Crystal Structures of Nickel(II) and Zinc(II) Complexes with 6-Ethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6-diene

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The nickel(II) and zinc(II) complexes of 6-ethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6-diene were synthesized and their crystal structures were determined by single-crystal X-ray diffractometry. The crystal system of NiLCl is monoclinic with the space group of $P2_1/c$ and $Z = 4$. The unit cell dimensions are $a = 8.452(2)\text{\AA}$, $b = 12.781(3)\text{\AA}$ and $c = 17.893(3)\text{\AA}$ with $\beta = 98.38(2)^\circ$, $V = 1912.2(7)\text{\AA}^3$. The crystal system of ZnLCl is monoclinic with the space group of $C2/c$ and $Z = 8$. The unit cell dimensions are $a = 24.860(3)\text{\AA}$, $b = 11.209(2)\text{\AA}$ and $c = 18.252(2)\text{\AA}$ with $\beta = 116.959(7)^\circ$, $V = 4533.4(9)\text{\AA}^3$. The nickel(II) ion of NiLCl is coordinated through four nitrogen atoms to form a square-planar geometry and the zinc(II) ion has a square-pyramid geometry with four nitrogen atoms in a plane and one chloride atom at an axial position.

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Our recent research has been concerned with structural and spectroscopic properties of tetraazamacrocyclic complexes. Although much attention has been paid to the chemistry of tetraaza[14]annulene having a conjugated π -electron system, 1,4,8,11-tetraazacyclotetradecane as saturated macrocycle and 1,4,8,11-tetraazacyclotetradeca-1,7-diene having an unconjugated π -electron system, there have been only a few studies of macrocycles having a partly conjugated π -electron system. We have already reported the syntheses and the spectral properties in organic solutions of 16-ethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6-diene and its nickel(II), zinc(II) and palladium(II) complexes.¹ Ansell *et al.* reported the synthesis and crystal structure of a nickel(II) perchlorate complex with 16-methyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6-diene.² In this paper, we describe the X-ray structure determination of nickel(II) and zinc(II) complexes of 16-ethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6-diene having counterions of chloride.

The preparative procedures for NiLCl and ZnLCl have been reported previously.¹ Recrystallization of NiLCl and ZnLCl·H₂O from ethanol and/or chloroform-ethanol (1:2 v/v) gave single crystals for X-ray diffraction study. Data collections were performed at room temperature with graphite monochromatized Cu- $K\alpha$ radiation on a Rigaku AFC7R diffractometer ($\lambda = 1.5418$

$\text{\AA}$). The structure was solved by direct methods (SIR92) and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms; all hydrogen atoms were

Table 1 Crystal and experimental data

	NiLCl	ZnLCl
Formula	C ₂₀ H ₂₃ N ₄ ClNi	C ₂₀ H ₂₃ N ₄ ClOZn
Formula weight	413.58	438.28
Crystal dimensions	0.04 × 0.2 × 0.7 mm	0.3 × 0.3 × 0.5 mm
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
<i>Z</i>	4	8
<i>a</i>	8.452(2) $\text{\AA}$	24.860(3) $\text{\AA}$
<i>b</i>	12.781(3) $\text{\AA}$	11.209(2) $\text{\AA}$
<i>c</i>	17.893(3) $\text{\AA}$	18.252(2) $\text{\AA}$
β	98.38(2) $^\circ$	116.959(7) $^\circ$
<i>V</i>	1912.2(7) $\text{\AA}^3$	4533.4(9) $\text{\AA}^3$
<i>D</i> _{calc}	1.437 g/cm ³	1.284 g/cm ³
Radiation	1.5418 $\text{\AA}$ (Cu $K\alpha$)	1.5418 $\text{\AA}$ (Cu $K\alpha$)
μ (Cu $K\alpha$)	28.24 cm ⁻¹	27.07 cm ⁻¹
No. of reflections used	2847	4097
$2\theta_{\text{max}}$	120.1 $^\circ$	136.2 $^\circ$
Residuals; <i>R</i> ; <i>R</i> _w	0.103; 0.194	0.147; 0.271
Residuals; <i>R</i> 1	0.065	0.071
Goodness of fit indicator	1.96	1.99
$(\Delta f)_{\text{max}}$	0.001	0.004
$(\Delta\rho)_{\text{max}}$	1.05 e $\text{\AA}^{-3}$	1.80 e $\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	-0.89 e $\text{\AA}^{-3}$	-0.60 e $\text{\AA}^{-3}$
Measurement	Rigaku AFC7R	Rigaku AFC7R
Program system	teXsan	teXsan
Structure determination	direct methods (SIR92)	direct methods (SIR92)
Refinement	full-matrix least-squares	full-matrix least-squares

Fig. 1 Chemical structure of the title complex.

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$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \text{ for } I > 2.0 \sigma(I)$$

Table 2 Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

atom	x	y	z	U_{eq}
NiLCl				
Ni(1)	0.23788(8)	0.14260(5)	0.01470(3)	5.42(3)
Cl(1)	0.0093(1)	0.24916(7)	-0.16973(5)	6.43(3)
N(1)	0.2233(4)	0.2037(3)	0.1067(2)	5.52(9)
N(2)	0.2097(4)	0.0077(2)	0.0468(2)	5.53(9)
N(3)	0.2596(5)	0.0838(3)	-0.0815(2)	6.1(1)
N(4)	0.2671(4)	0.2811(3)	-0.0226(2)	5.73(10)
C(1)	0.2377(5)	0.3569(3)	0.0346(3)	5.9(1)
C(2)	0.2282(6)	0.4633(4)	0.0211(3)	7.3(1)
C(3)	0.1927(7)	0.5289(4)	0.0771(3)	7.7(2)
C(4)	0.1643(6)	0.4885(4)	0.1449(3)	7.0(1)
C(5)	0.1755(6)	0.3818(4)	0.1589(2)	6.9(1)
C(6)	0.2144(5)	0.3152(3)	0.1036(2)	5.7(1)
C(7)	0.2146(6)	0.1539(3)	0.1706(2)	6.1(1)
C(8)	0.2101(5)	0.0466(3)	0.1790(2)	6.0(1)
C(9)	0.2028(5)	-0.0202(3)	0.1180(2)	5.7(1)
C(10)	0.2020(5)	-0.0676(3)	-0.0115(2)	5.7(1)
C(11)	0.1697(6)	-0.1742(4)	-0.0051(3)	6.9(1)
C(12)	0.1696(7)	-0.2381(4)	-0.0673(3)	7.7(2)
C(13)	0.1993(7)	-0.1984(5)	-0.1353(3)	8.7(2)
C(14)	0.2272(7)	-0.0934(4)	-0.1419(3)	8.2(2)
C(15)	0.2294(5)	-0.0296(3)	-0.0801(2)	6.3(1)
C(16)	0.4187(6)	0.1096(5)	-0.1034(3)	7.8(2)
C(17)	0.4403(8)	0.2247(5)	-0.1151(3)	7.8(2)
C(18)	0.4277(6)	0.2923(5)	-0.0472(3)	7.3(2)
C(19)	0.2108(7)	0.0004(4)	0.2574(3)	7.3(1)
C(20)	0.3735(9)	-0.0310(6)	0.2949(3)	10.1(2)
ZnLCl				
Zn(1)	0.28147(2)	0.02322(5)	0.57852(3)	5.03(2)
Cl(1)	0.25130(6)	0.0599(1)	0.44205(7)	6.63(4)
O(1)	0.3751(4)	-0.2237(6)	0.9418(4)	16.4(3)
N(1)	0.2603(2)	-0.1460(3)	0.5979(2)	5.16(9)
N(2)	0.3707(2)	-0.0222(3)	0.6335(2)	5.7(1)
N(3)	0.3226(2)	0.1894(4)	0.6363(2)	6.03(10)
N(4)	0.2061(2)	0.0569(4)	0.6040(2)	5.79(10)
C(1)	0.1701(2)	-0.0510(5)	0.5787(3)	6.0(1)
C(2)	0.1088(2)	-0.0480(6)	0.5581(4)	7.6(2)
C(3)	0.0760(2)	-0.1555(7)	0.5336(4)	9.0(2)
C(4)	0.1050(3)	-0.2612(6)	0.5333(4)	7.9(2)
C(5)	0.1647(2)	-0.2607(5)	0.5536(3)	6.7(1)
C(6)	0.1988(2)	-0.1560(4)	0.5771(2)	5.3(1)
C(7)	0.2968(2)	-0.2386(4)	0.6194(3)	5.8(1)
C(8)	0.3587(2)	-0.2354(4)	0.6436(3)	6.1(1)
C(9)	0.3922(2)	-0.1319(4)	0.6506(3)	5.9(1)
C(10)	0.4070(2)	0.0773(5)	0.6391(3)	6.2(1)
C(11)	0.4636(2)	0.0728(6)	0.6418(3)	7.4(2)
C(12)	0.4933(3)	0.1814(7)	0.6428(4)	8.7(2)
C(13)	0.4667(3)	0.2890(6)	0.6409(4)	9.0(2)
C(14)	0.4111(3)	0.2928(5)	0.6369(4)	8.0(2)
C(15)	0.3808(2)	0.1886(4)	0.6379(3)	6.3(1)
C(16)	0.3278(2)	0.1947(5)	0.7205(3)	7.3(1)
C(17)	0.2660(3)	0.1979(6)	0.7179(3)	7.8(2)
C(18)	0.2308(2)	0.0798(6)	0.6936(3)	7.5(2)
C(19)	0.3918(3)	-0.3538(5)	0.6632(4)	8.2(2)
C(20)	0.4176(4)	-0.3933(8)	0.7481(6)	12.2(3)

located from subsequent difference Fourier maps. The crystal and experimental data are given in Table 1. Atomic coordinates and equivalent isotropic parameters are listed in Table 2. The ORTEP drawings of nickel(II) and zinc(II) complexes are shown in Fig. 2. The crystal structure of NiLCl shows that the nickel(II) atom of NiLCl has a square-planar geometry with four N atoms of the macrocycle. The mean deviation from the 4N planes is 0.003 Å and the displacement of metal ion from the plane of four nitrogens is 0.088 Å. In addition, the slope for two benzene planes of the macrocycles is 1.8 degrees. This shows that the two benzene rings and the double bond chain N1-C7-C8-C9-N2 are nearly coplanar. The metal atom and the aliphatic chain N3-C16-C17-C18-N4 adopt a chair configuration. The chlorate anion is not bound to a nickel(II) atom but to two amine protons with hydrogen bonds: N-Cl 3.189, 3.234 Å. The bond lengths of Ni-N3 and Ni-N4 (aliphatic chain: 1.912(3) and 1.920(3) Å) of NiLCl are longer than those of Ni-N1 and Ni-N2 (double bond chain: 1.842(3) and 1.844 Å). On the other hand, the crystal structure of ZnLCl shows that the zinc ion has a square-pyramidal geometry with four nitrogen atoms in a plane and a chloride atom at an axial position. The water molecule is

Fig. 2 ORTEP drawing of the title complexes. a, NiLCl; b, ZnLCl·H₂O

bonded to an amine proton by a hydrogen bond (O(1)···N(4), 3.047(7) Å). Therefore, the displacement of Zn from the 4N atom plane of the macrocycle is 0.65 Å toward the Cl atom and the inclination of the two benzene planes is 16.7°. The bond lengths of Zn-N3 and Zn-N4 (aliphatic chain: 2.157(4) and 2.160(4) Å) of ZnLCl are longer than those of Zn-N1 and Zn-N2 (double bond chain: 2.042(4) Å). The displacement of Zn from the 4N atom plane of ZnLCl are larger than that of [ZnL'Cl](ClO₄) (0.453 Å, L' = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane³ and 0.542 Å, L' = 1,4,7,11-tetraazacyclotetradecane⁴) having aliphatic macrocycle, and/or [Zn(tmtaa)N(C₂H₅)₃] (0.563 Å, H₂tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecene) and [Zn(py)(TC-3,3)] (0.57 Å, TC-3,3 = 6,7,8,9,16,17,18,19-octahydrodicyclohepta[b,i]-[1,4,8,11]tetraazacyclotetradecene)⁵ having aromatic macrocycle.

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