Two Novel Cadmium Polymeric Metallamacrocyclic Complexes Constructed from a Pyridylmethyl-Functionalized Tetraaza Ligand

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A new octadentate ligand L was synthesized by tetrafunctionalization of 1,4,8,11-tetraazacyclotetradecane (L^1, cyclam) with 4-pyridylmethyl groups and its two novel cadmium polymeric metallamacrocyclic complexes, $[Cd_3L_{1.5}(C_6H_5O_7)_2\cdot 6H_2O]_n$ (**1**) and $[CdCl_2L_2\cdot 2.5H_2O]_n$ (**2**), were obtained by hydrothermal methods.

Macrocyclic and macrobicyclic compounds attract increasing interests of chemists owing to their interesting structures, properties and important roles in coordination chemistry and many other fields, such as material chemistry and medicinal chemistry.[1–6] Unlike polyoxa macrocyclic and macrobicyclic compounds, polyaza compounds can be functionalized by several groups, such as alkynyl,[7] phosphanylmethyl,[8] carboxyl,[9] and heterocyclic groups[10] on their secondary N-sites and thereby show some novel properties in coordination, electro-, photoluminescent and catalytic chemistry. Hence, we recently started the investigation on the complexes constructed from functionalized polyaza ligands, in order to prepare some novel structures and study their applications in material and medicinal chemistry. In this communication, we will report a new tetrafunctionalized octadentate ligand L and its two novel cadmium polymeric metallamacrocyclic complexes, $[Cd_3L_{1.5}(C_6H_5O_7)_2\cdot 6H_2O]_n$ (**1**) and $[CdCl_2L_2\cdot 2.5H_2O]_n$ (**2**), which were obtained by hydrothermal methods.

The ligand (L) was synthesized by the reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam, L^1) with 4-pyridylmethyl chloride according to a previously reported procedure (Figure 1).[10] Complex **1** was obtained from the hydrothermal reaction of cadmium nitrate, L and sodium citrate. Single-crystal X-ray analysis illustrates that **1** is an interesting polymeric metallamacrocyclic complex. There are three crystallographic independent Cd^{2+} ions: Cd(1) is coordinated by five oxygen and two nitrogen atoms in a pentagonal-bipyrimidal geometry, Cd(2) is coordinated by five oxygen and one nitrogen atoms in an octahedral geometry, while Cd(3) is coordinated by six oxygen and one nitrogen atoms in a pentagonal-bipyrimidal geometry. The citrate ligand shows an η^1-η^2-η^2-η^3-μ_4 coordination mode to connect four central metal ions by its six oxygen donors of three carboxylic groups and a hydroxy group (Supporting Information, Figure S1). One oxygen atom of it is uncoordinated and two oxygen donors coordinate to two central ions. The ligand L adopts two coordination modes: one acts as tetradentate ligand to coordinate four cadmium ions by its four pyridyl nitrogen atoms (η^1-μ_4, L^a), the other as bidentate ligand to two cadmium ions by its two *para*-pyridyl nitrogen atoms (η^1-μ_2, L^b) (Figure 1). The most striking feature of **1** is that its structure is built from seven interesting metallacycle units. The three Cd^{2+} ions form a novel M_3O_3 trinuclear heterocyclohexane-like metallacycle by the connection of citrate ligands (first metallacycle unit, C1; Figure 2). Every two of such trinuclear units are bridged by two citrate ligands to form a hexanuclear unit with a dinuclear 14-membered metallamacrocycle (C2; Figure 2). Every hexanuclear unit is connected with two other neighboring hexanuclear units by two citrate ligands to form columns of the structure with a dinuclear 12-membered metallamacrocycle (C3; Figure 2). Although several similar examples[11–16] of structures of the Cd_3O_3 unit have been reported, the major conformation is a heterocubane,[12,14,15] different from that in **1**. The fourth metallamacrocycle is a dinuclear 21-membered one formed by the linkage of two trinuclear Cd_3O_3 units through the two neighboring pyridyl

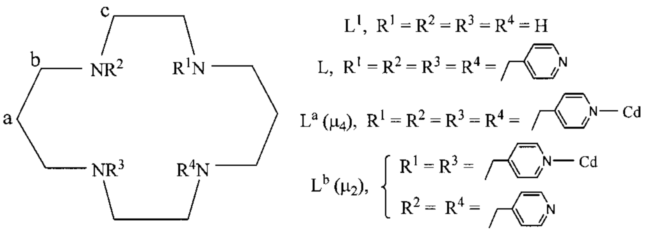

Figure 1. Schematic diagram of the ligands.

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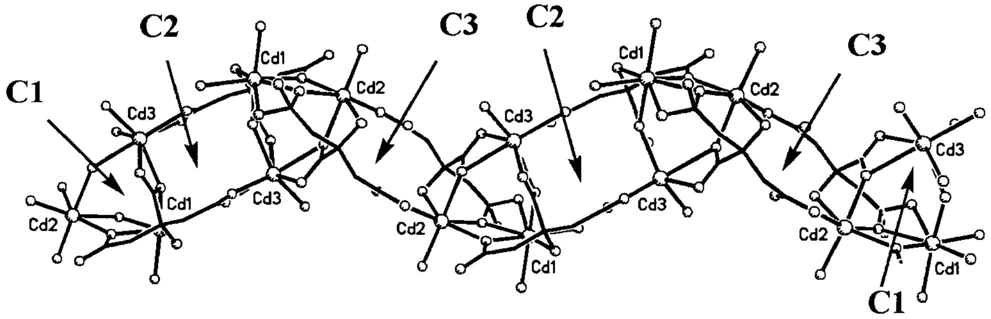

Figure 2. Structure of the two hexanuclear units linked by two citrate units in complex **1**. Selected bond lengths [Å]: Cd(1)–O(3) 2.289(3), Cd(1)–N(7) 2.290(4), Cd(1)–O(8) 2.301(4), Cd(1)–N(13A) 2.303(4), Cd(1)–O(12) 2.376(3), Cd(1)–O(10) 2.463(3), Cd(1)–O(7) 2.556(6), Cd(2)–O(10) 2.216(3), Cd(2)–N(12B) 2.249(4), Cd(2)–O(13) 2.253(4), Cd(2)–O(5) 2.272(3), Cd(2)–O(8) 2.441(4), Cd(2)–O(11) 2.461(3), Cd(3)–N(11) 2.254(4), Cd(3)–O(2) 2.288(5), Cd(3)–O(3) 2.310(3), Cd(3)–O(6) 2.356(4), Cd(3)–O(4) 2.461(4), Cd(3)–O(1) 2.484(4), Cd(3)–O(5), 2.570(3).

arms of an L^a ligand with the distance between the two Cd ions [Cd(1) and Cd(3)] being 6.546 Å (C4; Figure 3). The fifth macrocycle is a hexanuclear 50-membered metallamacrocycle (C5) formed by the linkage of four trinuclear units through four pyridyl arms from two L^a ligands in a parallelogram-type geometry as shown in Figure 3. The four corners of the parallelogram are occupied by cadmium ions, the side lengths are 15.293 and 11.092 Å, while the diagonals are 13.584 and 23.006 Å. The sixth macrocycle is a tetranuclear 42-membered parallelogram metallamacrocycle formed by the linkage of two trinuclear units through two L^b ligands (C6; Figure 3), the sides of the parallelogram are 3.761 and 20.160 Å and the diagonals are 20.434 and 20.582 Å. The seventh macrocycle is an octanuclear 68-membered parallelogram metallamacrocycle formed by the linkage of six trinuclear Cd_3O_3 units through two L^b ligands (C7), the sides of the parallelogram are16.448 and 20.161 Å and the diagonals are 21.343 and 29.974 Å. The columns formed by the hexanuclear units are linked by L^a and L^b ligands to result in a three-dimensional conforma-

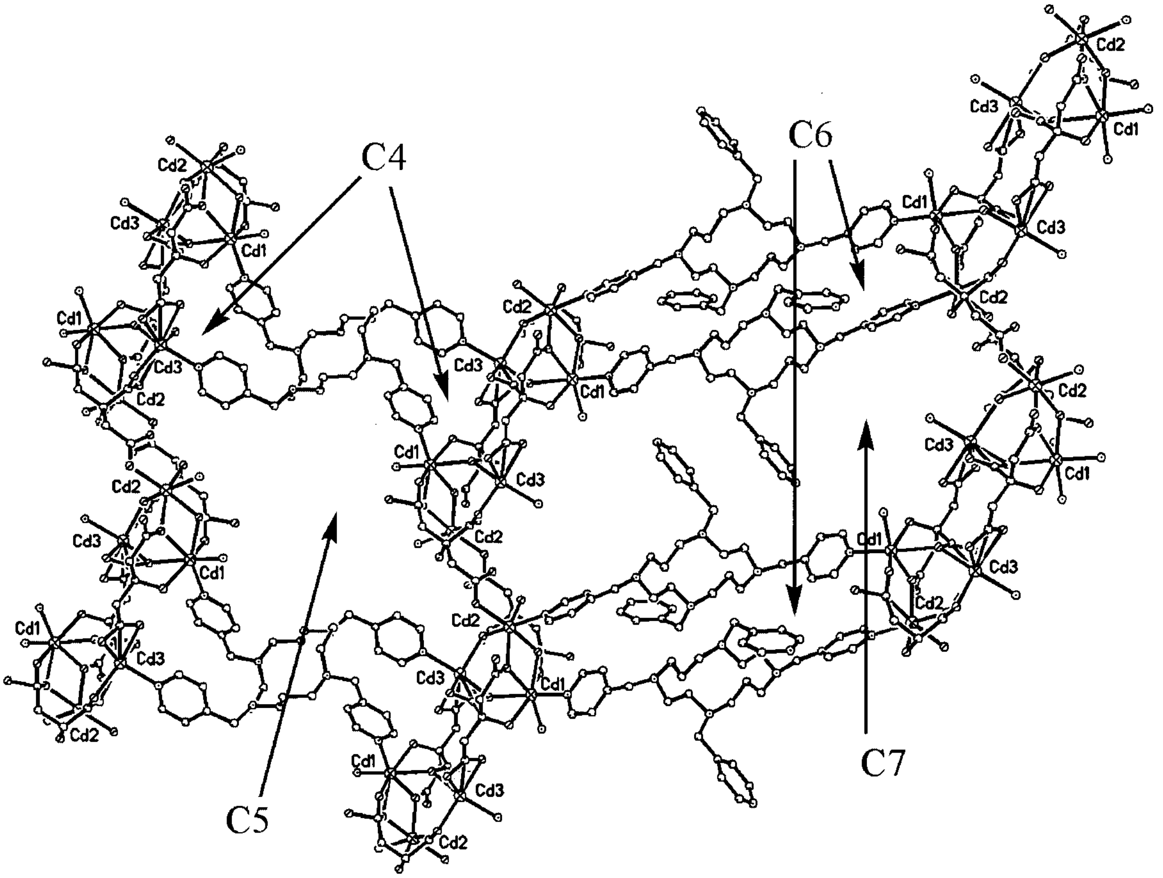

Figure 3. Molecular structure of complex **1**. Some molecules of L are omitted for clarity. There are four types of metallamacrocycles shown in this Figure: C4 and C5 (left) and C6 and C7 (right).

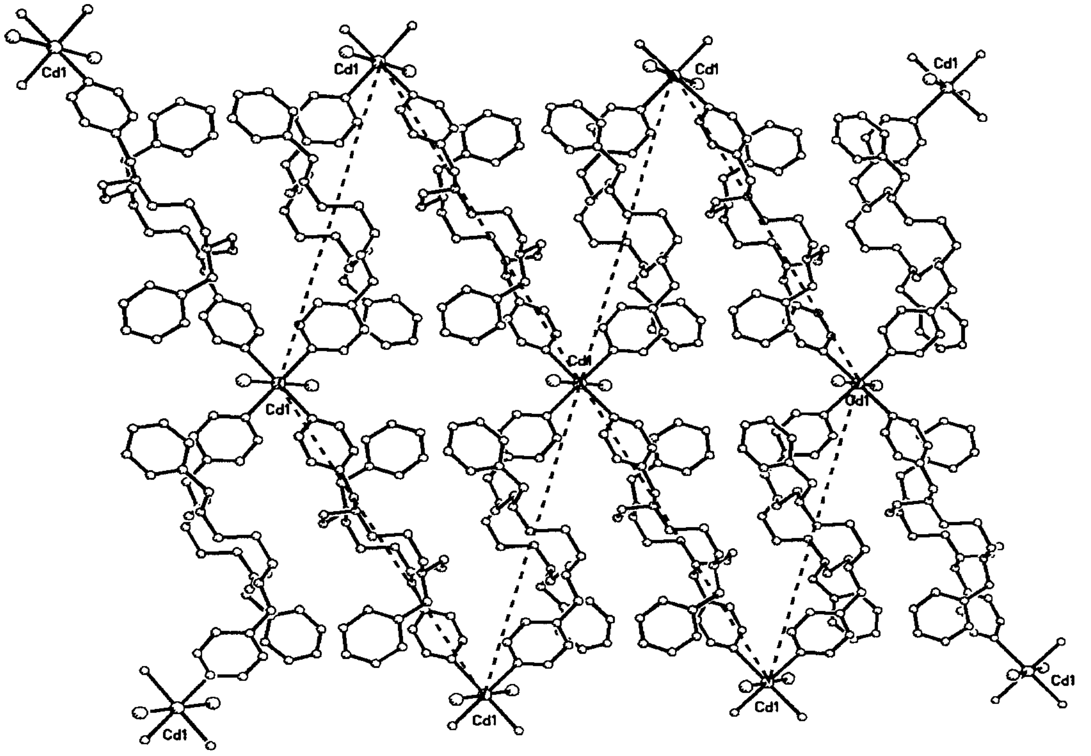

Figure 4. Molecular structure of complex **2**. Selected bond lengths [Å]: Cd(1)–N(6) 2.355(3), Cd(1)–N(5) 2.441(3), Cd(1)–Cl(1) 2.6145(9).

tion. Water molecules as guests exist in the structure and there are intermolecular hydrogen bonds O–H···O between neighboring water molecules.

Interestingly, when $CdCl_2$ was used as reactant, complex **2** was isolated, where no citrate ligands are observed because of the strong coordination ability of chloride ions to cadmium ions. A similar reaction without citrate ligand also resulted in **2**. This means that no substitution reaction between chloride ions and citrate ligands occurred under these hydrothermal conditions, and the citrate ligand did not play an important role in the formation of **2**. Compound **2** is a two-dimensional polymeric structure composed of $CdCl_2$ and ligand L (Figure 4). The ligand L shows only one conformation with two pendant pyridyl groups coordinated to cadmium ions and the other two being free (η^1-μ_2, L^b; Figure 1). In this structure, the cadmium ions are coordinated by four nitrogen atoms from four pyridyl groups of L^b and two chloride ions in a distorted octahedral geometry. The two chloride ions occupy the two apical positions and the basal plane consists of the four nitrogen atoms. The basic unit of this structure is a tetranuclear 76-membered metallamacrocycle in which four $CdCl_2$ units are connected by four L^b units in a parallelogram geometry with the two sides being 18.739 and 16.728 Å and the two diagonals being 13.508 and 32.856 Å. The metallamacrocycles are further extended into a planar structure by sharing cadmium ions. In both complexes **1** and **2**, the ligand L functions as a bridging ligand with the cyclam unit being uncoordinated, similar to the observation in the gold complex of *N*-phosphanylmethyl-functionalized cyclam reported by Che et al.[17]

In summary, two novel cadmium polymeric metallamacrocyclic complexes have been prepared from pyridyl-functionallized 1,4,8,11-tetraazacyclotetradecane by a hydrothermal method; different cadmium reactants influence the structures of the complexes dramatically. Further studies are underway and will be reported in a full paper.

Experimental Section

Synthesis of the Free Ligands L^1 and L: L^1 was prepared according to a reported procedure.[18] Free ligand L was prepared by tetrafunctionalization of L^1 with 4-pyridylmethyl chrolide according to a revised reported procedure.[10] Yield 41%; M.p. 152–153 °C. $C_{34}H_{44}N_8$ (564.77): calcd. C 72.30, H 7.85, N 19.84; found C 72.33, H 7.96, N 19.50. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ =1.77 (s, 4 H, a), 2.53 (s, 8 H, b), 2.61 (s, 8 H, c), 3.41 (s, 8 H, $-CH_2-$pyr), 7.24 (d, *J* = 3.5 Hz, 8 H, aryl), 8.47 (d, *J* = 4.0 Hz, 8 H, aryl) ppm. EI-MS: *m*/*z* (%) = 567.2, 566.3, 565.2 (100), 356.8, 256.4, 242.2, 178.7. IR (KBr disk): $\tilde{\nu}$ = 3073 (w), 3020 (w), 2958 (s, br.), 2797(m), 1596 (s), 1559 (m), 1467 (m), 1414 (s), 1366 (m), 1248 (m), 1155 (m), 1121 (m), 1103 (m), 1041 (m), 799 (s) cm^{-1}.

Synthesis of Complex 1: A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.044 g, 0.14 mmol), L (0.040 g, 0.071 mmol), $Na_3C_6H_5O_7\cdot 2H_2O$ (0.021 g, 0.071 mmol), and distilled water (20 mL) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 110 °C for 3 d. Colorless crystals of **1** were isolated by mechanical separation from the mixture of **1** and unidentified white powder. The yield of **1** was 12% based on Cd^{2+}. $C_{63}H_{88}Cd_3N_{12}O_{20}$ (1670.65): calcd. C 45.29, H 5.31, N 10.06; found C 45.32, H 5.29, N 10.02.

Synthesis of Complex 2: A mixture of $CdCl_2\cdot 2.5H_2O$ (0.032 g, 0.14 mmol), L (0.040 g, 0.071 mmol), $Na_3C_6H_5O_7\cdot 2H_2O$ (0.021 g, 0.071 mmol), and distilled water (20 mL) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 110 °C for 3 d. Colorless crystals of **2** were isolated by mechanical separation from a mixture of **2** and unidentified white powder. The yield of **2** was ca. 35% based on $CdCl_2$. $C_{68}H_{93}CdCl_2N_{16}O_{2.50}$ (1357.88): calcd. C 60.14, H 6.90, N 16.51; found C 60.23, H 6.85, N 16.26.

X-ray Crystallography: Crystal data for L: $C_{34}H_{44}N_8$ (564.77), monoclinic, space group $P2_1/n$, T = 130(2) K, a = 5.9649(4), b = 11.7400(7), c = 21.839(2) Å, β = 96.586(4)°, V = 1519.3(2) Å^3, Z = 2, $D_{calcd.}$ = 1.235 g·cm^{-3}, $F(000)$ = 608, μ(Mo-K_α) = 0.076 mm^{-1}, colorless from methanol, 0.75 × 0.50 × 0.25 mm, θ range for data collection 3.31–27.48°, 11320 collected, 3462 unique and 3150 observed (R_{int} = 0.0265) reflections, 190 parameters, R = 0.0435 and wR = 0.1049 for observed reflections with $I > 2\sigma(I)$, GOF = 1.058, $(\Delta\rho)_{max}$ = 0.262, $(\Delta\rho)_{min}$ = –0.205 e/Å^{-3}. Crystal data for **1**: $C_{63}H_{88}Cd_3N_{12}O_{20}$ (1670.65), triclinic, space group $P\bar{1}$, T = 130(2) K, a = 13.104(4), b = 16.448(5), c = 18.682(6) Å, α = 104.619(3), β = 102.754(1), γ = 106.923(2)°, V = 3534.2(18) Å^3, Z = 2, $D_{calcd.}$ = 1.570 g·cm^{-3}, $F(000)$ = 1708, μ = 0.974 mm^{-1}, colorless from water, 0.50 × 0.25 × 0.15 mm, θ range 3.02–25.00°, 22192 collected, 12317 unique and 10957 observed (R_{int} = 0.0220) reflections, 904 parameters, R = 0.0507 and wR = 0.1143 for observed reflections with $I > 2\sigma(I)$, GOF = 1.051, $(\Delta\rho)_{max}$ = 1.720, $(\Delta\rho)_{min}$ = –0.870 e/Å^{-3}. Crystal data for **2**: $C_{68}H_{93}CdCl_2N_{16}O_{2.50}$ (1357.88), triclinic, space group $P\bar{1}$, T = 130(2) K, a = 9.469(3), b = 13.271(4), c = 13.508(4) Å, α = 80.028(7), β = 78.940(8), γ = 86.796(7)°, V = 1640.3(8) Å^3, Z = 1, $D_{calcd.}$ = 1.375 g·cm^{-3}, $F(000)$ = 715, μ = 0.474 mm^{-1}, colorless, 0.30 × 0.25 × 0.05 mm, θ range 2.38–25.00°, 10544 collected, 5735 unique and 4813 observed (R_{int} = 0.0393) reflections, 411 parameters, R = 0.0483 and wR = 0.1013 for observed reflections with $I > 2\sigma(I)$, GOF = 1.093, $(\Delta\rho)_{max}$ = 0.873, $(\Delta\rho)_{min}$ = –0.472 e/Å^{-3}. Data collections for the three compounds were performed with a Rigaku Mercury-CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data sets were collected at 130 K (ω-scan mode). The structures of the three compounds were solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier syntheses and refined anisotropically. All hydrogen atoms were theoretically located. The structures were refined on F^2 by full-matrix least squares using the SHELXTL-97 program package. CCDC-262561, -262562, and -262563 (for L, **1**, and **2**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: Coordination modes of the citrate ligand (Figure S1); structural figures of the two complexes (Figures S2–S10); molecular structure (Figure S11), ^{1}H NMR spectrum (Figure S12), and EI mass spectrum (Figure S13) of ligand L.

Acknowledgments

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