrofuran (40 mL). After refluxing the reaction mixture for 12 h, the oil bath was removed. Water (5 mL) was carefully added to the hot reaction mixture in small portions followed by 3 M potassium hydroxide solution (20 mL). The reaction mixture was stirred for an additional hour without heating. The organic layer was decanted off from a white residue, which was rinsed with boiling tetrahydrofuran (2 × 50 mL). The solvent was removed by distillation under reduced pressure. The residue was treated with 3 M potassium hydroxide solution (50 mL) and the resulting mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried with potassium carbonate. Evaporation of the solvent gave the product as a colourless, foamy solid (568 mg, 98%). The crude material was purified by recrystallisation from a dichloromethane/ethanol (1:1) mixed solvent system. M.p. 146 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.87 (t, ^3J = 7 Hz, 12 H, NCH$_2$C*H*$_3$), 1.22 [s, 18 H, C(C*H*$_3$)$_3$], 2.19 (s, 6 H, NC*H*$_3$), 2.30 (q, ^3J = 7 Hz, 8 H, NC*H*$_2$CH$_3$), 2.42–2.52 (m, 16 H, NC*H*$_2$C*H*$_2$N), 2.83 (s, 4 H, ArSC*H*$_2$), 3.66 (s, 8 H, ArC*H*$_2$N), 7.36 ppm (s, 4 H, Ar*H*). ^{13}C{^{1}H}NMR (50 MHz, CDCl$_3$): δ = 11.9 (NCH$_2$*C*H$_3$), 31.3 [C(*C*H$_3$)$_3$], 34.6 [*C*(CH$_3$)$_3$], 36.5 (S*C*H$_2$), 43.6 (N*C*H$_3$), 47.6 (N*C*H$_2$CH$_3$), 51.4 (N*C*H$_2$CH$_2$N), 55.2 (Ar*C*H$_2$), 57.8 (NCH$_2$*C*H$_2$N), 125.2 (C^{Ar}H), 128.7 (C^{Ar}S), 144.2 (*C*^{Ar}CH$_2$N), 150.8 ppm (C^{Ar}*t*Bu). IR (KBr): $\tilde{\nu}$ = 3425 (vw), 2965 (vs), 2868 (s), 2798 (vs), 1595 (w), 1559 (vw), 1461 (w), 1407 (w), 1384 (m), 1366 (s), 1335 (w), 1312 (m), 1296 (w), 1274 (m), 1260 (m), 1217 (w), 1187 (m), 1163 (w), 1123 (s), 1100 (m), 1081 (m), 1039 (s), 1002 (w), 979 (w), 950 (w), 936 (w), 915 (w), 898 (w), 882 (w), 791 (w), 770 (w), 730 (vw), 683 (w), 653 (w), 607 (vw), 575 (vw), 555 (vw), 529 (vw), 475 cm^{-1} (vw). $C_{44}H_{76}N_6S_2$·H_2O (753.24 + 18.02): calcd. C 68.52, H 10.19, N 10.90, S 8.31; found C 68.35, H 10.16, N 10.57, S 7.92. This compound was additionally characterised by X-ray crystallography.

Preparation of H_2L^3·6HCl: A solution of **3** (3.80 g, 5.93 mmol) in tetrahydrofuran (50 mL) was added dropwise to a solution of sodium (2.0 g, 87 mmol) in liquid ammonia (150 mL). The resulting blue reaction mixture was stirred for a further 3 h at –76 °C. Solid ammonium chloride was then added to destroy the excess reducing agent. The resulting colourless suspension was warmed to room temperature. After 12 h, the remaining solvent was distilled off under reduced pressure. The residue was taken up in water (20 mL) and the solution was acidified to pH 1 with conc. hydrochloric acid. To remove sodium chloride and ammonium chloride from the product, the residue was triturated with methanol (3 × 50 mL) and filtered. The crude product was further purified by recrystallisation from a mixed methanol/ethanol (1:1) solvent system. This material (3.55 g, 72%) was used without further purification. M.p. 259 °C. ^{1}H NMR (400 MHz, CD$_3$OD): δ = 1.34 [s, 18 H, C(C*H*$_3$)$_3$], 3.00 (s, 6 H, NCH$_3$), 3.67 (m, 16 H, NC*H*$_2$C*H*$_2$N), 4.64 (s, 8 H, ArC*H*$_2$N), 7.80 ppm (s, 4 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$OD): δ = 31.5 [C(*C*H$_3$)$_3$], 35.9 [*C*(CH$_3$)$_3$], 42.1 (NCH$_3$), 43.4 (N*C*H$_2$), 52.2 (N*C*H$_2$), 53.6 (N*C*H$_2$), 130.4 (C^{Ar}H), 132.1 (C^{Ar}S), 135.8 (*C*^{Ar}CH$_2$N), 153.8 ppm (C^{Ar}*t*Bu). IR (KBr): $\tilde{\nu}$ = 3425 (vs), 2961 (vs), 2869 (s), 2640 (s), 1724 (vw), 1629 (w), 1601 (w), 1512 (vw), 1462 (s), 1366 (w), 1231 (w), 1161 (vw), 1019 (vw), 993 (vw), 895 (vw), 786 (vw), 753 (vw), 663 (vw), 557 cm^{-1} (vw). $C_{34}H_{64}Cl_6N_6S_2$·1.5EtOH (830.28 + 69.04): calcd. C 49.22, H 8.15, Cl 23.56, N 9.31, S 7.10; found C 48.8, H 8.38, Cl 23.53, N 9.13, S 7.55.

Preparation of H_2L^4·6HCl: The preparation of this ligand was analogous to that of H_2L^3·6HCl except that compound **5** was used instead of **3**. Yield: 672 mg (71%). The hexahydrochloride salt could not be obtained in analytically pure form, but it was pure enough for the preparation of the metal complexes. ^{1}H NMR (200 MHz, CD$_3$OD): δ = 1.24–1.70 [m, 30 H, C(C*H*$_3$)$_3$ and NCH$_2$C*H*$_3$], 2.67–3.05 (m, 6 H, NC*H*$_3$), 3.17–3.99 (m, 24 H, NC*H*$_2$), 7.42–8.15 ppm (m, 4 H, Ar*H*). ^{13}C{^{1}H}NMR (100 MHz, CD$_3$OD): δ = 9.04 (NCH$_2$*C*H$_3$), 31.6 [C(*C*H$_3$)$_3$], 35.2 [*C*(CH$_3$)$_3$], 41.3 (N*C*H$_3$), 47.7 (N*C*H$_2$CH$_3$), 50.1 (Ar*C*H$_2$N), 52.5 (N*C*H$_2$CH$_2$N), 59.5 (NCH$_2$*C*H$_2$N), 132.2 (C^{Ar}H), 132.6 (C^{Ar}S), 135.4 (*C*^{Ar}CH$_2$N), 148.9 ppm (C^{Ar}*t*Bu). IR (KBr): $\tilde{\nu}$ = 3404 (vs), 2964 (vs), 2870 (s), 2604 (vs), 1633 (w), 1602 (w), 1467 (vs), 1414 (s), 1398 (s), 1366 (m), 1232 (w), 1202 (vw), 1164 (w), 1081 (w), 1046 (m), 992 (vw), 959 (vw), 897 (vw), 795 (w), 737 cm^{-1} (vw).

Preparation of [(L^3)Ni$_2$(Cl)][ClO$_4$] (8[ClO$_4$]) and [(L^3)Ni$_2$(Cl)][BPh$_4$] (8[BPh$_4$]): A solution of NiCl$_2$·6H$_2$O (261 mg, 1.10 mmol) in methanol (2 mL) was added to a suspension of H_2L^3·6HCl (460 mg, 0.552 mmol) in methanol (15 mL). A solution of NEt$_3$ (448 mg, 4.43 mmol) in methanol (3 mL) was then added dropwise to give a dark red solution. The solution was stirred for a further 2 d at room to give a yellow solution. Solid LiClO$_4$·3H$_2$O (882 mg, 5.50 mmol) was added and half of the solvent was removed in vacuo. The resulting yellow precipitate was filtered off, recrystallised once from a few millilitres of acetonitrile, and dried in vacuo. Yield: 416 mg (87%). M.p. 299 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3430 (m), 3286 (w), 3256 (w), 3095 (vw), 2955 (m), 2870 (m), 2023 (vw), 1629 (w), 1461 (m), 1393 (w), 1363 (w), 1333 (vw), 1307 (vw), 1258 (w), 1229 (w), 1156 (m), 1094 [vs, ν(ClO$_4^-$)], 1000 (w), 975 (w), 957 (vw), 930 (w), 894 (vw), 871 (w), 854 (w), 806 (vw), 750 (w), 623 (m), 568 (vw), 546 (vw), 472 cm^{-1} (vw). UV/Vis (CH$_3$CN): λ_{max} (ε) = 623(76), 902 (63), 960 nm (68 M^{-1} cm^{-1}). $C_{34}H_{56}Cl_2N_6Ni_2O_4S_2$ (865.27): calcd. C 47.20, H 6.52, N 9.71, S 7.41; found C 47.20, H 6.29, N 9.32, S 7.10. The tetraphenylborate salt **8**[BPh$_4$] was prepared by adding NaBPh$_4$ (342 mg, 1.00 mmol) to a solution of **8**[ClO$_4$] (86.5 mg, 0.100 mmol) in methanol (40 mL). The yellow microcrystalline solid was isolated by filtration, washed with ethanol, and dried in air. Yield: 96.2 mg (89%). M.p. 249 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3440 (w), 3275 (m), 3055 (w), 2963 (m), 2872 (m), 1948 (vw), 1658 (w), 1578 (vs), 1479 (m), 1457 (s), 1426 (s), 1392 (w), 1362 (w), 1311 (w), 1260 (w), 1229 (w), 1151 (w), 1081 (m), 1057 (w), 1032 (w), 984 (w), 930 (w), 877 (w), 849 (w), 733 [m, ν(BPh$_4^-$)], 705 [s, ν(BPh$_4^-$)], 612 (m), 545 (vw), 464 (vw) cm^{-1}. $C_{58}H_{76}BClN_6Ni_2S_2$ (1085.05): calcd. C 64.20, H 7.06, N 7.75, S 5.91; found C 63.81, H 7.14, N 7.44, S 5.64. The tetraphenylborate salt was additionally characterised by X-ray crystallography.

Preparation of [(L^4)Ni_2(Cl)][ClO_4] (9[ClO_4]) and [(L^4)Ni_2(Cl)][BPh_4] (9[BPh_4]): A solution of $NiCl_2·6H_2O$ (59.4 mg, 0.250 mmol) in methanol (2 mL) was added to a suspension of $H_2L^4·6HCl$ (118 mg, 0.125 mmol) in methanol (15 mL). A solution of NEt_3 (101 mg, 1.00 mmol) in methanol (3 mL) was then added to give a dark red solution. The solution was stirred for a further 2 d at room temp. to give a yellow solution. Solid $LiClO_4·3H_2O$ (200 mg, 1.25 mmol) was added and half of the solvent was removed in vacuo. The resulting yellow precipitate was filtered off, recrystallised once from a few millilitres of acetonitrile, and dried in vacuo. Yield: 78 mg (64%). M.p. 296 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3438 (m), 2963 (s), 2891 (s), 2018 (vw), 1629 (w), 1460 (s), 1377 (m), 1363 (m), 1314 (w), 1259 (w), 1232 (w), 1201 (vw), 1158 (m), 1098 (vs, νClO_4^-), 1058 (m), 1023 (m), 988 (vw), 968 (vw), 955 (vw), 925 (vw), 907 (w), 883 (w), 809 (vw), 778 (m), 732 (w), 673 (vw), 624 (m) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 675 (31), 928 (62), 1013 (82 $M^{-1}cm^{-1}$). $C_{42}H_{72}Cl_2N_6Ni_2O_4S_2·H_2O$ (977.48 + 18.02): calcd. C 50.67, H 7.49, N 8.44, S 6.44; found C 50.5, H 7.51, N 8.09, S 6.56. The tetraphenylborate salt **9**[BPh_4] was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **9**[ClO_4] (100 mg, 0.100 mmol) in methanol (40 mL). The yellow microcrystalline solid was filtered, recrystallised from a few millilitres of acetonitrile, and dried in air. Yield: 113 mg (94%). M.p. 205 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3427 (m), 3055 (m), 3033 (m), 2963 (vs), 2894 (s), 2866 (s), 1816 (vw), 1615 (w), 1579 (w), 1478 (vs), 1461 (vs), 1429 (m), 1379 (m), 1362 (m), 1343 (w), 1312 (w), 1262 (w), 1233 (w), 1201 (vw), 1184 (vw), 1157 (w), 1096 (vs), 1058 (s), 1032 (s), 988 (w), 954 (w), 907 (w), 884 (w), 844 (w), 807 (w), 777 (m), 732 [vs, $\nu(BPh_4^-)$], 704 [vs, $\nu(BPh_4^-)$], 630 (w) 612 (m) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 658 (25), 928 (48), 1018 nm (63 $M^{-1}cm^{-1}$). $C_{66}H_{92}BClN_6Ni_2S_2·3H_2O·CH_3CN$ (1197.26 + 95.10): calcd. C 63.20, H 7.88, N 7.59, S 4.96; found C 62.90, H 7.64, N 7.73, S 5.36. The tetraphenylborate salt was additionally characterised by X-ray crystal structure analysis.

Preparation of [(L^1)Cd_2(Cl)][ClO_4] (10[ClO_4]): A solution of $CdCl_2·H_2O$ (402 mg, 2.00 mmol) in MeOH (10 mL) was added to a suspension of $H_2L^1·6HCl$ (806 mg, 1.00 mmol) in MeOH (30 mL). A solution of triethylamine (809 mg, 8.08 mmol) in MeOH (3 mL) was then added. After stirring at ambient temperature for 2 d, solid $LiClO_4·3H_2O$ (1.60 g, 10.0 mmol) was added. The precipitate was filtered and purified by recrystallisation from MeCN. Yield: 432 mg (46%). IR (KBr): $\tilde{\nu}$ = 3445 (m), 3229 [s, ν(NH)], 2953 (s), 2902 (s), 2855 (s), 1623 (m), 1456 (m), 1395 (w), 1363 (m), 1344 (w), 1297 (w), 1268 (vw), 1227 (m), 1151 (m), 1100 (s), 1078 (m), 1024 (m), 942 (m), 910 (m), 873 (m), 850 (m), 812 (w), 780 (w), 747 (vw), 627 (m) cm^{-1}. ^1H NMR (400 MHz, CD_3OD, for atom labels see inset of Table 2): δ = 1.26 (s, 9 H, C^1H_3 or C^4H_3), 1.32 (s, 9 H, C^1H_3 or C^4H_3), 2.40–3.70 (m, 20 H, $C^{6-9,6'-9'}H_2$ + $C^{5,5',10,10'}H$*H*), 4.30–4.40 (m, 4 H, $C^{5,5',10,10'}H$H), 7.16 (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$), 7.34 ppm (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$). $^{13}C\{^1H\}$NMR (100 MHz, [D_6]DMSO): δ = 31.2 (C^1 or C^4), 31.3 (C^1 or C^4), 33.7 (C^2 or C^3), 33.8 (C^2 or C^3), 47.4, 48.9, 49.2, 54.2, 55.2, 56.0 ($C^{5-10,5'-10'}$), 127.5, 127.8 ($C^{13,13',17,17'}$), 137.3, 137.4 ($C^{12,12',16,16'}$), 138.2, 139.1 ($C^{11,15}$), 145.0, 145.1 ($C^{14,18}$) ppm. ESI-MS: *m*/*z* 905.3 (100%) [(L^1)Cd_2(Cl)]$^+$. The tetraphenylborate salt **10**[BPh_4] was prepared by adding $NaBPh_4$ (674 mg, 1.97 mmol) to a solution of **10**[ClO_4] (186 mg, 0.197 mmol) in methanol (50 mL). The resulting colourless microcrystalline solid was isolated by filtration, washed with ethanol, and dried in air. Yield: 172 mg (74%). IR (KBr): $\tilde{\nu}$ = 3445 [m, ν(OH)], 3279 [s, ν(NH)], 3054 [m, ν(Ar)], [2962 (vs), 2864 (s)] [ν(CH)], 1616 (w), 1580 (w), 1477 (s), 1455 (s), 1394 (w), 1365 (w), 1300 (w), 1253 (w), 1227 (w), 1202 (vw), 1152 (w), 1098 (w), 1072 (w), 1033 (w), 909 (m), 849 (m), 735 (vs), 707 (vs), 612 (m) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 1.26 (s, 9 H, C^1H_3 or C^4H_3), 1.32 (s, 9 H, C^1H_3 or C^4H_3), 2.50–3.75 (m, 20 H, $C^{6-9,6'-9'}H_2$ + $C^{5,5',10,10'}H$*H*), 4.35–4.41 (m, 4 H, $C^{5,5',10,10'}H$H), 6.82 (t, *J* = 8 Hz, 4 H, BPh_4^-), 6.96 (t, *J* = 8 Hz, 8 H, BPh_4^-), 7.16 (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$), 7.29 (m, 8 H, BPh_4^-), 7.33 ppm (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$). $^{13}C\{^1H\}$NMR (100 MHz, [D_6]DMSO): δ = 31.1 (C^1 or C^4), 31.2 (C^1 or C^4), 33.7 (C^2 or C^3), 33.8 (C^2 or C^3), 47.4, 48.6, 49.1, 49.3, 54.2, 55.2 ($C^{5-10,5'-10'}$), 127.5, 127.8 ($C^{13,13',17,17'}$), 138.0, 138.2 ($C^{12,12',16,16'}$), 139.0, 139.9 ($C^{11,15}$), 140.0, 145.8 ($C^{14,18}$), 121.5 (BPh_4^-), 125.3 (BPh_4^-), 135.5 (BPh_4^-), 164.0 ppm (BPh_4^-). This salt was additionally characterised by X-ray crystallography.

Preparation of [(L^3)Cd_2(Cl)][ClO_4] (12[ClO_4]) and [(L^3)-Cd_2(Cl)][BPh_4] (12[BPh_4]): A solution of $CdCl_2·H_2O$ (223 mg, 1.10 mmol) in MeOH (2 mL) was added to a suspension of $H_2L^3·6HCl$ (460 mg, 0.552 mmol) in MeOH (15 mL). A solution of triethylamine (445 mg, 4.40 mol) in MeOH (3 mL) was then added to give a colourless solution. After stirring at ambient temperature for 4 d, solid $LiClO_4·3H_2O$ (118 mg, 0.735 mmol) was added to give the perchlorate salt **12**[ClO_4] as a white microcrystalline solid. The precipitate was filtered and purified by recrystallisation from MeCN. Yield: 432 mg (80%). M.p. 332 °C (decomp.). ^1H NMR (200 MHz, CD_3CN, for atom labels see inset of Table 2): δ = 1.25 (s, 9 H, C^1H_3 or C^4H_3), 1.29 (s, 9 H, C^1H_3 or C^4H_3), 2.65 [s, 6 H, $CH_3(R^1)$], 2.70–3.60 (m, 20 H, $C^{6-9,6'-9'}H_2$ + $C^{5,5',10,10'}H$), 4.25–4.43 (m, 4 H, $C^{5,5',10,10'}H$), 7.17 (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$), 7.32 ppm (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$). $^{13}C\{^1H\}$NMR (75 MHz, CD_3CN): δ = 31.61 (C^1 or C^4), 31.74 (C^1 or C^4), 34.84 (C^2 or C^3), 34.93 (C^2 or C^3), 49.48 (CH_3, R^1), 50.68, 55.19, 56.20, 58.06, 58.17, 60.37 ($C^{5-10,5'-10'}$), 129.01, 129.28 ($C^{13,13',17,17'}$), 138.95, 139.46 ($C^{12,12',16,16'}$), 138.45, 140.24 ($C^{11,15}$), 147.96, 148.21 ppm ($C^{14,18}$). IR (KBr): $\tilde{\nu}$ = 3453 (m), 3283 (m), 2953 (m), 2864 (m), 1629 (w), 1462 (m), 1363 (w), 1300 (vw), 1266 (vw), 1229 (w), 1202 (vw), 1154 (w), 1097 [vs, $\nu(ClO_4^-)$], 989 (w), 931 (w), 860 (w), 751 (vs), 624 (m) cm^{-1}. $C_{34}H_{56}Cd_2Cl_2N_6O_4S_2·2H_2O$ (972.70 + 36.03): calcd. C 40.48, H 6.00, N 8.33, S 6.36; found C 40.20, H 5.88, N 7.61, S 6.11. The tetraphenylborate salt **12**[BPh_4] was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **12**[ClO_4] (97 mg, 0.100 mmol) in methanol (40 mL). The colourless microcrystalline solid was isolated by filtration, washed with ethanol, and dried in air. Yield: 82 mg (69%). ^1H NMR (200 MHz, CD_3CN, for atom labels see inset Table 2): δ = 1.25 (s, 9 H, C^1H_3 or C^4H_3), 1.29 (s, 9 H, C^1H_3 or C^4H_3), 2.65 [s, 6 H, $CH_3(R^1)$] 2.65–3.60 (m, 20 H, $C^{6-9,6'-9'}H_2$ + $C^{5,5',10,10'}H$H), 4.20–4.45 (m, 4 H, $C^{5,5',10,10'}H$*H*), 6.83 (m, 4 H, BPh_4^-), 6.99 (m, 8 H, BPh_4^-), 7.17 (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$), 7.28 (m, 8 H, BPh_4^-), 7.32 ppm (s, 2 H, $C^{13,13'}H$ or $C^{17,17'}H$). $^{13}C\{^1H\}$NMR (75 MHz, CD_3CN): δ = 31.49 (C^1 or C^4), 31.61 (C^1 or C^4), 34.9 (C^2 or C^3), 35.0 (C^2 or C^3), 49.3 [$CH_3(R^1)$], 49.4, 50.6, 55.0, 56.1, 58.0, 60.2 ($C^{5-10,5'-10'}$), 128.9, 129.1 ($C^{13,13',17,17'}$), 138.5, 140.1 ($C^{12,12',16,16'}$), 139.0, 139.5 ($C^{11,15}$), 147.1, 147.8 ($C^{14,18}$); 122.7 (BPh_4^-), 126.5 (BPh_4^-), 136.7 (BPh_4^-), 165.04 (BPh_4^-) ppm. IR (KBr): $\tilde{\nu}$ = 3426 (m), 3275 (s), 3054 (m), 2965 (vs), 2867 (s), 2250 (vw), 1618 (vw), 1579 (w), 1479 (s), 1463 (s), 1427 (m), 1391 (w), 1363 (m), 1296 (w), 1267 (w), 1229 (w), 1201 (w), 1153 (m), 1086 (s), 1047 (s), 982 (w), 929 (w), 904 (w), 884 (w), 862 (m), 816 (vw), 749 (m), 735 [vs. $\nu(BPh_4^-)$], 706 [vs. $\nu(BPh_4^-)$], 680 (vw), 625 (w), 612 (m), 543 (vw), 469 (vw) cm^{-1}. $C_{58}H_{76}BCd_2ClNS_2·H_2O$ (1192.48 + 18.02): calcd. C 57.55, H 6.49, N 6.94, S 5.30; found C 57.20, H 7.13, N 7.54, S 5.56. The tetraphenylborate salt was additionally characterised by X-ray crystal structure analysis.

Preparation of [(L^4)Cd_2(Cl)][ClO_4] (13[ClO_4]) and [(L^4)-Cd_2(Cl)][BPh_4] (13[BPh_4]): A solution of $CdCl_2·H_2O$ (43.2 mg,

0.215 mmol) in MeOH (2 mL) was added to a suspension of H_2L^4·6HCl (101 mg, 0.107 mmol) in MeOH (20 mL). A solution of triethylamine (86.7 mg, 0.857 mmol) in MeOH (3 mL) was then added to give a colourless solution. After stirring at ambient temperature for 2 d, solid $LiClO_4$·$3H_2O$ (171 mg, 1.07 mmol) was added to give the perchlorate salt **13**[ClO_4] as a white microcrystalline solid. The precipitate was filtered and purified by recrystallisation from a mixed EtOH/MeCN (1:1) solvent system. Yield: 102 mg (88%). M.p. 328 °C (decomp.). ^{1}H NMR (200 MHz, CD_3CN, for atom labels see inset Table 2): δ = 1.12 [t, J = 14 Hz, 12 H, $NCH_2CH_3(R^2)$], 1.27 (s, 18 H, C^1H_3 + C^4H_3), 2.36–4.52 (m, 38 H, NCH_2), 2.83 [s, 6 H, $CH_3(R^1)$], 7.28 (s, 4 H, $C^{13,13',17,17'}H$) ppm. $^{13}C\{^1H\}$NMR (75 MHz, CD_3CN): δ = 6.63 [$CH_2CH_3(R^2)$], 31.5 ($C^{1,4}$), 34.7 ($C^{2,3}$), 50.00 [$CH_2CH_3(R^2)$], 50.30 [$CH_3(R^1)$], 55.74, 56.55, 58.13 ($C^{5-10,5'-10'}$), 130.18 ($C^{13,13',17,17'}$), 136.29 ($C^{12,12',16,16'}$), 142.13 ($C^{11,15}$), 146.78 ($C^{14,18}$) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (m), 2961 (s), 2867 (m), 1628 (w), 1465 (s), 1383 (m), 1367 (m), 1313 (w), 1268 (w), 1231 (w), 1203 (vw), 1100 (vs, νClO_4^-), 1052 (s), 985 (w), 948 (vw), 926 (vw), 887 (w), 778 (m), 624 (m) cm^{-1}. $C_{42}H_{72}Cd_2Cl_2N_6O_4S_2$·$7H_2O$ (1084.92 + 126.11): calcd. C 41.65, H 7.16, N 6.94, S 5.30; found C 42.1, H 7.01, N 7.09, S 5.54. The tetraphenylborate salt **13**[BPh_4] was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **13**[ClO_4] (108 mg, 0.100 mmol) in methanol (40 mL). The colourless microcrystalline solid was isolated by filtration, washed with ethanol, and dried in air. Yield: 119 mg (91%). M.p. 231 °C (decomp.). ^{1}H NMR (400 MHz, CD_3CN, for atom labels see inset Table 2): δ = 1.16 [m, 12 H, $CH_2CH_3(R^2)$], 1.28 (s, 18 H, C^1H_3 + C^4H_3), 2.86 [s, 6 H, $CH_3(R^1)$], 2.70–4.47 (m, 38 H, NCH_2), 6.85 (m, 4 H, BPh_4^-), 7.00 (m, 8 H, BPh_4^-), 7.23 ppm (m, 4 H + 8 H, $C^{13,13',17,17'}H$ + BPh_4^-). $^{13}C\{^1H\}$NMR (75 MHz, CD_3CN): δ = 6.56 [$CH_2CH_3(R^2)$], 31.5 ($C^{1,4}$), 34.65 ($C^{2,3}$), 49.91 [$CH_2CH_3(R^2)$], 50.21 [$CH_3(R^1)$], 55.64,

Table 5. Crystallographic data for **5**, **8**[BPh_4]·3EtOH, **9**[BPh_4]·5MeCN, **10**[BPh_4]·5MeOH, **12**[BPh_4]·2MeCN and {**13**[BPh_4]·3.5MeCN}$_2$.

	5	**8**[BPh_4]·3EtOH	**9**[BPh_4]·5MeCN
Formula	$C_{44}H_{76}N_6S_2$	$C_{64}H_{94}BClN_6Ni_2O_3S_2$	$C_{76}H_{107}BClN_{11}Ni_2S_2$
M_r [g mol^{-1}]	753.23	1223.25	1402.53
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	24.437(4)	14.872(3)	13.3420(5)
b [Å]	9.734(3)	14.949(3)	14.7530(5)
c [Å]	19.004(4)	16.132(3)	19.0750(7)
α [°]	90.00	71.14(3)	85.653(3)
β [°]	90.52(2)	78.41(3)	88.787(3)
γ [°]	90.00	71.92(3)	84.854(3)
V [Å^3]	4520.0(18)	3206.1(11)	3728.3(2)
Z	4	2	2
$D_{calcd.}$ [g cm^{-3}]	1.107	1.267	1.249
μ(Mo-K_α) [mm^{-1}]	0.154	0.742	0.646
θ limits [°]	1.67–28.86	1.34–28.82	3.26-31.99
Measured refl.	19600	29072	34637
Independent refl.	5472	14990	25571
Observed refl.[a]	2602	7750	17381
parameters	263	682	763
$R1$[b] ($R1$ all data)	0.0585 (0.1281)	0.0511 (0.1144)	0.0403 (0.0627)
$wR2$[c] ($wR2$ all data)	0.1579 (0.1908)	0.1197 (0.1461)	0.0999 (0.1054)
Max., min. peaks [e/Å^3]	0.443/–0.207	0.885/–0.532	1.226/–0.729
CCDC	600010	600011	600012
	10[BPh_4]·5MeOH	**12**[BPh_4]·2MeCN	{**13**[BPh_4]·3.5MeCN}$_2$
Formula	$C_{61}H_{92}BCd_2ClN_6O_5S_2$	$C_{62}H_{82}BCd_2ClN_8S_2$	$C_{146}H_{205}B_2Cd_4Cl_2N_{19}S_4$
M_r [g mol^{-1}]	1324.59	1274.54	2896.65
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	14.202(3)	15.283(3)	18.984(4)
b [Å]	17.019(3)	28.264(6)	20.143(4)
c [Å]	17.928(4)	16.995(3)	22.112(4)
α [°]	109.77(3)	90.00	98.55(3)
β [°]	105.85(3)	107.28(3)	115.29(3)
γ [°]	113.66(3)	90.00	95.67(3)
V [Å^3]	3288.1(11)	7010(2)	7434(3)
Z	2	4	2
$D_{calcd.}$ [g cm^{-3}]	1.338	1.208	1.294
μ(Mo-K_α) [mm^{-1}]	0.800	0.744	0.710
θ limits [°]	5.10–31.97	1.44–29.03	3.21–28.01
Measured refl.	49433	44336	137595
Independent refl.	22415	16567	34637
Observed refl.[a]	11546	5816	26501
parameters	741	655	1489
$R1$[b] ($R1$ all data)	0.0922 (0.1596)	0.0720 (0.1981)	0.0478 (0.0647)
$wR2$[c] ($wR2$ all data)	0.2259 (0.2670)	0.2013 (0.2551)	0.1313 (0.1447)
Max., min. peaks [e/Å^3]	2.841/–2.582	1.310/–0.829	1.331/–1.155
CCDC	622729	600013	600014

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

56.46, 59.02 ($C^{5–10,5'–10'}$), 130.10 ($C^{13,13',17,17'}$), 136.20 ($C^{12,12',16,16'}$), 142.06 ($C^{11,15}$), 146.67 ($C^{14,18}$); 122.79 (BPh_4^-), 126.58 (BPh_4^-), 136.77 (BPh_4^-), 164.82 (BPh_4^-) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (w), 3034 (m), 3054 (m), 2964 (vs), 2863 (s), 1748 (vw), 1616 (vw), 1580 (w), 1464 (vs), 1383 (m), 1367 (m), 1311 (w), 1267 (w), 1232 (w), 1185 (vw), 1159 (w), 1100 (m), 1053 (vs), 986 (vw), 949 (vw), 925 (vw), 886 (w), 845 (vw), 777 (m), 734 (s), 705 [vs. $\nu(BPh_4^-)$], 613 (m) cm^{-1}. $C_{66}H_{92}BCd_2ClN_6S_2$ (1304.69): calcd. C 60.76, H 7.11, N 6.44, S 4.92; found C 60.94, H 6.85, N 6.37, S 5.42. The tetraphenylborate salt was additionally characterised by X-ray crystal structure analysis.

Crystal Structure Determinations: Large single crystals of **5** were obtained by slow evaporation of a CH_2Cl_2/CH_3OH solution. Crystals of **8**[BPh_4]·3EtOH, **9**[BPh_4]·5MeCN, **12**[BPh_4]·2MeCN and {**13**[BPh_4]·3.5MeCN}$_2$ were obtained by slow evaporation from a mixed MeCN/EtOH (1:1) solvent system. Crystals of **10**[BPh_4]·5MeOH were grown by recrystallisation from MeOH. The diffraction experiments were carried out with Bruker CCD (for **5**, **8** and **12**) or STOE IPDS-2T X-ray diffractometers (for **9**, **10** and **13**). The intensity data were processed with the programs SAINT (**5**, **8**, **12**) or STOE X-AREA (**9**, **10**, **13**). Structures were solved by direct methods and refined by full-matrix least-squares on the basis of all data against F^2 using SHELXL-97.[31] PLATON was used to search for higher symmetry.[32] H atoms were placed in calculated positions and treated isotropically using the 1.2-fold U_{iso} value of the parent atom, except for methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent C atoms. Unless otherwise noted, all non-hydrogen atoms were refined anisotropically. ORTEP-3 was used for the artwork of the structures.[33] Experimental crystallographic data are summarised in Table 5. Further data are available in the Supporting Information.

In the crystal structure of **5** and **10**[BPh_4]·5MeOH a *tert*-butyl group is disordered over two positions. Two split positions were successfully refined to give the following site occupancies: C(19a)-C20(a)C(21a)/C(19b)C20(b)C(21b) = 0.60(1)/0.40(1) (for **5**), C(26a)C(27a)C(28a)/C(26b)C(27b)C(28b) = 0.60(2)/0.40(2) (for **10**[BPh_4]·5MeOH). The C, N, and O atoms of the solvates in **8**[BPh_4]·3EtOH, **9**[BPh_4]·5MeCN and {**13**[BPh_4]·3.5MeCN}$_2$ were refined isotropically.

CCDC-600010 to -600014 and -622729 (see Table 5 for assignments) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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