Syntheses and Crystal Structures of a Novel 20-Membered N₃O₂-Donor Macrocycle and Its Disilver(I) Bis(Macrocycle) and Monocadmium(II) Complexes

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In macrocyclic coordination chemistry, the cation to cavity size ratio is an important parameter for understanding complexation-based metal ion recognition.¹ For example, 16- to 19-membered ring ligands incorporating dibenzo subunits have been widely investigated because these ligands generally favor stable 1:1 complexation and show intermediate flexibility which limits the number of observed complex conformations.^{1,2}

Following these earlier studies, new synthetic results and applications for the related macrocyclic systems have continued up to the present.³ In terms of macrocyclic cavity sizes, macrocyclic rings greater than 24-membered are strong candidates for forming dinuclear complexes in both the synthetic and bioinorganic chemistry areas.⁴ However, their preparation and purification tend to be difficult, often leading to the formation of the target ring in low yield.

On the other hand, the preparation and structural characterization of the complexes with 20- to 23-membered macrocycles have been less investigated because their cavity sizes are too large for planar complexation with one metal ion but too small for coordination with two metal ions simultaneously.⁵ However, macrocycles with the 20–23 membered rings are expected to give the unusual coordination topologies, while another advantage is that the latter category is usually relatively easier to prepare than larger analogs. Recently, several kinds of 20- to 23-membered oxathia-tribenzo macrocycles and their discrete and polymeric complexes showing less common stoichiometric ratios have been reported.⁵ To the best of our knowledge, such 20-membered O₂N₃-donor analogs have not been reported so far.

In this work, we present a 20-membered O_2N_3 -macrocycle L incorporating a tribenzo-subunit (Scheme 1); L is a potentially pentadentate macrocyclic ligand which is expected to react with a wide range of metal species. In particular, d^{10} metal ions are free from formation of specific coordination geometries and often show favorable reactivity toward polyoxaaza ligand systems. Here we report the synthesis of L along with an X-ray study of its complexes incorporating the d^{10} -metal ions Cd(II) and Ag(I).

The novel tribenzo- O_2N_3 -macrocycle L was obtained directly in 75% yield from reaction of dialdehyde⁶ with

diethylenetriamine in methanol followed by sodium borohydride reduction. The ¹H and ¹³C NMR spectra together with elemental analysis and mass spectra were all in agreement with the proposed structure.



Scheme 1. Synthesis of L.

Reaction of L with Cd(NO₃)₂·4H₂O in dichloromethane/ methanol afforded a colorless crystalline product 1 suitable for X-ray analysis (Table 1). The crystal structure of 1 is shown in Figure 1 and its selected geometric parameters are presented in Table 2. The crystal structure of 1 has an anion-coordinated mononuclear arrangement with the formula being [Cd(L)](NO₃)₂]. Unlike our expectation, the Cd(II) center locates outside the macrocyclic cavity (Figure 1(a)). The Cd(II) center is in a hexa-coordinated environment, being bound to the three consecutive N atoms from L in a bent arrangement (Figure 1 (b)). The coordination environment is completed by three O atoms arising from monodentate and bidentate nitrate ions, with bond lengths [Cd1-O3 2.445(10), Cd1-O4 2.382(8), Cd1–O6 2.331(7) Å] that fall within the range observed for other nitrato complexes of Cd(II).⁷ The Cd–N bond lengths [Cd1-N1 2.312(9), Cd1-N2 2.332(7), Cd1-N3 2.373(9) Å] are also within the normal literature range for this bond type.8 Two O donors of L remain uncoordinated. As shown in Figure 1(c), the resulting geometry of the Cd(II) coordination sphere in 1 can be described as a distorted trigonal prism.⁹ The two trigonal faces of the trigonal prism are defined by O3-O4-O6 and N1-N2-N3.

The preference for the observed anion-coordinated mononuclear complex formation in which the metal center locates outside the macrocyclic cavity could be associated with the stronger affinity of the charged nitrate O atoms over the neutral O donors in the macrocycle toward Cd(II). In addition, the relatively larger cavity size of **L** compared with the Cd(II) ion

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radius is expected to lower the coordination affinity of the macrocycle for this ion.

When $AgPF_6$ was used in the reaction with L under similar conditions, a colorless crystalline product 2 suitable for X-ray analysis was isolated (Table 1). Interestingly, the crystal

Table 1. Crystal and experimental data for 1 and 2.

	1	2	
Formula	C26H31CdN5O8	C ₂₆ H ₃₁ AgF ₆ N ₃ O ₂ P	
Temperature (K)	173(2)	173(2)	
Formula weight	653.96	670.38	
Crystal system	Triclinic	Triclinic	
Space group	<i>P</i> -1	<i>P</i> -1	
a (Å)	10.99(5)	9.3365(2)	
<i>b</i> (Å)	11.07(4)	12.0608(2)	
<i>c</i> (Å)	12.09(5)	12.4584(2)	
α (deg)	72.37(7)	79.8460(10)	
β (deg)	84.78(4)	89.3030(10)	
γ (deg)	73.63(7)	83.9960(10)	
$V(\text{\AA}^3)$	1345(9)	1373.31(4)	
Ζ	2	2	
$D_{\rm calc}({\rm g/cm}^3)$	1.615	1.621	
μ (mm ⁻¹)	0.871	0.862	
$2\theta_{max}$ (deg)	56.00	56.00	
Reflections collected	24 778	24 741	
No. of reflection used	6482 ($R_{int} =$	6604 ($R_{int} =$	
$[>2\sigma(I)]$	0.0512)	0.0278)	
Goodness-of-fit on F^2	1.049	1.029	
$R_1, wR_2 [I > 2\sigma(I)]$	0.0459, 0.1154	0.0308, 0.0766	
R_1 , wR_2 (all data)	0.0559, 0.1212	0.0374, 0.0810	



Figure 1. Crystal structure of the mononuclear cadmium(II) complex **1**, $[Cd(L)(NO_3)_2]$: (a) front view, (b) side view, and (c) coordination environment of the cadmium(II) in **1** showing the distorted trigonal prismatic arrangement.

structure shows that **2**, $[Ag_2(L)_2](PF_6)_2$, is a dinuclear bis(macrocycle) complex with a 2:2 (metal-to-ligand) stoichiometry as shown in Figure 2. Selected geometric parameters are presented in Table 3. Unlike **1**, no anions are included in the coordination sphere in **2**. Since the structure shown in Figure 2(a) is generated through an inversion symmetry, the

Table 2. Selected bond length [Å] and bond angles [°] for 1, [Cd $(L)(NO_3)_2$].

Cd1–N1	2.312(9)	Cd1-N2	2.332(7)
Cd1-N3	2.373(9)	Cd1–O3	2.445(10)
Cd104	2.382(8)	Cd106	2.331(7)
N2-Cd1-O4	162.56(12)	N2-Cd1-O3	143.97(12)
N2-Cd1-O6	94.5(3)	N2-Cd1-N3	77.4(3)
N1-Cd1-N2	78.1(2)	N1-Cd1-N3	98.57(12)
N1-Cd1-O3	87.05(17)	N1-Cd1-O6	146.89(16)
N1-Cd1-O4	101.5(3)	N3-Cd1-O3	137.8(2)
N3-Cd1-O4	85.5(2)	O6-Cd1-N3	111.39(15)
O6-Cd1-O4	94.8(3)	O6-Cd1-O3	80.25(19)
O4-Cd1-O3	52.58(13)		



Figure 2. Crystal structure of the disilver(I) bis(macrocycle) complex 2, $[Ag_2(L)_2](PF_6)_2$: (a) front view and (b) side view. Noncoordinating anions are omitted.

Table 3. Selected bond length [Å] and bond angles [°] for 2, $[Ag_2(L)_2](PF_6)_2]$.

Ag1—N1	2.2268(17)	Ag1—N2A	2.3765(17)
Ag1–N3A	2.2951(18)	Ag1-O2A	2.8324(16)
N1—Ag1—N3A	154.04(6)	N1—Ag1—N2A	121.71(6)
N3A-Ag1-N2A	77.96(6)	N1-Ag1-O2A	110.36(6)
N3A-Ag1-O2A	76.63(6)	N2A-Ag1-O2A	104.81(6)

asymmetric unit in the complex part contains one L and one Ag(I).

In 2, the complex cation consists of a dimeric arrangement in which two macrocycles in a twist and bent arrangement sandwich two Ag(I) ions. Due to this sandwich structure, the Ag(I) ions are shielded by the macrocycles from further interaction with solvent or anions (Figure 2(b)). Each Ag(I) center is four-coordinate, being bound to an O and two N donors from one L. The coordination sphere is completed by an N donor from another L. The Ag–N bond lengths [Ag1–N1 2.2268(17), Ag1–N2A 2.3765(17), Ag1–N3A 2.2951(18) Å] are typical for such bonds¹⁰ and the Ag–O bond [2.8324(16) Å] falls at the longer end in the corresponding values (2.4–2.9 Å) for related systems.¹¹

The tetrahedral bond angles around the Ag atom vary from 76.6(6)° (N3A–Ag1–O2A) to 154.0(6)° (N1–Ag1–N3A). The observed large deviations from regular tetrahedral geometry are due to the formation of the hexagonal metallacycle as well as the steric hindrance between two adjacent macrocycles. The separation between the two Ag atoms (Ag1…Ag1A, 5.65 Å) is far outside the range expected for an agentophilic interaction.¹² The preferred formation of the dinuclear bis(macrocycle) complex appears mainly associated with the lower coordination affinity of the anion. It was not possible for us to prepare the corresponding AgNO₃ complex with **L**.

In summary, a 20-membered O_2N_3 -macrocycle L was synthesized in a reasonable yield via a cyclization reaction between dialdehyde and diethylenetriamine followed by reduction. Reaction of L with cadmium(II) nitrate yielded a 1:1 complex, in which the cadmium(II) locates outside the cavity assigned to the strong anion coordination and the larger cavity size of the macrocycle compared with the metal ion size. From the reaction of L with silver(I) hexafluorophosphate, a disilver(I) bis(macrocycle) complex without anion coordination was isolated. In both cases, all nitrogen donors are coordinated to the metal center, but depending on the anion coordination ability, the coordination behaviors of the cations afford different stoichiometric complexes. Further work on a wider range of metal complexes of L is in progress in our laboratory.

Experimental

General. All chemicals were purchased from commercial sources and used as received. All solvents used were of reagent grade. Elemental analyses were carried out on a LECO CHNS-932 elemental analyzer (LECO Corporation, St. Joseph, MI, USA). Electrospray ionization-mass (ESI-MS) spectra were recorded in positive ion mode from acetonitrile solution with Thermo Scientific LCQ Fleet spectrometer (Thermo Scientific, Waltham, MA, USA). The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using Thermo Fisher Scientific Nicolet *i*S 10 FT-IR spectrometer (Madison, WI, USA) with KBr pellets.

Synthesis of L. Dialdehyde⁶ (3.01 g, 8.66 mmol) prepared from the reaction of salicylaldehyde and 1,3-bis(bromomethyl)benzene was dissolved in methanol and slowly added to diethylenetriamine (1.59 g, 15.4 mmol) in methanol (50 mL). The reaction mixture was refluxed, and then sodium borohydride (0.984 g, 25.9 mmol) with small amount of borax was slowly added to the stirred solution. The reaction mixture was rapidly stirred for a further 6 h, allowed to cool to room temperature, and then filtered. Water was added, and the mixture was extracted with CH₂Cl₂. Removing the CH₂Cl₂ under a vacuum gave rise to crude oil. Treatment of the crude product on a silica gel column eluted with MeOH– $CH_2Cl_2(20:80 \text{ v/v})$ gave pure product L as a pale yellow glassy solid (yield 1.93 g, 75%). Mp: 78–80 °C. ¹H NMR (300 MHz, CDCl₃): $\delta =$ 7.76-6.95 (m, 12H, aromatic), 5.12 (s, 4H, ArCH₂O), 3.85 (s, 4H, ArCH₂NH), 2.68 (s, 8H, HNCH₂CH₂NH). ¹³C NMR (75 MHz, CDCl₃): $\delta = 155.9$, 136.4, 130.0, 128.2, 127.7, 127.3, 126.5, 125.6, 120.2, 110.9, 69.2, 46.8, 45.6, 45.3. IR (KBr pellet): 3062 (w), 3036 (w), 2941 (m), 2808 (m), 1664 (m), 1599 (s), 1494 (s), 1453 (s), 1378 (m), 1291 (w), 1237 (s), 1161 (w), 1113 (m), 1045 (m), 1009 (m), 845 (w), 756 (s), 698 (m) cm^{-1} . Anal. Calcd for [C₂₆H₃₁N₃O₂]: C, 74.79; H, 7.48; N, 10.06. Found: C, 74.72; H, 5.94; N, 10.08%. Mass (ESI) spectrum m/z: $418.42 (L)^+$.

Preparation of 1, [Cd(L)(NO₃)₂]. Cd(NO₃)₂·4H₂O (48.0 mg, 0.156 mmol) in dichloromethane was added to a solution of (60.2 mg, 0.144 mmol) in methanol. Slow evaporation of the solution at room temperature afforded a colorless crystal-line product **1** suitable for X-ray analysis. Mp: 230–232 °C (decomp.). IR (KBr pellet): 3064 (w), 2926 (m), 2871 (m), 1598 (m), 1495 (m), 1452 (m), 1384 (s, NO₃⁻), 1293 (m), 1238 (m), 1089 (w), 1022 (m), 901 (m), 840 (m), 758 (s), 692 (w) cm⁻¹. Anal. Calcd for [C₂₆H₃₁CdN₅O₈]: C, 47.75; H, 4.78; N, 10.71. Found: C, 47.63; H, 4.85; N, 10.43%. Mass (ESI) spectrum *m/z*: 593.17 [Cd(L)NO₃]⁺.

Preparation of 2, $[Ag_2(L)_2](PF_6)_2]$. AgPF₆ (33.6 mg, 0.133 mmol) in dichloromethane was added to a solution of L (45.4 mg, 0.101 mmol) in methanol. Slow evaporation of the solution afforded a colorless crystalline product **2** suitable for X-ray analysis. Bulk purity of **2** was confirmed by its PXRD patterns. Mp: 185–187 °C (decomp.). IR (KBr pellet): 2930 (m), 2861 (m), 1602 (m), 1494 (m), 1455 (m), 1380 (w), 1238 (m), 1173 (m), 1118 (m), 1008 (m), 913 (m), 841 (s, PF₆⁻), 759 (m), 672 (m) cm⁻¹. Mass (ESI) spectrum *m/z*: 524.33 [Ag(L)]⁺.

X-ray Crystallographic Analysis. Single crystals suitable for data collection were chosen under an optical microscope, mounted on glass fiber, and frozen under a stream of cryogenic nitrogen gas before data collection. Intensity data were collected on a Bruker SMART APEX II ULTRA diffractometer (Bruker, Billerica, MA, USA) attached with a CCD detector and graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.¹³ All of the calculations for the structure determination were carried out using the SHELXTL package.¹⁴ In all cases, all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with the their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures of 1-2 are summarized in Table 1.

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Supporting Information. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-1051140 (1) and CCDC-1051141 (2)). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

References

- (a) R. M. Izatt, K. Pawlak, J. S. Bradshaw, *Chem. Rev.* 1991, 91, 1721; (b) L. F. Lindoy, *The Chemistry of Macrocyclic Complexes*, Cambridge University Press, Cambridge, 1989; (c) R. M. Izatt, K. Pawlak, J. S. Bradshaw, *Chem. Rev.* 1995, 95, 2529.
- L. F. Lindoy, G. V. Meehan, I. M. Vasilescu, H. J. Kim, J.-E. Lee, S. S. Lee, *Coord. Chem. Rev.* 2010, 254, 1713.
- (a) S. Kim, L. F. Lindoy, S. S. Lee, *Coord. Chem. Rev.* 2014, 280, 176;
 (b) M. J. D. Champion, J. M. Dyke, W. Levason, M. E. Light, D. Pugh, H. Bhakhoa, L. Rhyman, P. Ramasami, G. Reid, *Inorg. Chem.* 2015, 54, 2497.
- (a) R. Menif, A. E. Martell, P. J. Squattrito, A. Clearfield, *Inorg. Chem.* **1990**, *29*, 4723; (b) S. Brooker, *Coord. Chem. Rev.* **2001**, 222, 33; (c) S. A. Cameron, S. Brooker, *Inorg. Chem.* **2011**, *50*, 3697.
- (a) H.-H. Lee, I.-H. Park, S. S. Lee, *Inorg. Chem.* 2014, *53*, 4763;
 (b) A. D. Siewe, H. Ju, S. S. Lee, *Bull. Korean Chem. Soc.* 2013, *34*, 725;
 (c) H. J. Kim, I. Yoon, S. Y. Lee, J. Seo, S. S. Lee, *Tetrahedron Lett.* 2007, *48*, 8464.

- (a) K. M. Atkinson, L. F. Lindoy, O. A. Matthews, G. V. Meehan, A. N. Sobolev, A. H. White, *Aust. J. Chem.* **1994**, 47, 1155; (b) A. H. M. Elwahy, A. A. Abbas, *Tetrahedron* **2000**, 56, 885.
- (a) K. R. Adam, S. P. H. Arshad, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, B. J. McCool, M. McPartlin, B. A. Tailor, P. A. Tasker, *Inorg. Chem.* **1994**, *33*, 1194;
 (b) L. H. Doerrer, S. J. Lippard, *Inorg. Chem.* **1997**, *36*, 2554;
 (c) K.-M. Park, S.-T. Moon, Y. J. Kang, H. J. Kim, J. Seo, S. S. Lee, *Inorg. Chem. Commun.* **2006**, *9*, 671;
 (d) K. S. Choi, D. Kang, J.-E. Lee, J. Seo, S. S. Lee, *Bull. Korean Chem. Soc.* **2006**, *27*, 747.
- (a) W. N. Setzer, Y. Tang, G. J. Grant, D. G. VanDerveer, *Inorg. Chem.* **1991**, *30*, 3652; (b) C.-D. Wu, P. Ayyappan,
 O. R. Evans, W. Lin, *Cryst. Growth Des.* **2007**, *7*, 1690;
 (c) L.-F. Ma, C.-P. Li, L.-Y. Wang, M. Du, *Cryst. Growth Des.* **2010**, *10*, 2641.
- (a) N. W. Alcock, E. H. Curzon, P. Moore, C. Pierpoint, J. Chem. Soc. Dalton Trans. 1984, 605; (b) U. Rajalingam, P. A. W. Dean, H. A. Jenkins, M. Jennings, J. M. Hook, Can. J. Chem. 2001, 79, 1330; (c) H. Keypour, R. Azadbakht, H. Khavasi, Polyhedron 2008, 27, 648; (d) W.-B. Lin, H.-C. Liang, J.-D. Chen, T.-C. Keng, J.-C. Wang, Inorg. Chim. Acta 2002, 336, 157.
- (a) Y. Habata, M. Ikeda, S. Yamada, H. Takahashi, S. Ueno, T. Suzuki, S. Kuwahara, *Org. Lett.* **2012**, *14*, 4576;
 (b) O.-S. Jung, Y. J. Kim, Y.-A. Lee, H. K. Chae, H. G. Jang, J. Hong, *Inorg. Chem.* **2001**, *40*, 2105.
- MOGUL, Cambridge Crystallographic Database, Cambridge, UK, 2006.
- (a) C. X. Cui, M. Kertesz, *Inorg. Chem.* **1990**, *29*, 2568;
 (b) V. Mckee, J. Nelson, D. J. Speed, R. M. Town, *J. Chem. Soc. Dalton Trans.* **2001**, 3641;
 (c) M. O. Awaleh, A. Badia, F. Bisse, *Cryst. Growth Des.* **2004**, *5*, 1897.
- Bruker, APEX2 Version 2009.1-0 Data Collection and Processing Software; Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
- Bruker, SHELXTL-PC Version 6.22: Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc., Madison, Wisconsin, USA, 2001.