

Synthesis and Characterization of Zinc(II) Tetraaza Macrocyclic Complexes with Aquo and Nitrate Ligands

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(Received November 16, 2017; Accepted December 26, 2017)

ABSTRACT. The complexes $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2] \cdot 2\text{NO}_2$ (**1**) and $[\text{Zn}(\text{L})(\text{NO}_3)_2]$ (**2**) ($\text{L} = 3,14\text{-dimethyl-2,6,13,17-tetraazatricyclo}[14,4,0^{1.18},0^{7.12}]$ docosane) have been synthesized and structurally characterized. The compound **1** crystallizes in the monoclinic system $P2_1/c$ with $a = 8.74650(10)$, $b = 18.6880(3)$, $c = 7.96680(10)$ Å, $\beta = 109.1920(10)^\circ$, $V = 1229.84(3)$ Å³, $Z = 2$. The compound **2** crystallizes in the monoclinic system $P1$ with $a = 8.1292(5)$, $b = 8.9244(5)$, $c = 9.1398(5)$ Å, $\alpha = 68.035(2)$, $\beta = 70.109(2)$, $\gamma = 75.649(3)^\circ$, $V = 572.70(6)$ Å³, $Z = 1$. The crystal structures of the compounds **1** and **2** show a distorted octahedral coordination geometry around the zinc(II) ion, with four secondary amines and two oxygen atoms of the two water and two nitrate ligands at the axial position. The TGA behaviors of the complexes are significantly affected by the nature of the tetraaza macrocycle and the axial ligands.

Key words: Zinc(II) complexes, Tetraaza macrocycle, Aquo ligand, Nitrite ligand, Nitrate ligand

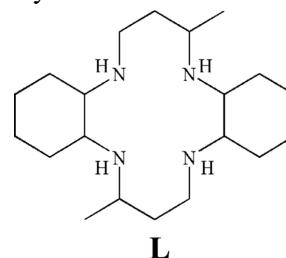
The transition metal(II) polyaza macrocyclic complexes with the axial ligands have attracted considerable interest due to their importance as models for metalloenzyme active sites^{1–4} and as selective complexing agents for metal ions.^{5–7} The structures and chemical properties of such compounds are affected by various factors, such as the type and synthetic difference of the axial ligands. For example, the complexes $[\text{Zn}(\text{L})(\text{NCS})]\text{NCS}$ and $[\text{Zn}(\text{L})(\text{H}_2\text{O})]\text{Cl} \cdot \text{INT} \cdot 3\text{H}_2\text{O}$ ($\text{L} = 3,14\text{-dimethyl-2,6,13,17-tetraazatricyclo}[14,4,0^{1.18},0^{7.12}]$ docosane, INT=isonicotinate) show that the zinc atoms are coordinated to the four secondary amines of macrocycle and to the nitrogen and oxygen atoms of the coordinated cyanate and water molecules,^{8,9} which reveal a five coordinate square pyramidal environment. However, the crystal structures of $[\text{Zn}(\text{L}1)]\text{X}_2$ ($\text{L}1 = 2,5,9,12\text{-tetramethyl-1,4,8,11-tetraazacyclo tetradecane}$; $\text{X} = \text{H}_2\text{O}$, N_3^- , NCS^-) have an axially elongated octahedral geometry with two axial ligands and adopt the *trans*-III conformation.^{10,11} The different molecular topologies in these complexes may be due to the different coordination modes of anions.

In order to better understand some aspects of zinc(II) complexes of tetraaza macrocycle with axial ligands, we report the syntheses, crystal structures and chemical properties of the zinc(II) complexes $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2] \cdot 2\text{NO}_2$ and $[\text{Zn}(\text{L})(\text{NO}_3)_2]$ ($\text{L} = 3,14\text{-dimethyl-2,6,13,17-tetraaza tri-cyclo}[14,4,0^{1.18},0^{7.12}]$ docosane).

EXPERIMENTAL

Materials and Physical Measurements

All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo $[14,4,0^{1.18},0^{7.12}]$ docosane (**L**) was prepared according to the literature method.¹² IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer (Perkin-Elmer, Waltham, MA, USA) using KBr pellets. DSC and TGA (Mettler Toledo, Lausanne, Switzerland) were performed under flowing nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$ using an SDT 2960 Thermogravimetric Analyzer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN analyzer.



3,14-dimethyl-2,6,13,17-tetraazatricyclo $[14,4,0^{1.18},0^{7.12}]$ docosane

Synthesis of $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2] \cdot 2\text{NO}_2$ (**1**)

ZnCl_2 (136 mg, 1.0 mmol) and KNO_3 (170 mg, 2.0 mmol) were added to a methanol solution (20 mL) of **L** (336 mg,

Table 1. Crystallographic data

	1	2
Empirical formula	C ₂₀ H ₄₄ N ₆ O ₆ Zn	C ₂₀ H ₄₀ N ₆ O ₆ Zn
Formula weight	529.98	525.95
Temperature (K)	100(2)	100(2)
Crystal color/habit	Silver/block	Silver/block
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
Unit cell dimensions		
<i>a</i> (Å)	8.74650(10)	8.1292(5)
<i>b</i> (Å)	18.6880(3)	8.9244(5)
<i>c</i> (Å)	7.96680(10)	9.1398(5)
α (°)		68.035(2)
β (°)	109.1920(10)	70.109(2)
γ (°)		75.649(3)
<i>V</i> (Å ³)	1229.84(3)	572.70(6)
<i>Z</i>	2	1
<i>D</i> _{calc} (Mg m ⁻³)	1.431	1.525
Absorption coefficient (mm ⁻¹)	1.046	1.122
<i>F</i> (000)	568	280
Crystal size (mm ³)	0.22×0.18×0.14	0.30×0.25×0.08
θ range (°)	2.18 to 28.42	2.48 to 28.72
Limiting indices	$-11 \leq h \leq 11, -24 \leq k \leq 24, -10 \leq l \leq 10$	$-10 \leq h \leq 10, -11 \leq k \leq 11, -12 \leq l \leq 12$
Reflection collected/unique	31542/3073 (<i>R</i> _{int} = 0.0210)	13509/5326 (<i>R</i> _{int} = 0.0421)
Absorption correction	SADABS	SADABS
Max./min. transmission	0.8674 and 0.8026	0.9156 and 0.7295
Data/restraints/parameters	3073/0/153	5326/3/223
Goodness of fit on <i>F</i> ²	1.076	1.065
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0833, <i>wR</i> ₂ ^b = 0.2031	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.1021
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0870, <i>wR</i> ₂ = 0.2060	<i>R</i> ₁ = 0.0407, <i>wR</i> ₂ = 0.1033
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 8.0273P]$ with $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0510P)^2 + 0.5283P]$ with $P = (F_o^2 + 2F_c^2)/3$
Largest difference peak and hole (eÅ ⁻³)	4.871 and -1.852	1.266 and -0.917

^a*R*₁ = $\|F_o - |F_c|\|/\Sigma|F_o|$.^b*wR*₂ = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

1.0 mmol). The mixture was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until colorless crystal formed. The product was recrystallized from a hot H₂O/CH₃CN (1:1 v/v, 20 mL) mixture. Yield: 65%. Calc. (found) for C₂₀H₄₄N₆O₆Zn: C, 45.33 (45.26); H, 8.37 (8.48); N, 15.86 (15.75)%. IR (KBr, cm⁻¹): ν(NH) 3158, ν_{as} (O₂N) 1445, ν_s (O₂N) 1058, cm⁻¹.

Synthesis of [Zn(L)(NO₃)₂] (2)

This compound was synthesized as colorless crystals by a reaction similar to that of **1**, except for the use of KNO₃ instead of KNO₂. The product was recrystallized from a hot H₂O/CH₃CN (1:1 v/v, 20 mL) mixture. Yield: 65%. Calc. (found) for C₂₀H₄₄N₆O₆Zn: C, 45.33 (45.26); H, 8.37 (8.48); N, 15.86 (15.75)%. IR (KBr, cm⁻¹): ν(NH) 3166, ν_s(O₃N) 1356 cm⁻¹.

Crystallography

Single crystal X-ray diffraction measurement for compound was carried out on a Bruker APEX II CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were measured at 100(2) K by ω-2θ technique. Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied with the SADABS program.¹³ The structure was solved by direct methods¹⁴ and the least-squares refinement of the structure was performed by the SHELXL-97 program.¹⁵ For **1**, all atoms except all hydrogen atoms were refined anisotropically. For **2**, all atoms except all hydrogen atoms and 15 atoms (N2, N3, N4, N5, O2, O3, O4, O6, C6, C8, C10, C11, C14, C18, C20) were refined anisotropically. The hydrogen atoms were placed in calculated

positions allowing them to ride on their parent C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1032374 for compound **1** and 1032375 for compound **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The macrocyclic ligand skeleton of the present compounds adopts the most stable *trans*-III (*R,R,S,S*) configuration with two chair six-membered and two gauche five-membered chelate rings. The N-Zn-N angles of the six-membered chelate rings for the complexes are larger than those of the five-membered chelate rings.

An ORTEP drawing¹⁶ of $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]\cdot 2\text{NO}_2$ (**1**) with the atomic numbering scheme is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The title

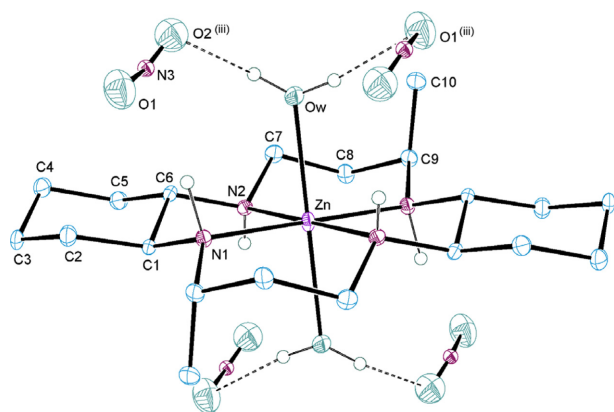


Figure 1. An ORTEP drawing (30% probability ellipsoids) of $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]\cdot 2\text{NO}_2$ (**1**) with the atomic numbering scheme. The hydrogen bonds are shown as dashed lines.

Table 2. Selected bond distances (Å) and angles (°) for $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]\cdot 2\text{NO}_2$ (**1**)

Zn-N(1)	2.118(3)	Zn-N(2)	2.087(3)
Zn-Ow	2.331(3)	N(3)-O(2)	0.767(5)
N(3)-O(1)#2	1.374(7)		
N(1)-Zn-N(2)	95.98(12)	N(1)-Zn-N(2)#1	84.02(12)
N(1)-Zn-Ow	94.17(12)	N(1)#1-Zn-Ow	85.83(12)
N(2)-Zn-Ow	90.67(12)	N(2)#1-Zn-Ow	89.33(12)
O(2)-N(3)-O(1)#2	135.6(6)		

Symmetry codes: (#1) $-x+1, -y+1, -z+1$ (#2) $-x+1, -y+1, -z$.

Table 3. Hydrogen bonding parameters (Å, °) for $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]\cdot 2\text{NO}_2$ (**1**)

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
Ow-HOw1...O(2)#3	0.84(7)	2.00(7)	2.826(6)	167(6)
Ow-HOw2...O(1)#3	0.81(6)	1.96(6)	2.759(6)	171(6)

Symmetry codes: (#3) $x, y, z+1$.

compound consists of a $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ cation and two nitrite anions. The coordination environment around Zn atom shows an axially elongated octahedron with four secondary amines of the macrocycle and two water molecules at the axial position. An inversion center exists on the central Zn atom. The Zn-N bond distances are 2.087(3) and 2.118(3) Å, which are similar to those found in $\text{Zn}(\text{O}_2\text{CoCH}_3)([\text{14}] \text{aneN}_4)(\text{ClO}_4)$ (2.088(3) and 2.111(3) Å).¹⁷ The Zn-Ow bond distance is 2.331(3) Å, which is comparable to that observed for *trans*- $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ (2.338(3) Å).¹⁸ The axial Zn-Ow linkage is not perpendicular to ZnN₄ plane as the Ow-Zn-N angles range from 85.83(12) to 94.17(12)°. Interestingly, the water molecules are hydrogen bonded to the nitrite anions [Ow-HOw1...O(2)#3 2.826(6) Å, 167(6)°; Ow-HOw2...O(1)#3 2.759(6) Å, 171(6)°; symmetry code #3: $x, y, z+1$ (Fig. 1 and Table 3).

An ORTEP drawing¹⁶ of $[\text{Zn}(\text{L})(\text{NO}_3)_2]$ (**2**) with the atomic numbering scheme is shown in Fig. 2. Selected bond distances and angles are listed in Table 4. The zinc(II) ion is coordinated by four nitrogen atoms of the macrocyclic ligand and two oxygen atoms of the nitrate ligand in a six-coordinated octahedral geometry. The average Zn-N (secondary amines) distance of 2.097(4) Å is very similar to that found for **1** and shorter than the axial Zn-O(1) and Zn-

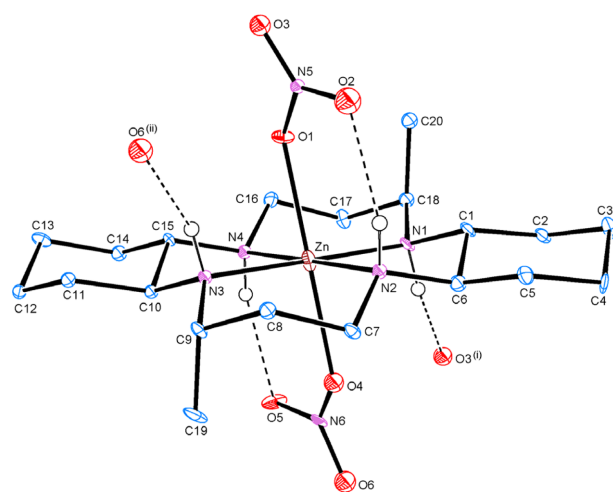


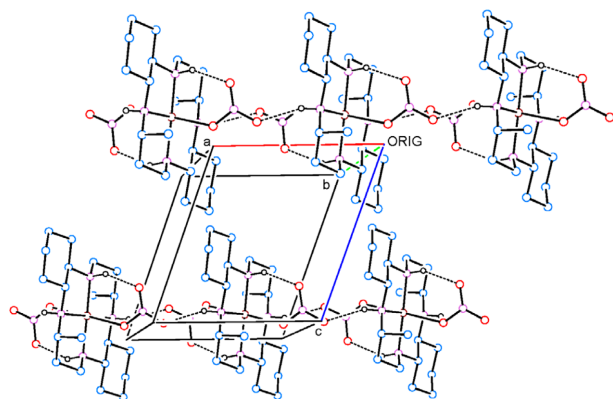
Figure 2. An ORTEP drawing (30% probability ellipsoids) of $[\text{Zn}(\text{L})(\text{NO}_3)_2]$ (**2**) with the atomic numbering scheme. The hydrogen bonds are shown as dashed lines.

Table 4. Selected bond distances (Å) and angles (°) for [Zn(L)(NO₃)₂] (**2**)

Zn-N(1)	2.125(5)	Zn-N(2)	2.044(4)
Zn-N(3)	2.107(5)	Zn-N(4)	2.111(4)
Zn-O(1)	2.299(4)	Zn-O(4)	2.306(4)
N(5)-O(1)	1.293(6)	N(5)-O(2)	1.240(7)
N(5)-O(3)	1.247(6)	N(6)-O(4)	1.204(7)
N(6)-O(5)	1.270(7)	N(6)-O(6)	1.254(6)
N(1)-Zn-N(2)	83.65(19)	N(1)-Zn-N(3)	179.4(3)
N(1)-Zn-N(4)	95.21(18)	N(2)-Zn-N(3)	96.63(17)
N(2)-Zn-N(4)	178.7(2)	N(3)-Zn-N(4)	84.52(19)
N(1)-Zn-O(1)	96.18(18)	N(2)-Zn-O(1)	94.72(16)
N(3)-Zn-O(1)	83.30(17)	N(4)-Zn-O(1)	86.03(16)
N(1)-Zn-O(4)	83.45(18)	N(2)-Zn-O(4)	86.34(16)
N(3)-Zn-O(4)	97.06(18)	N(4)-Zn-O(4)	92.90(16)
O(1)-Zn-O(4)	178.8(2)	Zn-O(1)-N(5)	133.1(3)
Zn-O(4)-N(6)	134.4(4)		

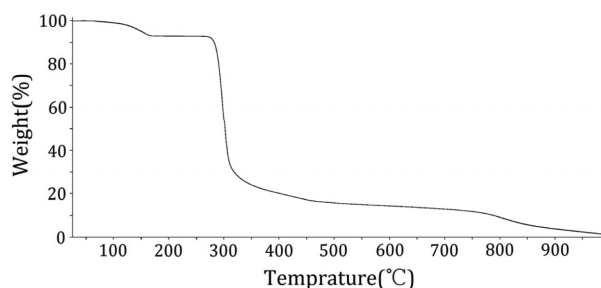
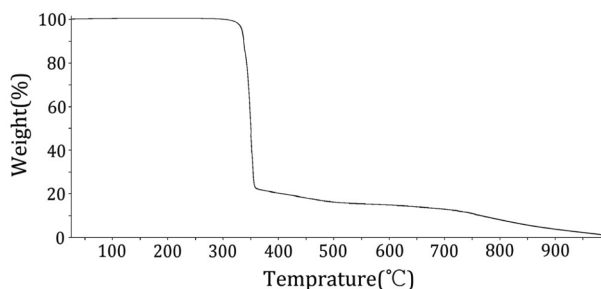
O(4) distances of 2.299(4) and 2.306(4) Å, giving an axially elongated octahedral geometry. Also, the axial Zn-O(1) and Zn-O(4) linkages are not perpendicular to the ZnN₄ plane with N-Zn-O(1) and N-Zn-O(4) angles of 83.30(17) and 97.06(18)°, respectively. The Zn-O(1)-N(5) and Zn-O(4)-N(6) angles related to the nitrate ligand are 133.1(3) and 134.4(4)°. Interestingly, the secondary amines of the macrocycle are also hydrogen bonded to the oxygen atoms of the nitrate groups [N(1)-H(1)···O(3)#1 2.997(6) Å, 152.1°; N(2)-H(2)···O(2) 2.998(7) Å, 152.4°; N(3)-H(3)···O(6)#2 3.020(6) Å, 150.2°; N(4)-H(4)···O(5) 2.970(6) Å, 149.7°], to form the one-dimensional hydrogen-bonded infinite chain (Fig. 3 and Table 5).

The IR spectra of the complexes **1** and **2** show bands at 3158 and 3166 cm⁻¹, corresponding to the ν(NH) of the coordinated secondary amines of the macrocycle. For **1**, the bands at 1445 and 1058 cm⁻¹ are assigned to the ν_{as}(O₂N)

**Figure 3.** A packing diagram of [Zn(L)(NO₃)₂] (**2**). The hydrogen bonds are shown as dashed lines.**Table 5.** Hydrogen bonding parameters (Å, °) for [Zn(L)(NO₃)₂] (**2**)

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)-H(1)···O(3)#1	0.93	2.14	2.997(6)	152.1
N(2)-H(2)···O(2)	0.93	2.14	2.998(7)	152.4
N(3)-H(3)···O(6)#2	0.93	2.18	3.020(6)	150.2
N(4)-H(4)···O(5)	0.93	2.13	2.970(6)	149.7

Symmetry code: (#1) x+1, y, z (#2) x-1, y, z.

**Figure 4.** Thermogravimetric curve of [Zn(L)(H₂O)₂].2NO₂ (**1**).**Figure 5.** Thermogravimetric curve of [Zn(L)(NO₃)₂] (**2**).

and ν_s(O₂N) of the nitrite group. For **2**, the strong band at 1356 cm⁻¹ is assigned to the ν_s(O₃N), which indicates the coordination of the oxygen atom between NO₃⁻ and Zn(II) atom. The TGA diagrams of **1** and **2** further support the structure determined by X-ray diffraction method (Fig. 4 and Fig. 5). The compounds were heated from 25 to 1000 °C in nitrogen gas. For **1**, the first weight loss is observed from 25 to 179 °C, which is due to the loss of two water molecules (observed 6.6%; calculated 6.8%). A second weight loss corresponding to the macrocycle and two nitrite ligands (observed 78.2%; calculated 77.8%) is found in the temperature range 242–581 °C. A final weight loss is observed above 581 °C corresponding to the black residue of ZnO (observed 15.2%; calculated 15.4%). For **2**, the first weight loss is observed from 251 to 546 °C, which is due to the loss of the macrocycle and two nitrate ligands (observed 84.7%; calculated 84.5%). Further weight loss is observed at 546–1000 °C and yields a black residue of ZnO (observed 15.3%, calculated 15.5%). The formation of ZnO accompanies the decomposition of the macrocycle ligand in the zinc(II) complex.¹⁹

CONCLUSION

The crystal structures of the compounds **1** and **2** show a distorted octahedral coordination geometry around the zinc(II) ion, with four secondary amines and two oxygen atoms of the two water and two nitrate ligands at the axial position. The secondary amines of the compound **2** are also hydrogen bonded to the oxygen atoms of the nitrate groups, to form the one-dimensional hydrogen-bonded infinite chain. The TGA behaviors of the complexes are significantly affected by the nature of the tetraaza macrocycle and the axial ligands.

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