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Syntheses and structural characterization of cadmium complexes constructed from a tetrakis(3-pyridylmethyl) functionalized ligand

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A functionalized ligand (L = 1,4,8,11-tetrakis(3-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) was synthesized by the reaction of 1,4,8,11-tetraazacyclotetradecane (*cyclam*, L¹) with 3-(chloromethyl)pyridine hydrochloride. Hydrothermal reactions between L and two Cd(II) salts (nitrate or chloride) led to the formation of [CdCl₂(μ_4 -4(pyridyl)L)]_n (1) and [Cd(μ -ONO₂)₂(μ_4 -4(pyridyl)L)]_n (2), which were characterized by elemental analysis and single-crystal X-ray diffraction. In 1, Cd is six-coordinate, with a CdN₄Cl₂ octahedral coordination environment forming two metallamacrocycles with the functionalized *cyclam*. In the structure of 2, the metal possesses a distorted CdN₄O₂ octahedral coordination geometry, also presenting two metallamacrocycles. In both structures, the ligand does not chelate, but forms extended polymeric structures.

Keywords: Cadmium complex; Functionalization; Metallamacrocycle; Hydrothermal method

1. Introduction

Functionalized by several groups, such as cyanoethyl [1–7], prop-2-ynyl [8–10], phosphanylmethyl [11–13], carbonylmethyl [14–21], carboxyethyl [22, 23], and heterocyclic groups, such as pyridylmethyl [24-27], bipyridyl [28], terpyridyl [29, 30], and acridinylmethyl [31, 32], or even two different chemical groups at one ligand, such as (phenanthrol-2-yl)methyl and carboxy-methyl [33], pyridylmethyl and carboxyl-methyl carboxylmethyl [35], [34]. phosphanylmethyl and (t-butoxycarbonyl) and (bis(2-pyridylmethyl)aminomethyl)-2-pyridylmethyl [36], and (morpholino-2-pyridyl)methyl and carboxylmethyl [37] on the secondary N-sites, macrocyclic and macrobicyclic compounds show novel properties in coordination, electro-, photoluminescent, and catalytic chemistry. Hence, this study aims to prepare functionalized macrocyclic and macrobicyclic complexes constructed from functionalized polyaza ligands and to investigate their coordination behavior. In this article, we report a new

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tetrafunctionalized octadentate ligand L and structures of cadmium polymeric metallamacrocyclic complexes, $[CdCl_2(\mu_4-4(pyridyl)L)]_n$ (1) and $[Cd(\mu-ONO_2)_2(\mu_4-4(pyridyl)L)]_n$ (2) (L = 1,4,8,11-tetrakis(3-pyridylmethyl)-1,4,8,11-tetraazacyclote-tradecane), which were obtained by hydrothermal methods.

2. Experimental

2.1. Instrumentation and reagents

¹H-NMR spectra were run on a Varian Unity 500 spectrometer. Elemental analyses were determined with an Elementar Vario EL III Elemental Analyser. IR spectra were measured with a Perkin-Elmer Spectrum 2000 in KBr pellets. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ Mass Spectrometer using dichloromethane–methanol as the mobile phase. All reagents used in the experiments were of analytical grade or purified by standard methods.

2.2. Syntheses

2.2.1. 1,4,8,11-Tetrakis(3-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (L). The synthetic process of this ligand is similar to that of the literature [24–26] and references cited therein. The one difference is that 2-(chloromethyl)pyridine hydrochloride or 4-(chloromethyl)pyridine hydrochloride was substituted by 3-(chloromethyl)pyridine hydrochloride. Yield of the ligand is 36%; m. p. 157–159°C. Anal. Calcd for $C_{34}H_{44}N_8$ (%): C, 72.30; H, 7.85; and N, 19.84. Found: C, 72.05; H, 7.95; and N, 19.58. The ¹H-NMR data δ (500 MHz, CDCl₃, 25°C) 1.74 (t, 4H, a), 2.46 (t, 8H, b), 2.57 (s, 8H, c), 3.38 (s, 8H, -CH₂-pyr), 7.17 (m, 4H, aryl), 7.58 (d, 4H, aryl), 8.45 (m, 4H, aryl), 8.48 (s, 4H, aryl). EI–MS (*m*/*z*): 566.6, 565.8 (100%), and 243.5. IR (KBr disk) (cm⁻¹): 3027 (m), 2952 (s, br), 2796 (vs), 1577 (s), 1474 (s), 1453 (m), 1426 (vs), 1365 (m), 1338 (m), 1319 (m), 1280 (m), 1251 (m), 1190 (m), 1159 (m), 794 (s), 775 (m), 717 (s), and 621 (m).

2.2.2. Synthesis of $[CdCl_2L]_n$ (1). A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.036 g, 0.16 mmol), L (0.030 g, 0.053 mmol), $Na_2C_4H_4O_6 \cdot 2H_2O$ (0.012 g, 0.052 mmol) and distilled water (20 mL) was sealed in a 25-mL stainless reactor with a Teflon liner and heated at 110°C for 3 days. Colorless crystals of 1 were isolated by mechanical separation from a mixture of 1 and unidentified white powder. The yield of 1 was *ca* 39% (15.5 mg) based on the ligand. Anal. Calcd for $[CdCl_2C_{34}H_{44}N_8]$ (%): C, 54.53; H, 5.93; and N, 14.97. Found: C, 54.29; H, 5.90; and N, 14.58.

2.2.3. Synthesis of $[Cd(NO_3)_2L]_n$ (2). A mixture of $Cd(NO_3)_2 \cdot 2.5H_2O$ (0.044 g, 0.14 mmol), L (0.040 g, 0.071 mmol), $Na_3C_6H_5O_7 \cdot 2H_2O$ (0.011 g, 0.037 mmol), and distilled water (20 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated at 110°C for 3 days. Colorless crystals of 2 were isolated by mechanical separation from a mixture of 2 and unidentified white powder. The yield of 2 was

ca 22% (12.7 mg) based on the ligand. Anal. Calcd for $[Cd(NO_3)_2C_{34}H_{44}N_8]$ (%): C, 50.97; H, 5.54; N, 17.48. Found: C, 51.29; H, 5.82; N, 17.61.

2.3. Crystal structure determinations

The single crystals of L, 1 and 2 were obtained as indicated above. The crystals with dimensions $0.72 \times 0.32 \times 0.31$, $0.79 \times 0.65 \times 0.35$, $0.53 \times 0.41 \times 0.36$ for L, 1 and 2 were mounted on glass fibers. Intensity data sets were collected on a Rigaku R-AXIS RAPID Weissenberg IP diffractometer or Rigaku Mercury-CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the ω scan mode at room temperature or at 130 K. Data reduction was made and ψ empirical absorption corrections carried out [38]. Structures were solved by direct methods using the SHELXS-97 package [39] and refined with SHELXL-97. All hydrogens were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for hydrogens were employed.

3. Results and discussion

The ligand (L) was synthesized by the reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam, L¹) with 3-pyridylmethyl chloride hydrochloride according to a previously reported procedure (figure 1) [24–26]; it belongs to the class of octaazamacrocyclic ligands derived from *cyclam*. The ligand has been characterized by elemental analyses, IR, NMR spectroscopy, EI-MS spectrometry, and X-ray diffraction analysis. The ¹H-NMR and IR spectra of L confirmed the integrity of the ligand and its stability in solution and solid state, showing that the four quadrants of the macrocyclic ligand are chemically equivalent, as one would expect with this kind of system. In the EI-MS spectrum, there are three m/z peaks, two molecular ion peaks at 566.6 and 565.8 (100%);another one typical fragment 243.5 for is its at $[NH(CH_2C_5H_4N)CH_2CH_2NH_2(CH_2C_5H_4N)]^+$. The structure of the ligand is shown in figure 2. The crystallographic summary is given in table 1 and selected bond lengths and angles are in table 2. There is a unique ligand in the asymmetric unit of the triclinic unit cell. The pseudocenter of the ligand is located at (0.25, 0.5, 0.25) with respect to the crystallographic centers. Bond lengths and angles determined for the structure fall within the normal ranges. The average bond length of the carbons and tertiary



Figure 1. Schematic diagram of ligand L and its coordination conformations in the three structures.



Figure 2. The molecular structure of the ligand.

nitrogens at cyclam is 1.468(2) Å and 1.335(2) Å for carbons and nitrogens at the four pyridyl groups. In its structure, the 14-membered tetraazamacrocyclic ring adopts a [34] conformation [40] with an RSSR pattern of chiralities at the nitrogens (the trans-IV configuration of Bosnich, Poon, and Tobe classification [41]). The four nitrogens of *cyclam* are nearly coplanar (with RMS deviation 0.0670), forming a parallelogram with the four nitrogens occupying the four corners of it with distances between every two nitrogens of 3.761(2) Å (N1-N2), 5.911(2) Å (N1-N3), 4.390(2) Å (N1-N4), 4.324(2) Å (N2-N3), 5.599(2)Å (N2-N4), and 3.774(2)Å (N3-N4), respectively. The four nitrogens of the four pyridyl groups are also nearly coplanar (with RMS deviation 0.3072), forming another parallelogram with the four nitrogens occupying the four corners of it by distances between these nitrogens being 9.096(2) Å (N5-N6), 13.659(2) Å (N5–N7), 10.052(2) Å (N5–N8), 9.252(2) Å (N6–N7), 12.235(2) Å (N6-N8), and 8.336(2)Å (N7-N8), respectively. Since the pyridine substituents are arrayed up, up, down, down, rather than alternating around the central macrocycle, the N4 plane (pyridines) is sharply tilted with respect to the N4 plane (macrocycle). The geometry is exodentate, assumed from these values according to the literature [40], with the nitrogens occupying positions around the perimeter of the macrocyclic skeleton.

When L was used in hydrothermal reactions to react with cadmium salts, 1 and 2 were isolated, in which the ligand connects the central ions, constructing 2-D polymeric metallamacrocyclic complexes with a conformation (η^1 – μ_4 , L^{a1}) with four pendant pyridyl groups coordinated to cadmium as shown in figures 3 and 4. Tables 1, 3, and 4 are the crystal data, selected bond lengths (Å) and angles (°) of the two complexes.

Compounds	L	1	2
Empirical formula	C34H44N8	C34H44CdCl2N8	C34H44CdN10O6
Formula weight	564.77	748.07	801.20
Temperature (K)	298	130	130
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	P2(1)/c	P2(1)/c
X-ray machine	Weissenberg IP	Mercury-CCD	Mercury-CCD
Unit cell dimensions (Å, °)	e	5	2
a	6.1908(5)	14.034(3)	13.482(3)
b	11.938 (1)	9.487(2)	9.491(2)
С	21.578(2)	14.579(3)	15.441(6)
α.	91,670(4)	90	90
ß	92.354(3)	118.29(3)	112.69(3)
r γ	92.680(5)	90	90
Volume (Å ³), Z	1590.8(2), 2	1709.1(6), 2	1693.9(8), 2
Calculated density (Mam $^{-3}$)	1 179	1 454	1 571
Absorption coefficient μ (mm ⁻¹)	0.072	0.832	0.707
F(000)	608	0.832	828
$\Gamma(000)$	$0.72 \times 0.32 \times 0.31$	$0.79 \times 0.65 \times 0.35$	$0.53 \times 0.41 \times 0.36$
(1) (1)	$0.72 \times 0.52 \times 0.51$	$0.79 \times 0.03 \times 0.33$	$0.33 \times 0.41 \times 0.30$
$U_{\text{max}}, U_{\text{min}}$	2/.40, 1.09 9 < h < 9	27.40, 2.07 18 $- h - 15$	27.75, 5.00 17 - h - 17
Limiting indices n	$-6 \le h \le 6$, $0 \le k \le 15$	$-10 \le n \le 10$, $12 \le k \le 11$;	$-17 \le n \le 17$, $12 \le k \le 12$;
	$-0 \le k \le 13$, 27 < l < 27	$-12 \le k \le 11$, $18 \le l \le 18$	$-12 \le k \le 12$, $20 \le l \le 18$
	$-21 \leq l \leq 21$	$-10 \leq l \leq 10$	$-20 \le l \le 18$
	(002	2077	20.40
Number of independent	5120	38//	3940
Number of observed	5139	3720	3491
Number of variables $C = 1$	380	205	232
Goodness-of-fit on F^-	1.003	1.015	1.028 D 0.0204
Final R indices	$R_1 = 0.04/1,$	$K_1 = 0.0269,$	$K_1 = 0.0394,$
	$wR_2 = 0.1239$	$wR_2 = 0.07/6$	$wR_2 = 0.1018$
Largest difference peak and hole (Δa) (e \mathring{A}^{-3})	0.213 and (-0.152)	1.217 and (-0.634)	0.736 and (-0.497)
CCDC number	797027	797028	797029

Table 1. Crystal data of the ligand and complexes.

Table 2. Selected bond lengths (Å) and angles (°) of the ligand.

N(1)-C(9)	1.464(2)	N(1)-C(13)	1.471(2)	N(1)–C(5)	1.477(2)
N(2)-C(27)	1.461(2)	N(2)-C(10)	1.465(2)	N(2)-C(11)	1.472(2)
N(3)-C(19)	1.466(2)	N(3)-C(20)	1.471(2)	N(3)-C(29)	1.472(2)
N(4)-C(16)	1.463(2)	N(4) - C(21)	1.467(2)	N(4) - C(18)	1.468(2)
N(5)-C(35)	1.329(2)	N(5)-C(22)	1.338(2)	N(8)-C(23)	1.338(2)
N(8)-C(38)	1.338(2)	N(6)-C(26)	1.332(2)	N(6) - C(42)	1.332(2)
C(30)–N(7)	1.338(2)	N(7)-C(37)	1.332(2)		
C(9)-N(1)-C(13)		111.7(1)	C(9)–N(1)–C	C(5)	111.7(1)
C(13)–N(1)–C(5)		113.4(1)	C(27)–N(2)–C	C(10)	112.1(1)
C(27)–N(2)–C(11)		111.8(1)	C(10)–N(2)–C	C(11)	113.6(1)
C(35)-N(5)-C(22)		116.6(1)	C(26)-N(6)-C	C(42)	116.6(1)



Figure 3. The molecular structure of 1.

In the structure of 1 (figure 3), there is a crystallographically independent cadmium and both the Cd ions and central macrocycles lie on inversion centers in the crystals. The cadmium is coordinated by four nitrogens from four pyridyl groups from four neighboring L and two chlorides in a slightly distorted CdN₄Cl₂ octahedral geometry [bond angle range for N-Cd-N or Cl-Cd-N is 88.04(5)-91.96(5)°]. The maximum deviation of these angles from the ideal value of 90° is 1.96° . The two chlorides occupy the two apical positions and the basal plane is comprised of four nitrogens. The average bond length of Cd-N is 2.387 Å. L shows only one conformation with four pendant pyridyl groups coordinated to the four cadmium ions and it functions as a tetradentate ligand with a coordination mode $(\eta^1 - \mu_4, L^{a1})$. This conformation results in a 2-D structure as a polymeric metallamacrocyclic complex. With differences of the four carbon strands at cyclam (3C-2C-3C-2C), the basic units of this structure are two dinuclear metallamacrocycles, where one is a 26-membered (type A) structure and the other a 28-membered one (type B) (figure 3). The distances between every cadmium and its eight neighboring cadmiums are 9.487, 9.487, 14.034, 14.034, 16.940, 16.940, 16.940 and 16.940 Å, respectively. The four cadmium central ions are coordinated by one ligand to form a parallelogram-geometry with the lengths of two sides being 14.034 and 9.487 Å and those of the two diagonals being 16.940 and 16.940 Å. The metallamacrocycles are further extended into a 2-D planar structure by sharing the cadmium ions with the four ligands. No substitution between chloride and citrate occurred under this hydrothermal condition. The structure does not include guest waters, although the crystals were obtained in water.

A cadmium structure, obtained by a hydrothermal method with $CdCl_2 \cdot 2.5H_2O$ and $Na_3C_6H_5O_7 \cdot 2H_2O$ with 1,4,8,11-tetrakis(4-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, functionalized on *cyclam* with 4-(chloromethyl)pyridine, was reported



Figure 4. The molecular structure of 2.

Table 3. Selected bond lengths (Å) and angles (°) of 1.

Cd(1)–N(5)	2.341(2)	Cd(1)–N(6)	2.432(2)	Cd(1)-Cl(1)	2.6490(7)
N(5)-Cd(1)-N(5A)	180.0		N(5)-Cd(1)-N(6A)	88.04(5)	
N(5A)-Cd(1)-N(6A)	91.96	(5)	N(5)-Cd(1)-N(6)	91.96(5)	
N(5A)-Cd(1)-N(6)	88.04	5)	N(6A)-Cd(1)-N(6)	180.00(7)	
N(5)-Cd(1)-Cl(1)	88.73	4)	N(5A)-Cd(1)-Cl(1)	91.27(4)	
N(6A)-Cd(1)-Cl(1)	88.80	4)	N(6)-Cd(1)-Cl(1)	91.20(4)	
N(5)-Cd(1)-Cl(1A)	91.27	4)	N(5A)-Cd(1)-Cl(1A)	88.73(4)	
N(6A)-Cd(1)-Cl(1A)	91.20	4)	N(6)-Cd(1)-Cl(1A)	88.80(4)	
Cl(1)-Cd(1)-Cl(1A)	180.00((3)			

Symmetry transformations used to generate equivalent atoms: A-x, -y-1, -z.

Table 4. Selected	bond	lengths	(A)	and	angles	(°)	of 2	2.
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Cd(1)–N(1)	2.317(2)	Cd(1)–N(3)	2.303(2)	Cd(1)–O(2)	2.338(2)
N(3A)-Cd(1)-N(3)	180.0		N(3)-Cd(1)-N(1A) 89.36(8)	
N(3)-Cd(1)-N(1)	90.64(8)		N(1A)-Cd(1)-N(1) 180.00(5)	
N(3A)-Cd(1)-O(2)	92.07(7)		N(3)-Cd(1)-O(2)	87.93(7)	
N(1A)-Cd(1)-O(2)	88.09(8)		N(1)-Cd(1)-O(2)	91.91(8)	
O(2A)-Cd(1)-O(2)	180.00(8)				

Symmetry transformations used to generate equivalent atoms: A-x, -y+1, -z.

[26]. In the reported structure, L shows only one conformation with two pendant pyridyl groups coordinated to cadmium and the other two being free $(\eta^1 - \mu_2)$, completely different from 1. The average bond length of the Cd-N in the reported complex (2.372(3) Å) is little shorter than that in 1 (2.387(2) Å), but the bond length of Cd–Cl (2.6594(7))Å is a little longer than that in 1 (2.6490(7)Å). Several structures of metal complexes with another similar ligand, which was functionalized on *cyclam* with 2-(chloromethyl)pyridine, were also reported [42–45]. All these compounds are monoor dinuclear compounds without metallamacropolymer obtained. The variations of these structures are caused by the difference of ligands, although they are tetra-2-pyridylmethyl, isomers (functionalized by tetra-3-pyridylmethyl or tetra-4-pyridylmethyl, respectively).

Complex 2 was obtained from the reaction of $Cd(NO_3)_2 \cdot 2.5H_2O$, L and $Na_3C_6H_5O_7 \cdot 2H_2O$ under hydrothermal conditions. In its structure (figure 4), there is an independent cadmium in the asymmetric unit cell and the Cd ions and central macrocycles also lie on inversion centers in the crystals. Each cadmium is coordinated by four nitrogens from the four pyridyl groups of $L^{a1}(\eta^1-\mu_4)$ and two oxygen donors from two nitrates in a slightly distorted octahedral geometry. The N-Cd-N or O-Cd-N angles in this distorted CdN_4O_2 octahedron deviate by a maximum of 2.07° from the ideal value of 90° as a consequence of the structure of the ligands and the range of these angles is $87.93(5)-92.07(5)^{\circ}$. In comparison with 1, the average bond length of the Cd–N (2.310(2) Å) is much shorter and the polymer with NO_3^- has a slightly different structure (more distorted and different bond lengths, see tables 3 and 4), resulting from the variation of the second ligand from Cl^- to NO_3^- . The phenomenon might be caused by the difference of the coordination abilities of NO₃⁻ and Cl⁻ to cadmium or the difference of the volumes of NO₃ and Cl⁻. Distances of cadmium ion and its eight neighboring cadmium ions are 9.491, 9.491, 14.349, 14.349, 17.204, 17.204, 17.204 and 17.204 Å, respectively. The parallelogram-geometry in this structure formed by the four cadmium atoms coordinated by one ligand is seen with the lengths of the two sides being 14.349 and 9.491 Å and those of two diagonals being 17.204 and 17.204 Å, respectively. Similar to that in 1, the basic units of this structure are also two dinuclear 26-membered (type A) and 28-membered metallamacrocycles (type B) and they are also further extended into a planar structure by sharing the cadmium ions of the ligands. Like 1, this structure also does not have water, although the crystals were obtained in water. The result shows that no crystal coordinated by a carboxylate was obtained in this reaction, unlike a structure obtained under similar hydrothermal conditions [26]. In that structure, the cadmium ions are coordinated not only by the functionalized ligands but also by citrates, which act as the second ligands [26], with formula $[Cd_{3}L_{1.5}(C_{6}H_{5}O_{7})_{2} \cdot 6H_{2}O]$ (L = 1,4,8,11-tetrakis(4-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane), giving an interesting structure composed of seven metallacycle units. The polymer with NO_3^- has a slightly different structure (more distorted and different bond lengths) compared to that of Cl⁻.

In conclusion, a new ligand functionalized on *cyclam* by 3-(chloromethyl)pyridine was synthesized. The ligand is a convenient N,N,N,N-tetrapodal ligand with easy synthesis of cadmium complexes with interesting structures. Two cadmium polymeric metallamacrocyclic complexes have been prepared from the functionalized ligand by a hydrothermal reaction with two cadmium salts. In both structures, the ligand does not chelate, but forms extended polymeric structures with Cd. Further studies of the ligand and other metal ions, especially transition metal ions and their properties, such as molar

conductance, electrochemistry, catalysis, or photoluminescence, are underway and will be reported in the future.

Supplementary Material

CCDC 797027–797029 contain the supplementary crystallographic data for this article. 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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