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Inorganica Chimica Acta 358 (2005) 1274-1278

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# Molecular interactions of zinc(II) cyclams with polycarboxylato ligands

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> Received 15 July 2004; accepted 17 October 2004 Available online 19 November 2004

### Abstract

Four new zinc(II) cyclams of the composition  $\{Zn(L)(tp^{2-}) \cdot H_2O\}_n$  (1),  $\{Zn(L)(H_2bta^{2-}) \cdot 2H_2O\}_n$  (2),  $[Zn_2(L)_2(ox^{2-})]$  2CIO<sub>4</sub> · 2DMF (3), and Zn(L)(H<sub>2</sub>btc<sup>-</sup>)<sub>2</sub> · 2DMF (4), where L = cyclam,  $tp^{2-} = 1,4$ -benzenedicarboxylate ion,  $H_2bta^{2-} = 1,2,4,5$ -benzenetetracarboxylate ion,  $ox^{2-} = oxalate$  ion, DMF = *N*,*N*-dimethylformamide, and  $H_2btc^- = 1,3,5$ -benzenetricarboxylate ion, have been synthesized and structurally characterized by a combination of analytical, spectroscopic and crystallographic methods. The carboxylato ligands in the complexes 1–4 show strong coordination tendencies toward zinc(II) cyclams with hydrogen bonding interactions between the pre-organized N–H groups of the macrocycle and oxygen atoms of the carboxylato ligands. The macrocycles in 1, 2, and 4 adopt *trans*-III configurations with the appropriate *R*,*R*,*S*,*S* arrangement of the four chiral nitrogen centers, respectively. However, the complex 3 shows an unusual *cis* V conformation with the *R*,*R*,*R*,*R* nitrogen configuration. The finding of strong interactions between the carboxylato ligands and the zinc(II) ions may provide additional knowledge for the improved design of receptor-targeted zinc(II) cyclams in anti-HIV agents. © 2004 Elsevier B.V. All rights reserved.

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Keywords: Zinc(II) complex; Crystal structure; Coordination polymer; Cyclam

# 1. Introduction

Cyclams and bicyclams exhibit anti-HIV activity [1,2]. Particularly, the bicyclams in which the cyclam moieties tethered via aliphatic or aromatic linkers are potent and selective inhibitors of HIV-1 and HIV-2 [3,4]. The phenylenebismethylene bridging bicyclam (AMD 3100) has recently been on clinical trials for the treatment of AIDS and also shows an ability to mobilize stem cells [5,6]. The cyclams block the entry of the virus into the white cells by specific binding to the co-receptor CXCR4, and co-receptor binding strength and anti-HIV activity enhance on the complexation of zinc(II) ions to

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cyclams. It has been suggested that the carboxylate groups of aspartate residues Asp 171 and Asp 262 of the CXCR4 co-receptor play key roles in the recognition of cyclams [7]. Therefore, the understanding of interactions between carboxylates and zinc(II) cyclams is significant in the design and development of more effective anti-HIV agents. Recently, several zinc complexes such as  $[Zn(L)(H_2O)_2](OAc)_2$  [8],  $\{Zn(L)(phthalate)\}_n \cdot (CH_3 OH_{2n}$  [8], [Zn(Bz-cyclam)Cl]Cl  $\cdot$  2.5CDCl<sub>3</sub> [4], and  $[Zn_2(Xyl-bicyclam)(OAc)_2]$  (OAc)<sub>2</sub> · 2CH<sub>3</sub>OH [4] have been prepared and structurally characterized to elucidate a selective recognition of zinc(II) cyclams by carboxylates. However, the zinc(II) cyclams having carboxylato ligands are still rare. During our efforts to expand such examples, which enable us to offer the knowledge of the nature of interactions between zinc(II) cyclams and carboxylates, we successfully prepared and

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<sup>0020-1693/</sup>\$ - see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2004.10.025

structurally characterized new carboxylato zinc(II) cyclams. In this report, we describe the synthesis, structures and properties of zinc(II) complexes 1, 2, 3, and 4 obtained from the reactions between  $Zn(L)(ClO_4)_2$  and various organic polycarboxylates.



# 2. Experimental

#### 2.1. Materials, methods and apparatus

All chemicals used in this work were of reagent grade and were used without further purification. Infrared spectra were measured as Nujol mulls between KBr plates using a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer over the range 4000 and 400 cm<sup>-1</sup>. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea. Suitable crystals of 1–4 for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope.

#### 2.2. Synthesis

The starting material  $Zn(L)(ClO_4)_2$  was synthesized according to the published procedures [7].

*Caution*: The perchlorate salts used in this study are potentially explosive and should be handled in small quantities.

# 2.2.1. Synthesis of $\{Zn(L)(tp^{2-}) \cdot H_2O\}_n$ (1)

To a DMF (10 mL) solution of  $Zn(L)(ClO_4)_2$  (166 mg, 0.357 mmol) was added dropwise an aqueous solution (10 mL) of 1,4-benzenedicarboxylic acid disodium salt (75 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent blocks formed. *Anal.* Calc. for  $C_{18}H_{30}N_4O_5Zn$  (1): C, 48.23; H, 6.70; N, 12.50. Found: C, 48.38; H, 6.83; N, 12.45%. IR (Nujol, cm<sup>-1</sup>): 3391 (OH), 3234, 3173 (NH), 1573, 1370 (COO).

# 2.2.2. Synthesis of $\{Zn(L)(H_2bta^{2-}) \cdot 2H_2O\}_n$ (2)

To a DMF (10 mL) solution of  $Zn(L)(ClO_4)_2$  (166 mg, 0.357 mmol) was added dropwise a DMF solution

(10 mL) of 1,2,4,5-benzenetetracarboxylic acid (91 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent plates formed. *Anal* Calc. for  $C_{20}H_{32}N_4O_{10}Zn$  (2): C, 43.33; H, 5.78; N, 10.11. Found: C, 43.74; H, 5.81; N, 10.09%. IR (Nujol, cm<sup>-1</sup>): 3449 (OH), 3224, 3164 (NH), 1693, 1572, 1340, 1310 (COO).

# 2.2.3. $[Zn_2(L)_2(ox^{2-})] 2ClO_4 \cdot 2DMF(3)$

To a DMF (10 mL) solution of  $Zn(L)(ClO_4)_2$  (166 mg, 0.357 mmol) was added dropwise an aqueous solution (10 mL) of potassium oxalate monohydrate (66 mg, 0.357 mmol). The solution was allowed to stand at room temperature. Transparent blocks were obtained after several days. *Anal.* Calc. for  $C_{28}H_{62}N_{10}O_{14}Cl_2Zn_2$  (3): C, 34.84; H, 6.42; N, 14.51. Found: C, 35.20; H, 6.44; N, 14.44%. IR (Nujol, cm<sup>-1</sup>): 3270, 3250 (NH), 1633, 1313, 790 (COO), 1095 (ClO<sub>4</sub>).

# 2.2.4. $Zn(L)(H_2btc^-)_2 \cdot 2DMF(4)$

To a DMF (10 mL) solution of  $Zn(L)(ClO_4)_2$  (166 mg, 0.357 mmol) was added dropwise a DMF solution (10 mL) of 1,3,5-benzenetricarboxylic acid (75 mg, 0.357 mmol). The solution was allowed to stand at room temperature for several days until transparent blocks formed. *Anal.* Calc. for  $C_{34}H_{48}N_6O_{14}Zn$  (4): C, 49.15; H, 5.78; N, 10.12. Found: C, 49.07; H, 5.78; N, 10.03%. IR (Nujol, cm<sup>-1</sup>): 3450 (OH), 3248, 3169 (NH), 1703, 1622, 1557 (COO).

#### 2.3. X-ray crystallography

A summary of selected crystallographic data for 1-4 is given in Table 1. X-ray data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A combination of 1°  $\phi$  and  $\omega$  (with kappa offsets) scans was used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [9]. The structures were solved and refined, using the SHELXL\PC V5.1 package [10]. Refinement was performed by full-matrix least-squares on  $F^2$ , using all data (negative intensities included). Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms of the carboxyl groups and those bonded to the nitrogen atoms, which were refined with isotropic thermal parameters.

# 3. Results and discussion

The crystals 1–4 retain their transparency for several weeks in a refrigerator, but they lose solvent molecules in a couple of days upon exposure to the atmosphere as evidenced by elemental analyses. The infrared spectra

	1	2	3	4
Empirical formula	$C_{18}H_{30}N_4O_5Zn$	$C_{20}H_{32}N_4O_{10}Zn$	C <sub>28</sub> H <sub>62</sub> Cl <sub>2</sub> N <sub>10</sub> O <sub>14</sub> Zn <sub>2</sub>	C <sub>34</sub> H <sub>48</sub> N <sub>6</sub> O <sub>14</sub> Zn
Formula weight	447.83	553.87	964.52	830.15
Temperature (K)	150(1)	150(2)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	C2/c	$P\overline{1}$	P2(1)/n	P2(1)/n
Unit cell dimensions				
a (Å)	16.3442(5)	8.5540(3)	13.2202(2)	8.4170(10)
b (Å)	16.2092(6)	8.7040(3)	12.0175(2)	20.7650(4)
<i>c</i> (Å)	8.9481(3)	9.4100(4)	13.3587(2)	11.3520(2)
α (°)		64.992(12)		
β (°)	119.435(2)	82.664(13)	103.819(10)	110.7621(10)
γ (°)		75.796(14)		
Volume (Å)	2064.58(12)	615.29(4)	2060.92(6)	1855.24(5)
Ζ	4	1	2	2
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0307, wR_2 = 0.0777$	$R_1 = 0.0375, wR_2 = 0.0875$	$R_1 = 0.0287, wR_2 = 0.0706$	$R_1 = 0.0383, wR_2 = 0.0903$
R indices (all data)	$R_1 = 0.0414, wR_2 = 0.0838$	$R_1 = 0.0487, wR_2 = 0.0959$	$R_1 = 0.0343, wR_2 = 0.0737$	$R_1 = 0.0545, wR_2 = 0.0974$

Table 1 Crystal data and details of structural determinations for 1–4

 $R_1 = \sum ||F_o - F_c|| / \sum |F_o|$  and  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

and microanalyses for 1–4 clearly support the structures determined by the X-ray diffraction studies as described in Section 2. Addition of 1,4-benzenedicarboxylate ion to a DMF solution of  $Zn(L)(ClO_4)_2$  produced the complex 1. The structure of 1 consists of a one-dimensional coordination polymer with a basic  $Zn(L)(tp^{2-})$  unit (Fig. 1). The macrocycle adopts *trans* III configuration in the solid state. The coordination environment around the central zinc(II) ion shows a slightly distorted octahedron in the chain direction with four Zn–N and two Zn– O bonds. The Zn atom sits on an inversion center. The four Zn–N distances are in the range 2.1083(15)– 2.1114(15) Å. The Zn–O distance of 2.1559(12) Å is



Fig. 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected bond distances (Å) and angles (°). Zn1–N1, 2.1083(15); Zn1–N2, 2.1114(15); Zn1–O(1), 2.1559(12); N1–Zn1–N2, 85.35(6); N1–Zn1–O1, 92.14(6); N2–Zn1–O1, 92.60(5).

slightly shorter than that found in {Zn(L)(phthalate)}<sub>n</sub>(CH<sub>3</sub>OH)<sub>2n</sub>; Zn–O=2.22 Å) [8]. One of the pertinent structural features found in **1** is the pre-organization of N–H groups of the macrocycle with its role in profacial selection of  $tp^{2-}$  binding through hydrogen bonding interactions (N1–H1···O2 = 2.971(2) Å). Similarly to other macrocyclic- $tp^{2-}$  systems [11], there are two different series of one-dimensional coordination polymers running toward different directions in **1**. The two different chains are interconnected by water molecules through hydrogen bonding interactions (O1W– H1W···O2 = 2.857(2) Å), resulting in the formation of an ultimate three-dimensional network.

In 2, the basic coordination pattern of the anion toward the zinc(II) is very similar to that found in 1. The polymeric one-dimensional chain is formed toward the axial direction of the Zn(L) (Fig. 2). The Zn atom is located on an inversion center. The Zn-O distance of 2.2839(14) Å is even longer than that observed in 1. It seems that the increased steric hindrance by the introduction of two more carboxyl groups in the H<sub>2</sub>bta<sup>2-</sup> prevents the anion from approaching closely to the zinc(II) macrocycle. Apart from the Zn-O bonds, the hydrogen bond between the pre-organized N-H groups of the macrocycle and the  $COO^-$  of the H<sub>2</sub>bta<sup>2-</sup> contributes to the formation of a polymer (N1- $H1 \cdots O2\#1 = 2.876(2)$  Å, symmetry codes: #1 - x + 1, -y + 1, -z + 1). The complex adopts *trans* III, as does complex 1. The salient structural feature of 2 is the observation of only a single series of one-dimensional coordination polymers running toward the crystallographic c directions. Water molecules mediate in interconnecting each polymeric chain through hydrogen bonding interactions to form two-dimensional plane (O4-H4O...O1W = 2.574(2) Å, O1W-H2W...O2#4 =



Fig. 2. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected bond distances (Å) and angles (°). Zn1–N1, 2.0971(19); Zn1–N2, 2.0978(19); Zn1–O1, 2.2839(14); N1–Zn1–N2, 85.47(8); N1–Zn1–O1, 87.54(6); N2–Zn1–O1, 90.78(7).

2.644(2) Å, O1W-H1W···O3#3 = 2.738(2) Å ; symmetry codes: #3 -x + 1, -y, -z + 2, #4 x, y - 1, z). The shape of the H<sub>2</sub>bta<sup>2-</sup> in **2** resembles that found in [Ni(L1)](H<sub>2</sub>bta<sup>2-</sup>) · (H<sub>4</sub>bta) {L1 = 3,10-bis(2-hydroxy-ethyl)-1,3,5,8,10,12-hexaazacyclotetradecane} [12]. As are often the examples [13–15], the carboxylato groups and carboxylic acid groups of the present H<sub>2</sub>bta<sup>2-</sup> do not lie in the phenyl ring plane, since the dihedral angle between the carboxylato and the aromatic ring (O1 C9 C6 C7) is 31.8° and the dihedral angle between the carboxylic acid sequence that and the aromatic ring the reported various shapes of the H<sub>4</sub>bta, H<sub>3</sub>bta<sup>-</sup>, and H<sub>2</sub>bta<sup>2-</sup>, where the shapes vary with the degree of deprotonation and the types of hydrogen bonding systems [16].

The structure of 3 consists of binuclear  $[Zn_2(L)_2(ox^{2-})]^{2+}$  cations, which are hydrogen bonded to perchlorate anions and solvent DMF molecules. There is a crystallographic inversion center at the middle of point of the C11–C11#1 bond of the bridging oxalato ligand. The oxalato ligand coordinates to the zinc(II) ion by a bis-bidentate mode. A view of the molecule is shown in Fig. 3. The coordination environment around the zinc(II) ion is described as a distorted octahedron with four nitrogen atoms from the macrocycle and two oxygen atoms from the bridging oxalato ligand. In 3, the macrocyclic ligand skeleton adopts an unusual cis V conformation in a manner observed in [Zn<sub>2</sub>(Xyl-bicy $clam)(OAc)_2](OAc)_2 \cdot 2CH_3OH$ [4], cis-[Ni<sub>2</sub>(L)<sub>2</sub>( $\mu$  $ox^{2-})$ ]2NO<sub>3</sub> [17] and [(NiL1)<sub>2</sub>(µ-ox<sup>2-</sup>)]2ClO<sub>4</sub> [18],



Fig. 3. Molecular structure of **3** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected bond distances (Å) and angles (°). Zn1–N1, 2.1598(14); Zn1–N2, 2.1490(13); Zn1–N3, 2.1429(14); Zn1–N4, 2.1658(14); Zn1–O1, 2.1175(11); Zn1–O2, 2.1397(11); O1–Zn1–O2, 78.74(4); O1–Zn1–N3, 92.43(5); O2–Zn1–N3, 95.50(5); O1–Zn1–N2, 166.71(5); O2–Zn1–N2, 88.31(5); N3–Zn1–N2, 91.78(5); O1–Zn1–N1, 95.20(5); O2–Zn1–N1, 92.86(5); N3–Zn1–N1, 169.64(5).

showing the R, R, R, R set of nitrogen configurations. The two Zn–O distances of 2.1175(11) and 2.1397(11) Å are comparable to those found in a related macrocyclic zinc(II) system  $[Zn_2(Xyl-bicyclam)(OAc)_2](OAc)_2$ .  $2CH_{3}OH (Zn-O = 2.089(2), 2.407(2) \text{ Å})$  [4]. Apart from the bridging oxalato ligand, two  $ClO_4^-$  anions play a role in mediating the two macrocycles by weak hydrogen bonds. The four N-H groups in 3 are also pre-organized, however, the patterns of the pre-organization observed in 3 are different from those observed in 1, 2 and 4 as the macrocycles are folded. The two hydrogen atoms on nitrogen atoms N1 and N3 as hydrogen bond donors face the oxygen atoms of perchlorate anions, and the remaining two hydrogen atoms on N2 and N4 face the oxygen atoms of solvent DMF molecules, assisting in the formation of an ultimate dimeric compound 3.

The structure of 4 consists of Zn(L), two H<sub>2</sub>btc<sup>-</sup> ligands, and two solvent DMF molecules. The coordination geometry around the zinc(II) ion reveals a sixcoordinated axially distorted octahedron with four nitrogen atoms from the macrocycle and two oxygen atoms from the carboxylato ligands of H<sub>2</sub>btc<sup>-</sup>. An inversion center exists on the central zinc(II) ion. Fig. 4 shows a drawing of **4** with the atom labeling scheme. The Zn–O distance of 2.2222(12) Å and the Zn–N distances of 2.0923(16)-2.1128(15) Å are normal and fall on those found in complexes 1-3. The H<sub>2</sub>btc<sup>-</sup> is always involved in the formation of the complex 4 although an acid form H<sub>3</sub>btc is used during the synthesis. Two sets of N-H are observed in 4 and each set participates in the formation of hydrogen bonding interactions as hydrogen bond donors (N1–H1···O2 = 2.9287(19) Å, N2–  $H2 \cdot \cdot \cdot O5\#3 = 3.0674(19)$  Å; symmetry code: #3 x - 1, y, z - 1).



Fig. 4. Molecular structure of **4** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected bond distances (Å) and angles (°). Zn1–N1, 2.0923(16); Zn1–N2, 2.1128(15); Zn1–O1, 2.2222(12); N1–Zn1–N2, 84.76(6); N1–Zn1–O(1), 91.07(5); N2–Zn1–O1, 90.59(5).

In conclusion, we have prepared and fully characterized four new carboxylato zinc(II) cyclams. The carboxylato ligands in the complexes 1-4 show strong coordination tendency toward the zinc(II) cyclams with hydrogen bonding interactions between the pre-organized N-H groups of the macrocycle and oxygen atom of the carboxylato ligands, respectively. The complexes 1, 2, and 4 adopt *trans*-III configurations with the appropriate *R*,*R*,*S*,*S* arrangement of the four chiral nitrogen centers. However, the complex 3 adopts an unusual *cis* V conformation with the *R*,*R*,*R*,*R* nitrogen configuration. This understanding may provide a new basis for the improved design of receptor-targeted zinc(II) cyclams.

# Appendix A. Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC Nos. 208587–208590 for 1–4. Supplementary data associated with this article can be found, in the on-line version at doi:10.1016/j.ica.2004.10.025.

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