Synthesis, X-ray Characterization, NMR and A*b Initio* Molecular-Orbital Studies of Some Cadmium(II) Macrocyclic Schiff-Base Complexes with Two 2-Aminoethyl Pendant Arms

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Three new pendant arm Schiff-base macrocyclic complexes, $[CdL^n]^{2+}$ (n = 5, 6, 7), have been prepared via cyclocondensation of 2,6-diacetylpyridine with three different branched hexaamines in the presence of Cd(II). The ligands are 15-, 16- and 17-membered pentaaza macrocycles having two 2-aminoethyl pendant arms [L^5 = 2,13-dimethyl-6,9-bis(aminoethyl)-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, L^6 = 2,14-dimethyl-6,10-bis(aminoethyl)-3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene and L^7 = 2,15-dimethyl-6,11-bis(aminoethyl)-3,6,11,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene]. All complexes were investigated by IR, ^{1}H and ^{13}C NMR, COSY(H,H) and HETCOR(H,C) spectroscopy and X-ray diffraction. In the solid state structure of each complex the Cd(II) ion is situated centrally within an approximately planar pentaaza macrocyclic ring, binding to the five nitrogen atoms, and also to the two pendant amines which are located on opposite sides of the macrocyclic plane. *ab initio* HF-MO calculations using a standard 3-21G* basis set have been used to verify that these similar basic structures correspond to energy minima in the gas phase.

Keywords: Cadmium(II) complexes, Schiff-base macrocyclic ligand, Pendant arm, Seven coordinate, *Ab initio* studies

INTRODUCTION

The preparation of macrocyclic polyamine ligands bearing functional pendant donor groups and their ligation to metal ions has been an active area of research for many years [1-4] and, stemming from this, a variety of different applications for these ligands and their complexes are now emerging [5]. We have been interested for some time in the synthesis of CR-type, [6], macrocyclic Schiff-base complexes formed from Cu(II) and Ni(II) templated [1+1] cyclocondensations of 2,6-diacetylpyridine (hereafter DAP) with tripodal tetraamines. These reactions produce tetraaza macrocycles carrying a single 2-aminoethyl pendant arm [7]. However, when Cd(II) was used as the templating metal ion

in those reactions ring closure could not be effected, which may be due to the ring size of these macrocycles being smaller than is appropriate for the occurrence of a successful [1+1] cyclocondensation around Cd(II) [8]. As an extension of this idea, we have developed a method for producing pentaaza macrocycles with two pendant 2-aminoethyl arms, using branched hexaminees with DAP. This is successful, in the presence of Mn(II), Mg(II) and Zn(II) (seven coordinate ionic radius <0.90 Å [9]), in producing ligands L^5-L^7, shown in Chart 1, which impose unusual pentagonal bipyramidal coordination geometries on these metal ions [10]. It was of interest, therefore, to determine whether L^5-L^7 would form using the larger Cd(II) ion as the metal template (seven coordinate ionic radius = 1.03 Å [9]) since, if successful, this approach would allow the investigation of the chemistry of

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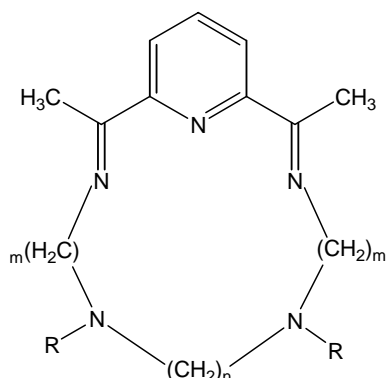
	n	m	R	
L^1	2	2	H	[15]pydieneN$_5$
L^2	3	2	H	[16]pydieneN$_5$
L^3	4	2	H	[17]pydieneN$_5$
L^4	2	3	H	[17]pydieneN$_5$
L^5	2	2	EtNH$_2$	(NH$_2$Et)$_2$[15]pydieneN$_5$
L^6	3	2	EtNH$_2$	(NH$_2$Et)$_2$[16]pydieneN$_5$
L^7	4	2	EtNH$_2$	(NH$_2$Et)$_2$[17]pydieneN$_5$

Chart 1

heptadentate Cd(II) complexes coordinated by a single heptaaza ligand.

Cd(II) complexes of L^1, L^2 and L^4 (Chart 1) have been reported [11,12] and in the case of L^2 and L^4 the structures of the bromo-complexes have been determined by X-ray diffraction: $[CdL^2Br]_n^{n+}$ is a polymeric cation in which the Cd(II) ion is seven-coordinate with a pentagonal bipyramidal arrangement of donor atoms. L^2 occupies the equatorial coordination sites and bridging bromo-moieties are arranged axially. $[CdL^4Br]^+$ involves a six-coordinate Cd(II) ion at the centre of a pentagonal pyramidal arrangement of donor atoms with L^4 occupying the basal positions and the bromo group at the apex.

In this report we describe the Cd(II) templated [1+1] cyclocondensation of DAP with the branched hexaamines ten, ttn, and ttmd which gave the complexes $[CdL^n]^{2+}$ n = 5, 6, 7, respectively, as shown in Scheme 1. These complexes are based on the 15-, 16- and 17-membered pentaaza macrocycles (L^1-L^3, Chart 1) but have 2-aminoethyl pendant arms attached to the two secondary amines. The pattern of methylene groups present in $[CdL^7]^{2+}$, results in a pair of five-membered chelate rings flanking a seven-membered chelate ring, making it a derivative of the

n=2, ten
n=3, ttn
n=4, ttmd
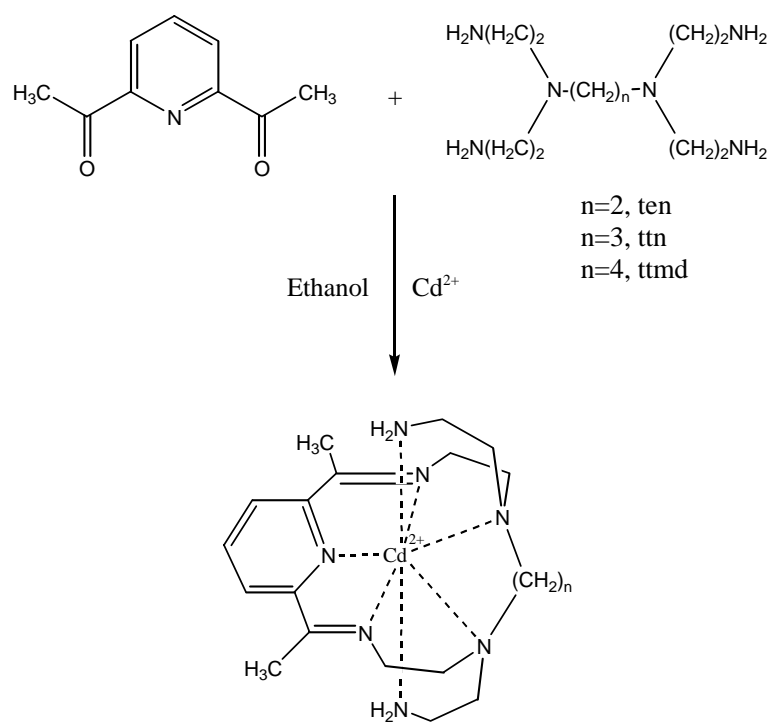
Scheme 1. The template condensation between DAP and various hexaamines in the presence of Cd(II).

unknown 17-membered pydieneN$_5$, shown as L^3 in Chart 1, rather than the known 17-membered pydieneN$_5$, L^4, complexes which have a central five-membered chelate ring flanked by two six-membered rings.

EXPERIMENTAL

Starting Materials

All reagents and solvents were of analytical grade quality and purchased commercially. DAP was obtained from Aldrich and used without further purification.

Physical Measurements

NMR spectra were obtained on a Varian 300 MHz spectrometer. Infrared spectra were recorded as liquid films between NaCl plates, using BIO-RAD FTS-40A spectrophotometer in the range 4000-600 cm^{-1}.

Hexamine Synthesis

The branched hexaamines were prepared by reaction of the appropriate linear diamines with N-tosylaziridine, in benzene at room temperature for 3 days, followed by detosylation with HBr/AcOH, as described previously using N-benzenesulfonyl aziridine [13]. (1) N,N,N',N'-tetrakis(2-aminoethyl)ethane-1,2-diamine hexahydrobromide (ten. 6HBr), ^{13}C NMR (D$_2$O): δ_C 37.37, 51.14, 51.97 ppm. (2) N,N,N',N'-tetrakis(2-aminoethyl)propane-1,3-diamine hexa hydrobromide (ttn. 6HBr), ^{13}C NMR (D$_2$O): δ_C 19.39, 36.01, 50.24, 50.82 ppm. (3) N,N,N',N'-tetrakis(2-aminoethyl)butane-1,4-diamine hexahydrobromide (ttmd. 6HBr), ^{13}C NMR (D$_2$O): δ_C 22.43, 36.25, 51.85, 55.33 ppm.

Complex Synthesis

Warning: Perchlorate complexes are potentially explosive. While we have not experienced any problems with the compounds described, they should be treated with caution and handled only in small quantities.

A solution of NaOH (3 mmol) in absolute EtOH (10 ml) was added to a suspension of hexaamine. 6HBr (0.5 mmol) in absolute EtOH (10 ml) and the mixture was stirred at room temperature. The mixture was then filtered to remove the precipitated sodium bromide, which was washed well with absolute EtOH (10 ml). The combined filtrate and washings were added dropwise to a hot solution of Cd(NO$_3$)$_2$.4H$_2$O (0.5 mmol) and 2,6-diacetylpyridine (0.5 mmol) in absolute EtOH (20 ml) over a period of 2 h. After refluxing for 15 h, the solution was filtered whilst hot and solid NaClO$_4$

(1 mmol) added to the filtrate. On cooling, the product was precipitated as a powder which was recrystallized from CH$_3$CN/EtOH.

[CdL^5](ClO$_4$)$_2$. Yield 0.16g (48%). Anal. Calcd. for C$_{19}$H$_{33}$Cd Cl$_2$N$_7$O$_8$: C, 34.02; H, 4.96; N, 14.61. Found: C, 34.2; H, 5.0; N, 14.3. IR (Nujol); 3364, 3302, 1653, 1594, 1077, 1018, 656, 622 cm^{-1}. ^{13}C NMR (CD$_3$CN, ppm): δ_C 165.8 (apt ↓), 148.6 (apt ↓), 142.6 (apt ↑), 125.4 (apt ↑), 58.5 (apt ↓), 57.2 (apt ↓), 53.8 (apt ↓), 46.7 (apt ↓), 39.5 (apt ↓), 15.7 (apt ↑).

[CdL^6](ClO$_4$)$_2$ 0.5 H$_2$O. Yield 0.16 g (45%). Anal. Calcd. for C$_{20}$H$_{36}$CdCl$_2$N$_7$O$_{8.5}$: C, 34.62; H, 5.23; N, 14.13. Found: C, 34.5; H, 5.0; N, 14.3. IR (Nujol); 3550, 3355, 3296, 1653, 1593, 1091, 1014, 658, 623 cm^{-1}. ^{13}C NMR (CD$_3$CN, ppm): δ_C 166.5 (apt ↓), 149.0 (apt ↓), 142.2 (apt ↑), 125.3 (apt ↑), 61.2 (apt ↓), 56.4 (apt ↓), 52.6 (apt ↓), 45.9 (apt ↓), 38.3 (apt ↓), 24.9 (apt ↓), 15.8 (apt ↑).

[CdL^7](ClO$_4$)$_2$ .0.25 H$_2$O. Yield 0.14g (40%). Anal. Calcd. for C$_{21}$H$_{37.5}$CdCl$_2$N$_7$O$_{8.25}$: C, 35.86; H, 5.37; N, 13.94. Found: C, 35.9; H, 5.5; N, 14.0. IR (Nujol); 3530, 3333, 3276, 1644, 1587, 1085, 1012, 658, 622 cm^{-1}. ^{13}C NMR (CD$_3$CN, ppm): δ_C 167.2 (apt ↓), 149.5 (apt ↓), 142.1 (apt ↑), 125.5 (apt ↑), 55.2 (apt ↓), 53.4 (apt ↓), 50.2 (apt ↓), 46.3 (apt ↓), 38.0 (apt ↓), 24.1 (apt ↓), 15.9 (apt ↑).

The dihexafluorophosphate salts of the complexes were prepared in the same way as the diperchlorate salts, but by using NH$_4$PF$_6$ instead of NaClO$_4$ at the final stage.

[CdL^5](PF$_6$)$_2$. Yield: 0.16 g (42%). Anal. Calcd. for C$_{19}$H$_{33}$CdF$_{12}$N$_7$P$_2$: C, 29.95; H, 4.37; N, 12.87. Found: C, 30.0; H, 4.6; N, 12.7. IR (Nujol); 3385, 3324, 1654, 1588, 1019, 841, 656, 556 cm^{-1}.

[CdL^6](PF$_6$)$_2$. Yield: 0.12 g (31%). Anal. Calcd. for C$_{20}$H$_{35}$CdF$_{12}$N$_7$P$_2$: C, 30.96; H, 4.55; N, 12.64. Found: C, 31.1; H, 4.4; N, 12.5. IR (Nujol); 3382, 3326, 1651, 1592, 1015, 842, 672, 556 cm^{-1}.

[CdL^7](PF$_6$)$_2$. Yield: 0.14 g (35%). Anal. Calcd. for C$_{21}$H$_{37}$CdF$_{12}$N$_7$P$_2$: C, 31.93; H, 4.72; N, 12.41. Found: C, 32.0; H, 4.6; N, 12.3. IR (Nujol); 3379, 3320, 1648, 1589, 1012, 838, 658, 556 cm^{-1}.

Crystal Structure Determination

Vapor diffusion of diethyl ether into a solution of [CdL^n](ClO$_4$)$_2$ (n = 5, 6) or [CdL^7](PF$_6$)$_2$ in acetonitrile afforded crystals of suitable size for study by X-ray crystallography. Unit-cell and intensity data were measured on a Bruker CCD diffractometer [14] using graphite-monochromated MoKα X-radiation and corrected for

Table 1. Crystal Data and Structure Refinement Data for $[CdL^5](ClO_4)_2$ and $[CdL^7](PF_6)_2$ and Crystal Data for $CdL^6](ClO_4)_2$.

	$[CdL^5](ClO_4)_2$	$[CdL^6](ClO_4)_2$	$[CdL^7](PF_6)_2$
Empirical formula	$C_{19}H_{33}Cl_2CdN_7O_8$	$C_{20}H_{35}Cl_2CdN_7O_8$	$C_{21}H_{37}CdF_{12}N_7P_2$
Formula weight	670.83	684.863	789.93
System, space group	Orthorhombic, $Pca2_1$	Orthorhombic, $Pca2_1$	Orthorhombic, $Pca2_1$
a (Å)	16.338(4)	16.302(4)	17.175(4)
b (Å)	11.505(3)	11.777(3)	12.113(3)
C (Å)	13.973(3)	14.340(4)	14.049(3)
V (Å^3)	2626(1)	2753(1)	2923(1)
Z	4	4	4
Color and shape	Yellow, block	Yellow, plate	Colorless, wedge
Size (mm)	$0.21 \times 0.42 \times 0.60$	$0.12 \times 0.35 \times 0.41$	$0.24 \times 0.78 \times 0.85$
Wavelength (Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.696	1.647	1.795
F(000)	1368	1400	1592
Temp (K)	168(2)	168(2)	168(2)
μ (mm^{-1})	1.092	1.044	0.961
T_{min}, T_{max}	0.642, 0.790	0.650, 1.000	0.635, 0.794
θ_{max} (deg)	26.38	26.36	26.44
Index ranges	$-20 \leq h \leq 17$	$-19 \leq h \leq 20$	$-21 \leq h \leq 21$
	$-14 \leq k \leq 14$	$-9 \leq k \leq 14$	$-15 \leq k \leq 15$
	$-8 \leq l \leq 17$	$-17 \leq l \leq 12$	$-17 \leq l \leq 11$
No. reflections measured	21295	23868	36756
R_{int}	0.066	0.053	0.024
No. unique reflections	2800	2931	3111
No. reflections used in refinement ($F^2 > 0$), NV	2765, 328		3073, 388
R,[a] wR_2,[b] S	0.033, 0.100, 1.649	0.071, -, -	0.018, 0.051, 1.027
Final shift/error$_{max}$	0.002		0.003
$\Delta\rho$ max., min. (e Å^{-3})	0.919, -0.795		0.42, -0.43

[a] $R=\sum||F_o|-|F_c||/\sum|F_o|$ for $F^2 > 2\sigma F^2$. [b] $wR_2=[[\sum w(F_o^2-F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where w = $[\sigma^2(F_o^2) + (pF_o^2)^2]^{-1}$ and p = 0.05 for $[CdL^5](ClO_4)_2$ and 0.04 for $[CdL^7](PF_6)_2$.

absorption using SADABS [15] at the University of Canterbury, New Zealand. Parameters associated with unit cell dimensions, intensity data collection and refinement for the structures are given in Table 1.

The structures were solved by using SIR97 [16], otherwise, computer programs of the XTAL system [17] were used for all calculations. Non-hydrogen atomic coordinates and anisotropic displacement parameters for all atoms were refined by full-matrix least-squares on F2 minimizing $\sum w(|Fo^2|-|Fc^2|)^2$ where w is defined in Table 1. Neutral atom scattering factors with anomalous dispersion corrections were used. All hydrogen atoms were placed at calculated positions

and, although their coordinates and isotropic displacement parameters were not refined, the coordinates were recalculated several times during the refinements. In $[CdL^5](ClO_4)_2$, the perchlorate ion centered on Cl(1) is disordered. This feature was modeled by placing two rigid perchlorate groups on the site and refining a population parameter appropriately constrained for each contributor.

The structure of $[CdL^6](ClO_4)_2$ could not be refined to a satisfactory conclusion. Some displacement ellipsoids indicated large deviations from a mean position and there was major disorder in the perchlorates. The atomic coordinates will not be submitted to the CCDB.

Ab Initio Molecular-Orbital Calculations

A full minimization of the structure of each macrocyclic complex was performed at the *ab initio* HF level of theory using gradient techniques with the Gaussian 98 set of programs [18], on a Pentium-PC computer with a 1400 MHz processor. The effective core potential (ECP) standard basis set LanL2DZ [19], was utilized for cadmium. The full-electron standard basis set 3-21G* [20] was used for all other atoms. A starting semiempirical structure for the *ab initio* calculation, was arrived at by performing a minimization using the HyperChem 5.02 program [21].

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis of the $[CdL^n]^{2+}$ (n = 5, 6, 7) Schiff-base macrocyclic complexes were carried out as shown in Scheme 1 via Cd(II) templated [1+1] cyclocondensation of DAP and the hexaamines ten, ttn, and ttmd, respectively. These three hexaamines constitute dimethylene-, trimethylene- and tetramethylene-linked 1,5-diamino-3-aza pentane units. The complexes were characterized by X-ray crystallography and spectroscopic methods, which will be discussed below. While it is theoretically possible for the hexaamines to condense with DAP to give either linked 12-membered tetraaza macrocycles [22,23], or an X-membered pentaaza macrocycle (X = 15, 16 or 17) with two pendant 2-aminoethyl arms, in practice only products of the second type were observed. These compounds are air stable solids, moderately soluble in CH_3CN and had elemental analyses consistent with the formulations given in Experimental Section.

The infrared spectra of $[CdL^n]^{2+}$ (n = 5, 6, 7) taken in the region 4000-600 cm^{-1} are all very similar and provide some information regarding the bonding in the complexes. The data are consistent with the presence of imine bonds, each complex exhibiting the ν(C=N) mode at 1644-1654 cm^{-1}, which is diagnostic for the Schiff-base condensation, while no bands attributable to C=O groups are detected. The spectra exhibit medium to strong bands at 1587-1594 cm^{-1} as expected for the high energy ring vibrations of the coordinated pyridine. The 3385 cm^{-1} (for PF_6^- salts) assigned to the symmetric and asymmetric NH_2 bonding of the pyridine nitrogen atom is also shown by the presence of the bands at 1012-1019 cm^{-1} and 656-672 cm^{-1} attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively [24]. The presence of unreacted pendant primary amine groups, and hence the non-macrobicyclic nature of the complexes, is evident in the IR spectra by the appearance of two strong peaks at 3276-3364 cm^{-1} (for ClO_4^- salts) and 3320-stretching modes. The IR spectra of perchlorate complexes exhibit a strong absorption band centered at 1077-1091 cm^{-1} suggesting the presence of non-coordinated perchlorate groups. The strong absorption band at 838-842 cm^{-1}, shown by the hexafluorophosphate salts is assigned to P-F stretching mode.

Description of the Crystal Structures

The structure of the cation in $[CdL^5](ClO_4)_2$ and $[CdL^7](PF_6)_2$, determined by single crystal X-ray diffraction, is shown in Figs. 1 and 2, respectively. Selected bond lengths, bond angles and torsion angles are given in Tables 2 and 3. In general terms the geometry of each complex can be considered as that of a distorted pentagonal bipyramid with the metal ion and five nitrogen atoms lying in an approximately pentagonal plane and one of the two 2-aminoethyl nitrogen atoms coordinated at each axial position.

The structures show that in each case the macrocyclic ring is not strictly planar. The deviations from the least-squares plane calculated through Cd and N(2)-N(6) are, for $[CdL^5]^{2+}$, -0.01(2), -0.33(2), 0.35(2), -0.21(2), 0.01(2), 0.22(2) and, for $[CdL^7]^{2+}$, -0.030(1), -0.380(2), 0.517(2), -0.290(2), 0.034(2), 0.275(2), respectively. In both complexes it is noticeable that the two nitrogen atoms to which the pendant arms are attached deviate the most from the plane, and lie on opposite sides of it. This type of distortion provides a means for shortening the pendant amine to metal ion separation over what it otherwise would be. While the Cd-pendant amine distances are the longest of all the Cd-N distances in $[CdL^5]^{2+}$, they are the shortest in $[CdL^7]^{2+}$. This is interesting since in the structures of $[MgL^5]^{2+}$ and $[ZnL^5]^{2+}$ [10], the M-pendant amine l 57 lengths are shorter than those to the ring nitrogen atoms suggesting that the binding cavity presented by the fifteen-membered macrocycle is somewhat smaller than optimum for Cd(II). This is also suggested by the more puckered structure of $[CdL^5]^{2+}$, as indicated by the torsion angles (Table 3), compared to $[CdL^7]^{2+}$. The angle between the CdN_5 plane, and the plane including the metal and the two axial nitrogen atoms is 97° and 93° for $[CdL^5]^{2+}$ and $[CdL^7]^{2+}$, respectively. The pyridine ring forms an angle of 7.1° and 8.2° with the CdN5 plane. As indicated by the torsion angles (Table 3) the two five-membered rings which

Table 2. Selected Bond lengths (Å) and Bond angels (deg) for $[CdL^5]^{2+}$, $[CdL^6]^{2+}$, $[CdL^7]^{2+}$

	$[CdL^5]^{2+}{}_{MO}$[a]	$[CdL^5]^{2+}{}_{XRD}$[b]	$[CdL^6]^{2+}{}_{MO}$	$[CdL^7]^{2+}{}_{MO}$	$[CdL^7]^{2+}{}_{XRD}$
Cd-N(1)	2.497	2.431(12)	2.535	2.357	2.3283(18)
Cd-N(2)	2.333	2.394(12)	2.337	2.585	2.592(2)
Cd-N(3)	2.333	2.399(16)	2.337	2.584	2.497(2)
Cd-N(4)	2.325	2.37(2)	2.349	2.504	2.4570(19)
Cd-N(5)	2.300	2.334(5)	2.318	2.505	2.4560(17)
Cd-N(6)	2.325	2.37(2)	2.348	2.504	2.450(2)
Cd-N(7)	2.497	2.412(11)	2.535	2.357	2.348(2)
C(12)-N(4)	1.262	1.256(9)	1.262	1.263	1.278(3)
C(19)-N(6)	1.262	1.252(10)	1.262	1.263	1.265(3)
N(1)-Cd-N(2)	73.7	73.9(4)	72.7	73.2	72.73(7)
N(1)-Cd-N(3)	111.9	97.7(6)	118.3	109.1	109.91(7)
N(1)-Cd-N(4)	92.0	92.7(7)	94.0	94.3	95.28(6)
N(1)-Cd-N(5)	86.5	96.0(3)	82.5	88.2	93.23(6)
N(1)-Cd-N(6)	85.7	91.8(5)	80.8	84.1	87.30(6)
N(1)-Cd-N(7)	173.1	171.2(4)	165.0	176.4	169.27(7)
N(7)-Cd-N(2)	111.8	100.2(5)	118.3	109.0	97.22(7)
N(7)-Cd-N(3)	73.7	74.3(4)	72.7	73.3	74.10(7)
N(7)-Cd-N(4)	85.6	88.9(5)	80.8	84.1	95.45(7)
N(7)-Cd-N(5)	86.5	92.6(3)	82.5	88.2	91.22(6)
N(7)-Cd-N(6)	92.0	93.0(8)	94.0	94.4	85.72(7)
N(2)-Cd-N(3)	81.2	78.5(4)	94.2	104.6	95.08(7)
N(2)-Cd-N(4)	140.0	147.7(8)	140.2	152.8	156.51(6)
N(2)-Cd-N(5)	139.4	141.0(8)	132.9	127.7	134.11(6)
N(2)-Cd-N(6)	75.2	74.0(6)	72.7	68.4	70.58(7)
N(3)-Cd-N(4)	75.2	74.3(6)	72.7	68.4	69.56(7)
N(3)-Cd-N(5)	139.4	140.5(7)	132.9	127.7	130.45(6)
N(3)-Cd-N(6)	140.1	147.1(7)	140.2	152.8	153.75(7)
N(4)-Cd-N(5)	70.3	68.2(5)	69.8	64.8	65.03(6)
N(4)-Cd-N(6)	140.6	136.9(3)	139.5	129.5	130.22(6)
N(5)-Cd-N(6)	70.3	68.7(6)	69.8	64.8	65.19(6)

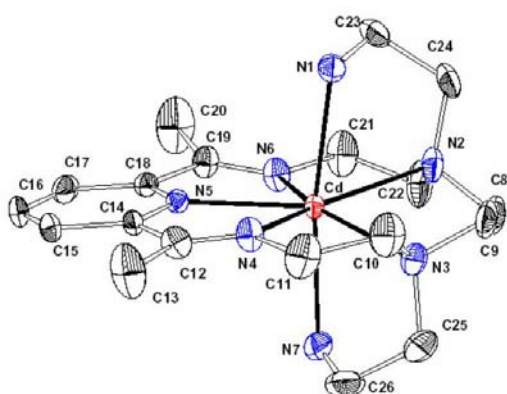[a] MO, *ab initio* gas state calculations. [b] XRD, X-ray diffraction solid state experimental results.

Fig. 1. Structure of the $[CdL^5]^{2+}$ cation. The atoms are drawn with 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.
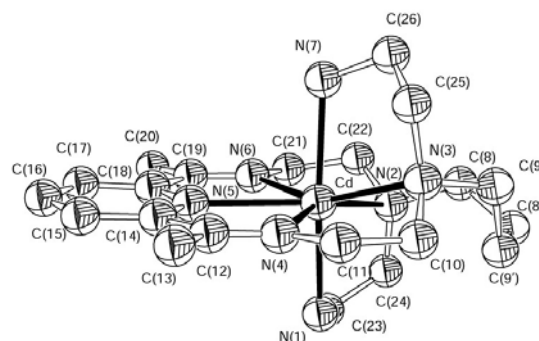

Fig. 2. Structure of the $[CdL^7]^{2+}$ cation. The atoms are drawn with 50% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Torsion Angles (deg) for $[CdL^5]^{2+}$, $[CdL^6]^{2+}$, $[CdL^7]^{2+}$

	$[CdL^5]^{2+}{}_{MO}{}^a$	$[CdL^5]^{2+}{}_{XRD}{}^b$	$[CdL^6]^{2+}{}_{MO}$	$[CdL^7]^{2+}{}_{MO}$	$[CdL^5]^{2+}{}_{XRD}$
Cd-N(2)-C(8)-C(9)	32.8	-44.6(10)	-	-	-
Cd-N(2)-C(8)-C(8')	-	-	57.8	30.8	71.8(3)
Cd-N(2)-C(22)-C(21)	57.2	51.0(8)	57.8	57.6	-53.7(2)
Cd-N(3)-C(9)-C(8)	32.8	-43.3(10)	-	-	-
Cd-N(3)-C(9)-C(8')	-	-	57.9	-	-
Cd-N(3)-C(9)-C(9')	-	-	-	30.8	-44.1(3)
Cd-N(3)-C(10)-C(11)	57.2	52.2(8)	57.8	57.5	-54.0(2)
Cd-N(4)-C(11)-C(10)	4.4	14.4(13)	-3.9	1.7	-8.1(3)
Cd-N(4)-C(12)-C(14)	-1.2	-8.4(12)	-0.8	0.5	4.7(3)
Cd-N(5)-C(14)-C(12)	-0.6	4.5(12)	-0.7	-1.1	-0.5(2)
Cd-N(5)-C(18)-C(19)	-0.6	-6.4(11)	-0.7	-1.1	3.6(2)
Cd-N(6)-C(21)-C(22)	4.3	19.0(13)	-3.9	1.7	-17.9(2)
Cd-N(6)-C(19)-C(18)	-1.3	-12.6(14)	-0.8	0.5	4.2(3)
N(2)-C(8)-C(9)-N(3)	-47.6	64.9(9)	-	-	-
N(2)-C(8)-C(8')-C(9)	-	-	-35.8	-	-
N(2)-C(8)-C(8')-C(9')	-	-	-	-89.0	-53.5(4)
N(2)-C(22)-C(21)-N(6)	-43.3	-48.8(12)	-37.1	-42.4	51.6(3)
N(3)-C(9)-C(8')-C(8)	-	-	-35.9	-	-
N(3)-C(9)-C(9')-C(8')	-	-	-	-88.9	119.5(3)
N(3)-C(10)-C(11)-N(4)	-43.3	-47.0(12)	-37.1	-42.4	43.6(3)
N(4)-C(12)-C(14)-N(5)	1.2	2.6(14)	1.0	0.4	-2.6(3)
N(6)-C(19)-C(18)-N(5)	1.3	12.6(15)	1.1	0.4	-5.1(3)

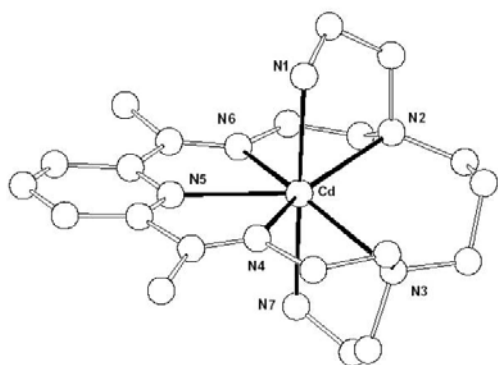^{a} MO, *ab initio* gas state calculations. ^{b} XRD, X-ray diffraction solid state experimental results.

Fig. 3. Structure of the $[CdL^6]^{2+}$ cation. The atoms are drawn as arbitrary spheres. Hydrogen atoms are omitted for clarity.

include the imine bonds are closer to planarity in $[CdL^7]^{2+}$ than in $[CdL^5]^{2+}$, the small deviations in the planarity of these two rings are probably due to the puckered configuration of the adjacent five-membered rings and the effect of the metal interaction with the imine nitrogen lone pairs [25].

Although the crystal structure of $[CdL^6](ClO_4)_2$ could not be refined to publication standard, the general features of the molecule were obvious from the direct methods solutions (Fig. 3). The structure of the $[CdL^6]^{2+}$ ion is similar to the other cations with the two 2-aminoethyl pendant arms bonded trans to the pentagonal plane. The six-membered chelate ring is in the strained half-chair conformation which arises as a consequence of positioning the two pendant arms on opposite sides of the macrocyclic plane. The accuracy of the atomic coordinates does not warrant further discussion of the structura details.

NMR Studies

The NMR data for all complexes at ambient temperature in CD_3CN are consistent with the macrocycle adopting a solution conformation similar to that indicated by the solid state study. Hydrogen and carbon atoms were assigned by APT, COSY(H,H) and HETCOR(H,C) techniques (Chart 2). The chemical shift assignments are summarised in Table 4.

For all three complexes, only a single ^1H methyl resonance, appearing as a triplet at ca 2.50 ppm, is observed. This demonstrates the equivalence of the two

methyl environments. The triplet, which simplified to a singlet after irradiation of the resonance at ca 3.80 ppm, is a result of long range coupling with the methylene group adjacent to imino nitrogen atom ($^5J_{He-Hf} \approx 1.20$ H$_z$). The ^{1}H NMR spectra of [CdL^5]$^{2+}$ shows a doublet of doublet (8.36 ppm) and a doublet (8.24 ppm) assigned to the para-(H$_a$) and meta-(H$_b$) pyridyl protons respectively ($^3J_{Ha-Hb} \approx 7.85$ H$_z$). A broad singlet at 1.85 ppm is assigned to the NH$_2$ groups on the basis of the deuterium exchange noted when D$_2$O was added to the CD$_3$CN solution. The complex nature of the resonances arising from the aliphatic regions of the molecules most likely stems from magnetic inequivalence of the geminal hydrogen pairs caused by restricted rotation about the C-C bonds, which strongly suggests that coordination of the primary amine nitrogen atoms to the Cd(II) ion is retained in solution [26,27].

While the ^{1}H NMR spectra of the pyridine region of [CdL^6]$^{2+}$ and [CdL^7]$^{2+}$ are similar to [CdL^5]$^{2+}$, the aliphatic regions are more complicated. The protons of the ethyl regions of macrocyclic ring and pendant arms give rise to some multiplets (Table 4), but the close similarity of many of the geminal H$_\alpha$ and H$_\beta$ chemical shifts leads to multiple overlaps of signals. The ^{13}C spectra are more informative [CdL^7]$^{2+}$ and are consistent with all complexes having the twofold symmetry axis that is closely approximated in the solid state, although they do not exclude the possibility N of planar structures with neither of the pendant donors coordinated.

These observations are similar to the previous observations reported for the corresponding Zn(II) and Mg(II) complexes [9] and are in agreement with the complexes having pentagonal bipyramidal geometry in solution. The proposed coupling relationships shown in Table 4 have been corroborated by the ^{1}H-^{1}H two dimensional correlation (COSY) NMR spectra. The 2D HETCOR and COSY(H,H) spectra of [CdL^5]$^{2+}$ are shown in Fig. 4.

Ab Initio Modelling Studies

As we were unable to prepare a crystal containing the [CdL^6]$^{2+}$ cation suitable for completely satisfactory X-ray diffraction work, we chose to assess its structural parameters by undertaking *ab initio* molecular orbital calculations. To do this, we assumed that the same mode of [1+1] cyclization as found for [CdL^5]$^{2+}$ and [CdL^7]$^{2+}$ had occurred, and undertook a full geometry optimization at the HF/3-21G* level of theory, using LanL2DZ basis set for Cd. We also undertook the same level of *ab initio* calculations for [CdL^5]$^{2+}$ and
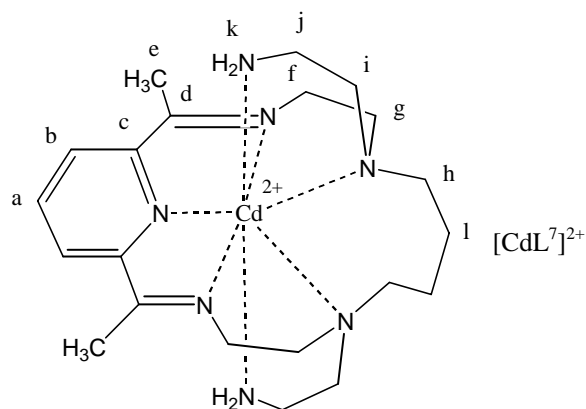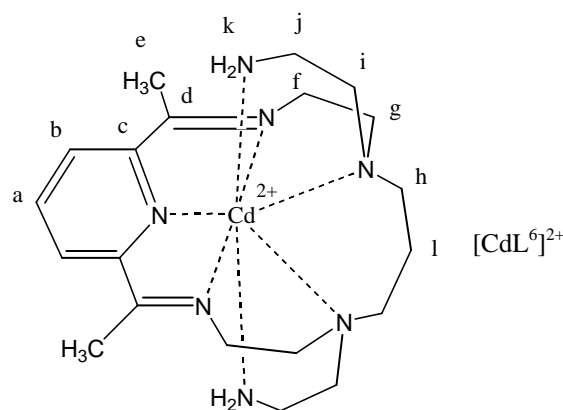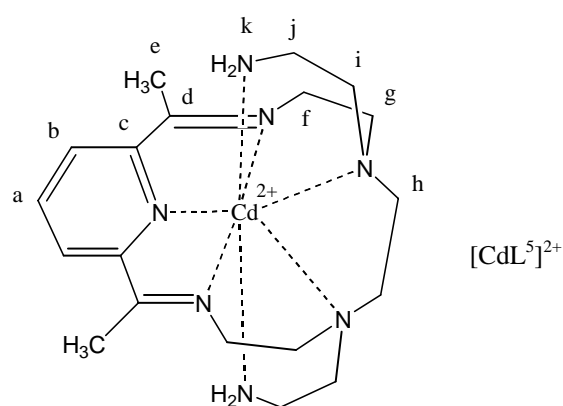

[CdL^5]$^{2+}$

[CdL^6]$^{2+}$

[CdL^7]$^{2+}$

Chart 2

Table 4. ^{1}H NMR and ^{13}C{H} NMR spectral assignments for $[CdL^5]^{2+}$, $[CdL^6]^{2+}$ and $[CdL^7]^{2+}$ recorded at 300 MHz in CD_3CN.

Hydrogen atom	δ_H (ppm)	J/Hz	Carbon atom	δ_C
$[CdL^5]^{2+}$				
H_a(1H)	8.36(dd)	^3J (H_a, H_b)≈7.85	C_a(1C)	142.6
H_b(2H)	8.24(d)	^3J (H_a, H_b)≈7.85	C_b(2C)	125.4
H_e(6H)	2.50(t)	^5J (H_e, H_f)≈1.16	C_c(2C)	148.6
$H_{f\alpha}$(2H)	3.85(m)		C_d(2C)	165.8
$H_{f\beta}$(2H)	3.71(m)		C_e(2C)	15.7
$H_{g\alpha}$, $H_{g\beta}$(4H)	3.30-3.15(m)		C_f(2C)	46.7
$H_{h\alpha}$, $H_{h\beta}$, $H_{j\alpha}$, $H_{i\alpha}$, $H_{i\beta}$(10H)	2.95-2.70(m)		C_g(2C)	58.5
$H_{j\beta}$(2H)	2.40(m)		C_h(2C)	57.2
H_k(4H)	1.85(br)		C_i(2C)	53.8
			C_j(2C)	39.5
$[CdL^6]^{2+}$				
H_a(1H)	8.32(dd)	^3J (H_a, H_b)≈7.90	C_a(1C)	142.2
H_b(2H)	8.21(d)	^3J (H_a, H_b)≈7.90	C_b(2C)	125.3
H_e(6H)	2.50(t)	^5J (H_e, H_f)≈1.20	C_c(2C)	149.0
$H_{f\alpha}$, $H_{f\beta}$(4H)	3.83-3.79(m)		C_d(2C)	166.5
$H_{g\alpha}$(2H)	3.50(m)		C_e(2C)	15.8
$H_{h\alpha}$, $H_{h\beta}$(4H)	3.05-2.81(qt)		C_f(2C)	45.9
$H_{g\beta}$, $H_{i\alpha}$, $H_{j\alpha}$, $H_{j\beta}$(8H)	2.80-2.53(m)		C_g(2C)	56.4
$H_{i\beta}$(2H)	2.43(m)		C_h(2C)	61.2
H_l(2H)	1.87(qu)	^3J (H_h, H_l)≈ 4.50	C_i(2C)	52.6
H_k(4H)	2.32(br)		C_j(2C)	38.3
			C_l(1C)	24.9
$[CdL^7]^{2+}$				
H_a(1H)	8.31(dd)	^3J (H_a, H_b)≈8.0	C_a(1C)	142.1
H_b(2H)	8.21(d)	^3J (H_a, H_b)≈8.0	C_b(2C)	125.5
H_e(6H)	2.49(t)	^5J (H_f, H_e)≈1.20	C_c(2C)	149.5
$H_{f\alpha}$(2H)	3.81(m)		C_d(2C)	167.2
$H_{f\beta}$(2H)	3.77(m)		C_e(2C)	15.9
$H_{g\alpha}$(2H)	3.44(m)		C_f(2C)	46.3
$H_{g\beta}$, $H_{h\alpha}$, $H_{h\beta}$, $H_{j\alpha}$, $H_{j\beta}$, $H_{i\alpha}$(12H)	2.81-2.58(m)		C_g(2C)	55.2
$H_{i\beta}$(2H)	2.40(m)		C_h(2C)	53.4
$H_{l\alpha}$(2H)	1.98(m)		C_i(2C)	50.2
$H_{l\beta}$(2H)	1.70(m)		C_j(2C)	38.0
H_k(4H)	2.31(br)		C_l(2C)	24.1

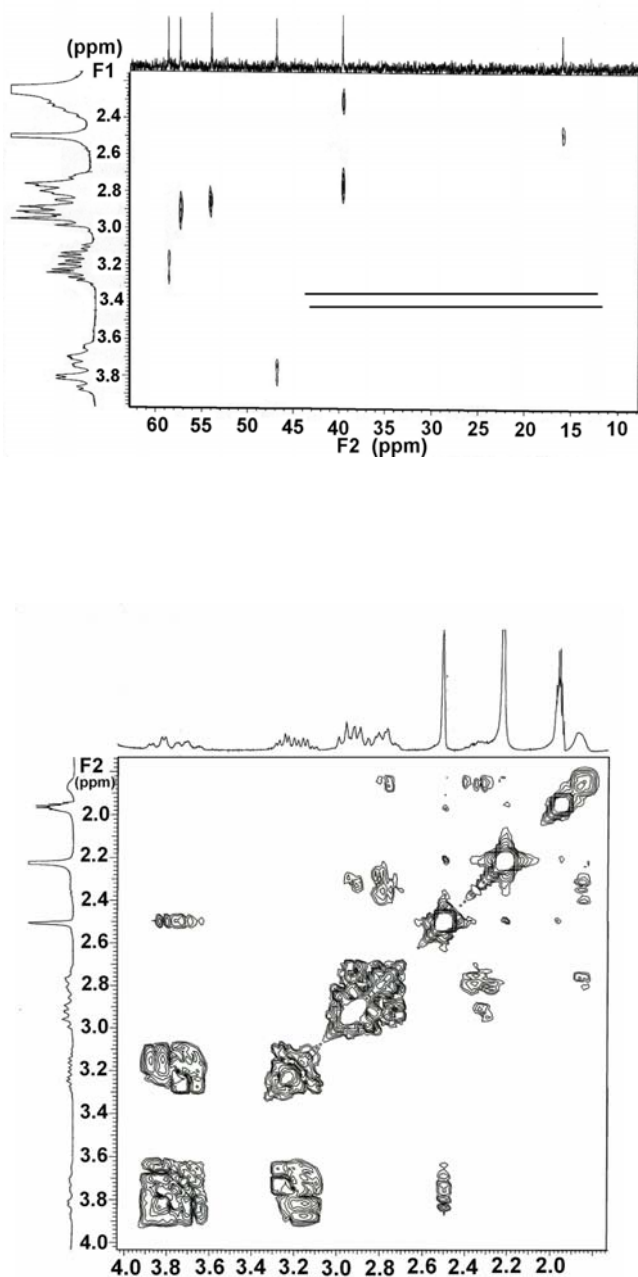d, doublet; t, triplet; qt, quartet of triplet; qu, quintet; m, multiplet

Fig. 4. 2D HETCOR(H,C) (upper) and COSY(H,H) (lower) spectra of the aliphatic region of $[CdL^5]^{2+}$ in CD_3CN.

$[CdL^7]^{2+}$ to observe the comparability of the predicted gas phase structure with that seen in the solid state.

For all three complexes, the calculations predicted

structures with C2 symmetry as shown in Fig. 5, with bond lengths and angles broadly in agreement with those determined for the solid state. Selected calculated bond distances, angles and torsion angles for the three complexes are presented in Tables 2 and 3.

Interestingly, of the three complexes, $[CdL^6]^{2+}$ is predicted to have the longest pendant nitrogen to Cd(II) distance and the N(1)-Cd-N(7) alignment the least linear. This is despite the fact that the planar region of the six-membered chelate ring achieves the greatest angular rotation with respect to the remainder of the molecule, 29°, P.C. Hellier, P.D. Hempstead, J.M. Latour, J. Chem. compared to the other two complexes (22° and 24° for $[CdL^5]^{2+}$ and $[CdL^7]^{2+}$, respectively). This suggests that the six-membered chelate ring is the least accommodating of the three chelate ring sizes in terms of allowing the pendant nitrogen to Cd(II) ion interaction to optimize, and in situations where a labile pendant amine is desired this would be the molecular arrangement of choice.

CONCLUSION

Cd(II) is effective as a template for the Schiff-base condensation of DAP with three hexaamine ligands yielding heptaaza macrocyclic complexes based on the [X]pydieneN$_5$ rings (X = 15, 16, 17). Five-membered chelate rings adjacent to the pyridine head unit are common in all the complexes. It appears that this arrangement causes stability of the ternary complex precursor and partially condensed intermediates, which facilitate cyclization of the complex resulting in the pentagonal bipyramidal environment for the metal ion. Thus, the size of the metal ion may not be the only factor determining the success of the cyclization reaction.
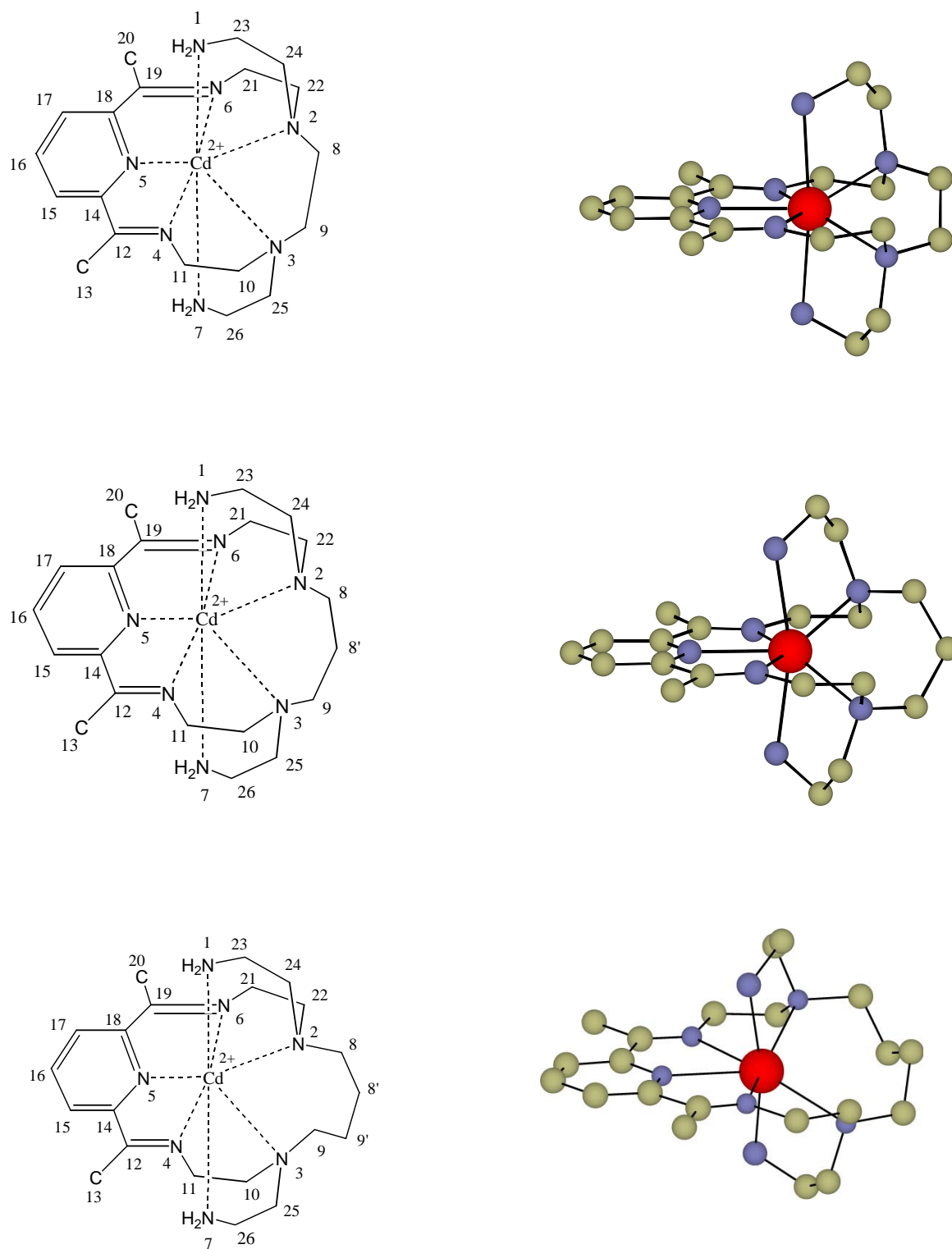
ACKNOWLEDGMENTS

Fig. 5. The *ab initio* optimized structures of the cations.

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