Pergamon

Polyhedron Vol. 16, No. 14, pp. 2393–2396, 1997

0277–5387/97 $17.00+0.00

PII: S0277–5387(96)00578–5

Preparation and structure of a macrocyclic thiocyanatotetraamine zinc(II) complex

Ki-Young Choi[a]* and Il-Hwan Suh[b]

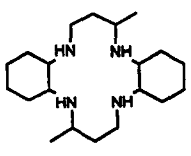
[a]Department of Chemistry, Mokwon University, Taejeon 301-327, Korea; [b]Department of Physics, Chungnam National University, Taejeon 305-764, Korea

(Received 24 October 1996; accepted 20 November 1996)

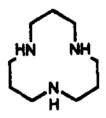
Abstract—The complex [Zn(L^1)(NCS)][NCS] (**1**) (L^1 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$, $0^{7.12}$]docosane) has been prepared from the reaction of [Zn(L^1)(H_2O)$_2$][Cl]$_2$ with sodium thiocyanate. The new complex has been characterized by spectroscopic and X-ray crystallographic methods. The crystal structure of **1** has revealed a five-coordinate, square-pyramidal geometry with an axial thiocyanate. © 1997 Elsevier Science Ltd

Keywords: macrocyclic thiocyanatotetraamine zinc(II) complex.

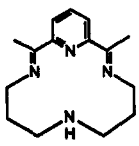
Macrocyclic polyamine complexes of zinc(II) have been of great interest for their importance as models of zinc-containing active centers in enzymes, such as carbonic anhydrase(CA) [1–4]. The thiocyanate anion is one of the typical CA inhibitors [5], which is due to the strong binding to the zinc ion [6]. Recent X-ray crystal analysis of the thiocyanate binding to the 1,5,9-triazacyclododecane (L^2) complex of zinc(II) showed a trigonal bipyramidal structure with two inequivalent thiocyanates (the equatorial Zn—NCS^- bond distance of 2.012 Å and the axial Zn—NCS^- bond distance of 2.119 Å) [7]. The zinc(II) complex of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadecane-1(17),2,11,13,15-pentaene (L^3) was also introduced as a CA model [8], since this model clearly displayed the essential role of the zinc ion. Recently, we have synthesized the zinc(II) chloride complex with modified cyclam, 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane(L^1) [9]. The crystal structure of this complex indicated that the zinc ion adopts an axially elongated octahedral environment with two water molecules (Zn—O bond distance 2.388 Å) and four equatorial nitrogens from the macrocycle. In this study we describe the preparation and structure of the zinc(II) complex of L^1 with thiocyanate ligands.



L^1



L^2



L^3

EXPERIMENTAL

Measurements

IR spectra were recorded as KBr pellets on a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer and ^{13}C NMR spectra with a Bruker GRX 300 spectrometer. High-resolution fast atom bombardment mass spectrometry (FAB-MS) was performed using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejeon, Korea.

Materials

All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocyclic ligand L^1 and complex [Zn(L^1)(H_2O)$_2$][Cl]$_2$ were prepared as described previously [9,10].

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*Author to whom correspondence should be addressed.

Synthesis of [Zn(L^1)(NCS)][NCS] (1)

To a methanol solution (20 cm^3) of [Zn(L^1)(H$_2$O)$_2$][Cl]$_2$ (200 mg, 0.39 mmol) was added KSCN (76 mg, 0.78 mmol) and the mixture refluxed for 1 h. The solution was then taken to dryness and the resulting solid dissolved in acetonitrile/water (1 : 1, 10 cm^3). When this mixture was allowed to stand for a few days, a quantity of colorless crystals were deposited. These were filtered off, washed with diethylether and desiccated until dry (230 mg, 76%). Found: C, 50.8; H, 7.7; N, 16.3. $ZnC_{22}H_{40}N_6S_2$ requires: C, 51.0; H, 7.8; N, 16.2%. IR (KBr, cm^{-1}): 3155 (νNH), 2031 (νC≡N), 1995 (νC≡N) 1309, 1271, 1168, 1098, 1005, 991, 949, 894, 786, 668. FAB mass (m/z): 460.04 $(M-NCS)^+$. ^{13}C NMR (CDCl$_3$, TMS reference, 25°C): δ 136.551 (NCS$^-$), 60.153, 56.728 (cyclohexane ring carbon), 47.500, 40.519, 34.560 (N—C—C—C—N), 29.309, 28.964, 24.173, 24.164 (cyclohexane ring carbon), 14.385 (CH$_3$).

X-ray crystallography

A summary of the data collection and details of the structure refinement is given in Table 1. A colorless crystal was mounted on an Enraf–Nonius CAD-4 diffractometer at 291 K. The unit-cell parameters and orientation matrix were obtained by the least-squares fit of 25 reflections. The intensity data were reduced using Lorentz and polarization corrections, but no absorption correction was applied. After the reduction step all calculations were performed using the NRCVAX PC software package [11]. The structure was solved by the heavy-atom method. All non-hydrogen atoms were placed with a combination of difference Fourier and least-squares calculations. Hydrogen atoms in methyl groups were located from difference-Fourier maps, other hydrogen atoms were placed in calculated positions. Anisotropic thermal parameters were used for all non-hydrogen atoms and isotropic thermal parameters were used with the hydrogen atoms. Hydrogen-atom positions were fixed during the least-squares process. Full crystallographic details, atomic coordinates, interatomic distances and angles, hydrogen-atom coordinates and anisotropic displacement parameters for **1** have been deposited with the editor as supplementary material. Structure factor tables may be obtained directly from the authors.

Table 1. Crystallographic data for [Zn(L^1)(NCS)][NCS] (1)

Formula	$ZnC_{22}H_{40}N_6S_2$
Formula weight	518.09
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.918(3)
b (Å)	18.816(2)
c (Å)	10.425(3)
β (°)	93.73(2)
V (Å^3)	2528.6(10)
Z	4
F(000)	1106.18
Crystal size (mm)	0.2 × 0.3 × 0.2
D_c (g cm^{-3})	1.361
Diffractometer	Enraf–Nonius CAD-4
λ (Mo-K_α) (Å)	0.71069
μ (Mo-K_α) (mm^{-1})	1.17
Scan method	ω–2θ
Scan width	0.8 + 0.34tanθ
2 θ range (°)	22.74 – 28.70
h,k,l range	−14–14, 0–20, 0–11
No. of unique reflections	2869
No. of observed reflections [$F_o > 3\sigma(F_o)$]	1846
No. of parameters	320
R^a	0.068
$R_w{}^b$	0.077
GoF^c	2.88

$^a R = \Sigma(F_o - F_c)/\Sigma(F_o)$.

$^b R_w = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o{}^2)]^{1/2}$.

$^c \mathrm{GoF} = [\Sigma w(F_o - F_c)^2/(\text{no. of rflns} - \text{no. params})]^{1/2}$.

RESULTS AND DISCUSSION

A drawing of **1** with the atomic numbering scheme is shown in Fig. 1 and selected bond lengths and angles in Table 2. The crystal structural analysis of **1** reveals a five-coordinate, square-pyramidal geometry with one bound thiocyanate ion. The zinc ion is 0.417(5) Å above the N$_4$ square plane and shifted toward the thiocyanate nitrogen atom (N5), which occupies the axial position at 2.028(11) Å. The Zn—N(5)—C(21) angle of 131.2(10)° is less bent than that found in [Zn(L^2)(NCS)$_2$] (152.1°) [7]. This fact implies that a donation of SCN$^-$ of **1** is stronger than that of the axial SCN in [Zn(L^2)(NCS)$_2$]. The nitrogen atom [N(6)] of the other thiocyanate is located 2.992(18) Å from the N$_4$ plane, but displaced from the axial position of the N$_4$ plane to the point where it is closer to N(4) than to zinc(II) [N(6)—N(4) = 3.048(16) Å *vs* N(6)—Zn = 4.102(14) Å]. This is most likely a result

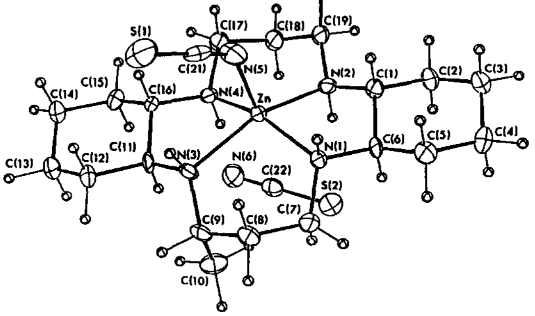

Fig. 1. ORTEP drawing of **1**, showing the atomic labeling scheme.

Table 2. Selected bond lengths (Å) and angles (°) for $[Zn(L^1)(NCS)][NCS]$ (**1**)

Zn—N(1)	2.095(9)	N(1)—C(7)	1.503(16)
Zn—N(2)	2.130(10)	N(2)—C(1)	1.482(17)
Zn—N(3)	2.197(10)	N(2)—C(19)	1.514(16)
Zn—N(4)	2.074(11)	N(3)—C(9)	1.526(16)
Zn—N(5)	2.028(11)	N(3)—C(11)	1.446(16)
Zn···N(6)	4.102(14)	N(4)—C(16)	1.508(16)
S(1)—C(21)	1.620(17)	N(4)—C(17)	1.513(16)
S(2)—C(22)	1.655(17)	N(5)—C(21)	1.144(20)
N(1)—C(6)	1.507(15)	N(6)—C(22)	1.123(22)

N(1)—Zn—N(2)	83.2(4)	Zn—N(4)—C(17)	112.4(9)
N(1)—Zn—N(3)	95.0(4)	C(16)—N(4)—C(17)	112.2(9)
N(1)—Zn—N(4)	158.9(4)	Zn—N(5)—C(21)	131.2(10)
N(1)—Zn—N(5)	100.7(5)	Zn—N(6)—C(22)	113.0(10)
N(2)—Zn—N(3)	155.6(4)	N(1)—C(6)—C(1)	108.9(9)
N(2)—Zn—N(4)	92.3(4)	N(1)—C(6)—C(5)	111.2(11)
N(2)—Zn—N(5)	109.5(4)	N(1)—C(7)—C(8)	111.2(10)
N(3)—Zn—N(4)	80.6(4)	N(2)—C(1)—C(2)	108.0(10)
N(3)—Zn—N(5)	94.8(4)	N(2)—C(1)—C(6)	108.6(10)
N(4)—Zn—N(5)	100.2(5)	N(2)—C(19)—C(18)	109.0(11)
N(5)—Zn—N(6)	146.0(5)	N(2)—C(19)—C(20)	111.4(12)
Zn—N(1)—C(6)	109.2(7)	N(3)—C(9)—C(8)	108.5(10)
Zn—N(1)—C(7)	117.1(8)	N(3)—C(9)—C(10)	111.4(11)
C(6)—N(1)—C(7)	111.1(9)	N(3)—C(11)—C(12)	112.8(11)
Zn—N(2)—C(1)	104.3(7)	N(3)—C(11)—C(16)	111.8(9)
Zn—N(2)—C(19)	115.6(7)	N(4)—C(16)—C(11)	105.0(9)
C(1)—N(2)—C(19)	116.2(10)	N(4)—C(16)—C(15)	113.6(11)
Zn—N(3)—C(9)	119.4(8)	N(4)—C(17)—C(18)	107.7(10)
Zn—N(3)—C(11)	108.7(7)	S(1)—C(21)—N(5)	177.9(14)
C(9)—N(3)—C(11)	116.7(10)	S(2)—C(22)—N(6)	176.1(14)
Zn—N(4)—C(16)	107.9(7)		

of hydrogen-bonding interactions rather than coordinate covalent interactions with the zinc atom. The nonbonded thiocyanate ion forms hydrogen bonds N(6)···H—N(4) 3.048(16) Å with the macrocycle and N(6)···H—N(1)^i ($-0.5+x$, $0.5-y$, $-0.5+z$) 3.016(17) Å with an adjacent zinc(II) complex (Fig. 2). The average Zn—N distance (2.124 Å) in the N_4-donor complex is slightly longer than that observed in $[Zn(L^1)(H_2O)_2][Cl]_2$ (2.099 Å) [9]. The IR CN stretching frequencies ν_{CN} of 2031 and 1995 cm^{-1} are assigned to the nonbonded shorter N≡C distance of 1.123(22) Å and the axial N≡C distance of 1.144(20) Å, respectively. This is as expected by comparison with FAB mass spectra of $[Zn(L^1)(NCS)]^+$ (*m/z* 460.04). The ^{13}C NMR spectrum of complex **1** in $CDCl_3$ clearly shows 11 resolved singlets, indicating that **1** contains 11 different types of carbon atoms. The N—Zn—N angles of the six-membered chelate rings of **1** are larger than those of the five-membered chelate rings. The methyl group on a six-membered chelate ring is *anti* with respect to the N_4 plane. As in the solid-state structure of $[Zn(L^1)(H_2O)_2][Cl]_2$ [9], **1** also adopts a thermodynamically most stable *trans*-III conformations in the solid state.

Acknowledgment—This work was supported by the Research Fund of Mokwon University, 1996.

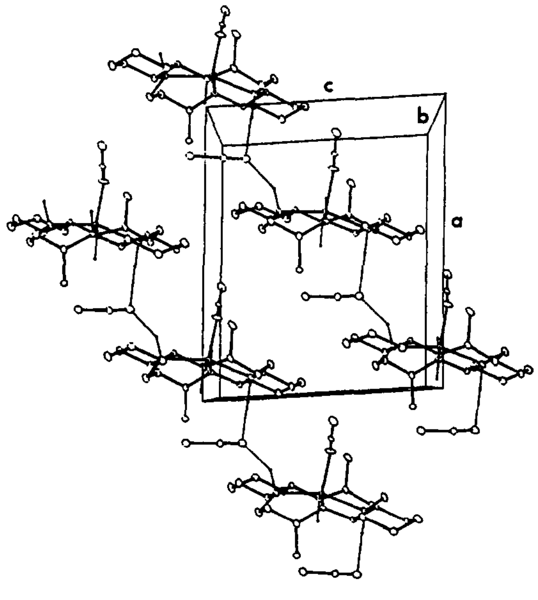

Fig. 2. Crystal packing in the unit cell of **1**, showing the hydrogen bonds. The *a* axis is vertical, whereas the *c* axis runs horizontally.

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