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mer-R,S-[ZnL_2]($(NO_3)_2$), New Zinc Complex with *N*-(2-Aminoethyl)-1,3-propanediamine: Spectral and Structural Study

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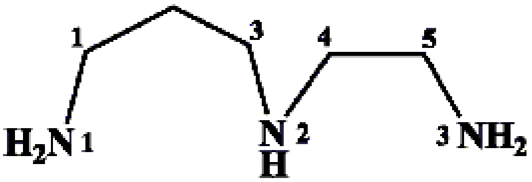
ABSTRACT

In this work, a new zinc complex of *N*-(2-aminoethyl)-1,3-propanediamine (L), *mer-R,S*-[ZnL_2]$(NO_3)_2$ (**1**), was prepared and identified by elemental analysis, FT-IR and Raman spectroscopy and single-crystal X-Ray diffraction. The zinc atom in **1** which is coordinated by four nitrogen atoms of the NH_2 groups and two nitrogen atoms of the NH groups has a distorted octahedral geometry. If the distortion in the $[ZnL_2]^{2+}$ cation is disregarded, it has a C_2 axis and C_2 symmetry. The dihedral angle between two planes of the coordinated atoms of each ligand confirms the *mer* conformation. The N–H···O hydrogen bonds between the nitrate and amine groups are presented in the crystal network of **1**.

Key words: Zinc Complex, *mer* Conformation, X-ray Crystal Structure, C_2 Symmetry.

INTRODUCTION

N-(2-Aminoethyl)-1,3-propanediamine (aepn) is a rather common tridentate amine ligand. It usually forms three coordination bonds with the same central atom[1] and only rarely aepn adopts bridging function[2]. In the past few years we have studied complexation of multi N-donor ligands[3"6]. In continuation of our previous studies, in this work the preparation of new zinc(II) complex, *mer-R,S*-[ZnL_2]$(NO_3)_2$ (1), with *N*-(2-aminoethyl)-1,3-propanediamine (L, scheme 1) was described. This complex was characterized by elemental analysis, FT-IR and Raman spectroscopy and X-ray crystallography.



Scheme 1: The structure of ligand

General methods

All starting chemicals and solvents were reagent or analytical grade and used as received. Raman spectra were obtained using a Nicolet Model 910 Fourier-transform spectrometer. The infrared spectrum of a KBr pellet was recorded in the range 4000–400 cm^{-1} using a FT-IR 8400-Shimadzu spectrometer. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Melting point was determined using a Barnsted Electrothermal 9200 electrically heated apparatus.

Synthesis of *mer-R,S*-$[ZnL_2](NO_3)_2$, 1.

$Zn(NO_3)_2.6H_2O$ (1 mmol, 0.30 g) was dissolved in EtOH (15 mL) and added with stirring to a solution of L (2 mmol, 0.23 g) in EtOH (5 mL). A colorless precipitate was formed and after 3 h was filtered and recrystallized from 1:1 H_2O/EtOH. Colorless crystals suitable for X-ray diffraction were obtained after 6 days. Yield (0.35 g) 82%; m.p.: 219 °C. Anal. Calcd for $C_{10}H_{30}N_8O_6Zn$ (%): C, 28.34; H, 7.14; N, 26.44. Found: C, 28.12; H, 7.11; N, 26.58. IR (KBr, cm^{-1}): 3313 s (ν_{as} NH_2), 3263 s (ν_s NH_2), 3163 s (ν NH), 2916 and 2870 m (ν CH_2), 1597 m (δ NH_2), 1381 vs (ν_4 NO_3), 1291 m (ν_1 NO_3), 1157 m (ν CN), 1088 m (ν_2 NO_3), 833 w (ν_6 NO_3), 625 w (ν ZnN). Raman (cm^{-1}): 2904 m and 2810 w (ν CH_2), 1534 m (δ NH_2), 1420 s (ν_4 NO_3), 1235 s (ν_1 NO_3), 1079 s (ν_2 NO_3), 600 m (ν ZnN).

Crystal structure determination and refinement

Suitable crystals of **1** were placed on an Oxford Diffraction Gemini Ultra diffractometer, and kept at 150.0 K during data collection. Using OLEX-II[7], the structures were solved with the SHELXS[8] structure solution program using Direct Methods and refined with the SHELXL[8] refinement package using least squares minimization. Table 1 contains crystallographic data and details of the data collection and structure refinement. Selected bond lengths (Å) and angles (°) and dimensions of the hydrogen bonds (Å and °) for complex are listed in table 2 and table 3, respectively.

RESULTS AND DISCUSSION

The reactions between L and ethanolic solution of zinc(II) nitrate provided colorless crystals of 1. This complex was characterized by IR and Raman spectroscopy and X-ray crystallography. It is air-stable and soluble in DMSO.

Presence of the RNH_2 group in **1** affect IR spectrum in two regions including 3313 and 3263 cm^{-1} for asymmetric and symmetric NH_2 stretches and 1597 cm^{-1} for NH_2 bending. Four bands in the IR spectrum near 1381, 1291, 1088, and 833 $cm^{˝1}$ for **1** can be assigned to vibrations of the nitrate groups ($í_4$, $í_1$, $í_2$ and $í_6$)[9]. The free nitrate ion has D_{3h} symmetry and three infrared active vibrations, but this symmetry is lowered to C_{2v} and C_s in metal complexes[10], to give up to six infrared active vibrations. In **1**, the nitrate groups are involved in hydrogen bonds lowering the symmetry. In the Raman spectrum of **1**, a band at 600 cm^{-1} was assigned to the Zn–N stretching vibration.

Description of the crystal structure

The crystal structure of **1** was determined by X-ray single-crystal diffraction. The molecular graphics were drawn with ORTEP-III[12] and Diamond [13].

Table 1: Crystal data and structure refinement for 1

Empirical formula	$C_{10}H_{30}N_8O_6Zn$
Formula weight (g $mol^{˝1}$)	423.79
Temperature (K)	150.0
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	11.3391(3)
b	12.3777(3)
c	13.4039(4)
β	90.284(3)
Volume ($Å^3$), *Z*	1881.24(9), 4
Calculated density (g cm^{-3})	1.496
Absorption coefficient (mm^{-1})	1.349
F(000)	896.0
Crystal size (mm^3)	0.09×0.08 ×0.01
2θ range for data collection (°)	6.58– 58.6
h, *k*, *l* ranges	-15:13, -13:16, -18:12
Reflections collected	9733
Independent reflections	4386
R_{int}	0.0273
Data / restraints / parameters	4386 / 0 / 226
Goodness-of-fit on F^2	0.941
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0605, wR_2 = 0.1576
R indices (all data)	R_1 = 0.0772, wR_2 = 0.1712
Largest diff. peak and hole (e.$Å^{-3}$)	1.55 and -0.53

Table 2: Selected bond length (Å) and angles (°) for 1 with estimated standard deviations in parentheses

Distances			
Zn1–N1	2.182(4)	N7–O1	1.250(6)
Zn1–N3	2.179(3)	N7–O2	1.236(6)
Zn1–N4	2.152(5)	N7–O3	1.224(6)
Zn1–N5	2.206(4)	N8–O4	1.225(7)
Zn1–N6	2.217(4)	N8–O5	1.247(7)
		N8–O6	1.235(7)
Angles			
N1–Zn1–N2	82.76(19)	O1–N7–O2	121.2(4)
N1–Zn1–N4	90.76(16)	O1–N7–O3	120.6(4)
N1"Zn1"N5	103.35(16)	O2–N7–O3	118.1(4)
N1–Zn1–N6	88.57(15)	O4–N8–O5	120.9(5)
N5–Zn1–N6	78.27(18)	O4–N8–O6	118.3(6)
N5–Zn1–N4	87.4(2)	O5–N8–O6	120.7(5)

Table 3: Dimensions of the hydrogen bonds (Å and °) in 1

D–H···A	*d*(D–H)	*d*(H···A)	<(DHA)	*d*(D···A)	Symmetry code
N1–H1A···O4	0.920	2.113	151.2	2.953(7)	*x, y, z*
N3–H3A···O2	0.921	2.102	174.6	3.020(6)	*x*, 0.5 - *y*, -0.5 + *z*
N3–H3B···O3	0.920	2.101	162.5	2.992(5)	*x, y, z*
N4–H4B···O6	0.920	2.121	167.1	3.025(7)	1 - *x*, 0.5 + *y*, 0.5 - *z*
N5–H5···O1	0.930	2.133	150.7	2.980(6)	*x*, 0.5 - *y*, -0.5 + *z*
N6–H6D···O1	0.920	2.126	178.3	3.046(6)	*x, y, z*

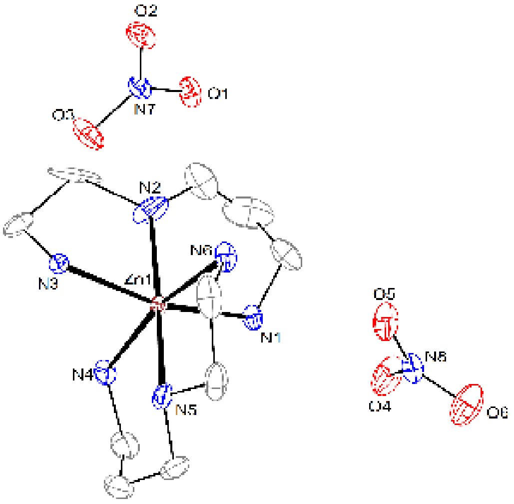


Fig. 1: The ORTEP-III diagram of the molecular structure of 1. The ellipsoids are drawn at the 50 % probability level

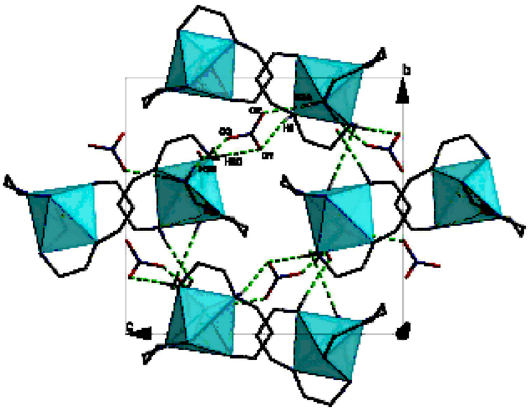


Fig. 2: Packing of 1, showing N–H···O hydrogen bonds in *bc* plane. Only the hydrogen atoms involved in hydrogen bonding are shown. Each ZnN_6 unit is shown as an octahedron

In the crystal structure of **1** (figure 1), zinc atom with coordination number six has a distorted octahedral geometry. Four sites are occupied by nitrogen atoms of the NH_2 groups with the Cd–N bond lengths in the range of 2.152(5)–2.217(4) Å. The two other sites are occupied by nitrogen atoms of the NH groups with the Cd–N bond lengths in the range of 2.202(7)–2.206(4) Å. Two ligands in **1** which act as tridentate forming two five- and two six-membered chelate rings with the zinc atom and not any of them are planar. The dihedral angle between two N1/N2/N3/Zn1 and N4/N5/N6/Zn1 plans is 89.78° that confirm the *mer* form. If the distortion in the $[ZnL_2]^{2+}$ cation is disregarded, it has a C_2 axis and C_2 symmetry. The ligands have no chiral center, but two new one (N2, N5) are formed after coordination[14] and have different enantiomeric forms. In the crystal network of **1** (figure 2), there are intermolecular N–H···O hydrogen bonds (table 3). The oxygen atoms in hydrogen bonds act as proton acceptors whereas the nitrogen atoms participate in hydrogen bonding as proton donors.

Supplementary material

CCDC 917541 for *mer-R,S*-$[ZnL_2](NO_3)_2$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving. html.

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