

**THE CRYSTAL AND MOLECULAR STRUCTURE OF A ZINC(II) COMPLEX WITH A NEW NON-SYMMETRICAL TETRADENTATE SCHIFF BASE, [Zn(C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O)Br]**

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The structure of (1-(2-(2-aminoethylamino)ethylimino)methyl-2-naphtholato-*O,N,N',N''*)bromozinc(II), [Zn(naden)Br], containing a new Schiff base ligand, naden, was solved by Patterson and Fourier techniques and refined anisotropically to  $R = 0.047$  for 1 426 unique observed reflections. The complex crystallizes in the space group *Pbca* with lattice parameters  $a = 14.024(1)$ ,  $b = 10.699(1)$ ,  $c = 21.635(2)$  Å,  $Z = 8$ . The structure of [Zn(C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O)Br] complex molecule consists of two six-membered aromatic rings and one six-membered and two five-membered chelate rings. The distorted coordinate polyhedron around Zn atom is formed by N1, N2, N3 and O atoms of the naden ligand and Br anion. Unusually short C–C bond in five-membered rings as well as small N–C–C–N torsion angles and somewhat large C4–C3–N2 and N2–C2–C1 angles are probably connected with intense thermal vibrations of C2 and C3 atoms. The structure is held together by weak hydrogen bonds.

The complexes with non-symmetrical multidentate Schiff bases are interesting model systems for investigation of various metalloenzymes<sup>1</sup>. So far the structures of these type of complexes have been described with so-called saden<sup>2</sup>, saltrien<sup>3</sup>, baden<sup>4</sup>, and aden<sup>5</sup> ligands. Molecules of the first three ligands contain one benzene aromatic ring, which influences both structure and properties of related complexes. The present paper describes the structure of the complex containing a new tetradentate Schiff base ligand, naden, prepared by a condensation of diethylenetriamine with 2-naphthol-1-carbaldehyde. The aim of the present study is to demonstrate, whether, and in which way, the second aromatic ring of the naden ligand influences the structure of coordination compounds.

## EXPERIMENTAL

To the methanolic solution of ZnBr<sub>2</sub> (2.25 g, 0.01 mol) was slowly added equivalent amount of diethylenetriamine and then 2-naphthol-1-carbaldehyde in the same solvent. Resulting solution was neutralized by NaOH and after filtration allowed to stand in air. Small yellowish crystals were separated during several days; yield 1.2 g (30%). Density was determined by flotation method in cold

carbon tetrachloride. For  $C_{15}H_{18}BrN_3OZn$  (401.6) calculated: 44.9% C, 4.5% H, 19.9% Br, 10.5% N, 16.3% Zn; found: 45.2% C, 4.7% H, 19.6% Br, 10.5% N, 16.1% Zn.

### Crystal Structure Determination

Orthorhombic system, space group  $Pbca$ ,  $a = 14.024(1)$ ,  $b = 10.699(1)$ ,  $c = 21.635(2)$  Å,  $V = 3\ 246.0(6)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calc}} = 1.644$ ,  $D_{\text{exp}} = 1.63$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 39.9$  cm<sup>-1</sup>,  $F(000) = 1\ 616$ . The structure was solved by the heavy atom method and subsequent standard Fourier techniques. Atoms H were fixed in calculated positions with fixed  $U_{\text{iso}}$  values of 1.3 times of the  $U_{\text{eq}}$  value of the attached atoms. All non-H atoms were refined anisotropically by block-diagonal least-squares based on  $F$  magnitudes. Empirical correction for absorption was made<sup>6</sup>. Data collection and structure refinement are listed in Table I.

TABLE I  
Data collection and refinement parameters

Crystal dimension	0.35 × 0.20 × 0.25 mm
Diffractometer and radiation used	Enraf-Nonius C4D4, MoK $\alpha$ , $\lambda = 0.71073$ Å
Scan technique	$\omega/2\theta$
No. and $\theta$ range of reflections for lattice parameter refinement	25; 21 – 22°
Range of $h$ , $k$ and $l$	0 → 16, -12 → 12, 0 → 24
Maximum value of $(\sin \theta)/\lambda$	0.572
Standard reflections	3 0 -2, 2 2 -2
Standard reflections monitored in interval; intensity fluctuation	120 min; -0.2%
Total number of reflections measured; $2\theta$ range	4 938; 0 – 48°
Value of $R_{\text{int}}$	0.051
No. of unique observed reflections	1 426
Criterion for observed reflections	$I \leq 1.96 \sigma(I)$
Function minimized	$\sum w ( F_o  -  F_c )^2$
Weighting scheme	$w = 0.38/[\sigma^2 F_o + 0.0009 F_c^2]$
Parameters refined	190
Value of $R$ , $wR$ and $S$	0.047, 0.046, 0.58
Ratio of max. LS shift to e.s.d. in the last cycle	0.001
Max. and min. heights in final $\Delta\rho$ map	0.71, -0.49 e Å <sup>-3</sup>
Source of atomic scattering factors	SHELX76 (ref. 7)
Programs used	SDP (ref. <sup>8</sup> ), SHELX76 (ref. <sup>7</sup> ), SHELX86 (ref. <sup>9</sup> ), PARST (ref. <sup>10</sup> )
Computer used	PDP 11/73, PC 486

## RESULTS AND DISCUSSION

The final positional and thermal parameters for non-H atoms are listed in Table II. Bond distances and angles are summarized in Table III. Figure 1 shows the studied complex molecule, the crystal packing is depicted in Fig. 2. The coordination polyhedron around Zn atom is formed by N1, N2, N3, O and Br atoms and can be described either as a distorted trigonal bipyramid (Zn, N1, N3, Br are approximately in plane) or square pyramid (N1, N2, N3, O in basal plane). The first four atoms lie better in the minimum squares plane (with the maximum deviation of 0.219(6) Å for N1, compared with the deviation of 0.253(8) Å for N2 from the best N1, N2, N3, O plane), which somewhat favours the trigonal bipyramidal arrangement. According to the values of bond angles around the central atom, however, the pyramidal arrangement seems to be more

TABLE II  
Atomic coordinates ( $\cdot 10^4$ ) for non-H atoms and their equivalent isotropic thermal parameters ( $\cdot 10^3$ ) with estimated standard deviations (e.s.d.'s) in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
Br	2256.0(6)	321.1(9)	84.2(4)	63.6(3)
Zn	991.9(6)	1022.3(8)	766.1(5)	45.7(3)
O	350(4)	-570(5)	1049(2)	51(2)
N1	1337(5)	1301(6)	1662(3)	57(2)
N2	1266(5)	3058(6)	770(4)	63(3)
N3	-166(4)	1614(6)	234(3)	52(2)
C1	1626(9)	2565(9)	1810(6)	107(5)
C2	1391(12)	3402(11)	1379(7)	153(7)
C3	471(9)	3595(10)	491(11)	250(12)
C4	-217(7)	2969(9)	217(5)	79(4)
C5	537(5)	-1238(7)	1529(4)	45(3)
C6	1061(5)	-808(7)	2050(4)	41(2)
C7	1368(5)	466(7)	2099(4)	51(3)
C8	181(6)	-2496(8)	1544(4)	56(3)
C9	399(6)	-3277(8)	2015(4)	58(3)
C10	941(6)	-2921(8)	2518(4)	50(3)
C11	1203(6)	-3749(9)	3001(5)	67(4)
C12	1746(7)	-3403(11)	3484(5)	78(4)
C13	2081(7)	-2190(11)	3527(4)	74(4)
C14	1833(6)	-1342(9)	3076(4)	61(3)
C15	1274(5)	-1685(8)	2558(4)	47(3)

appropriate. The value of the parameter  $t$  (ref.<sup>11</sup>) is 0.381, which is also closer to the value for square pyramidal ( $t = 0.0$ ) than trigonal bipyramidal ( $t = 1.0$ ) structure.

The complex molecule consists of two six-membered aromatic rings, containing only carbon atoms, one six-membered and two five-membered chelate rings containing the metal ion. Five-membered Zn,N2,C3,C4,N3 ring has an almost symmetrical envelope

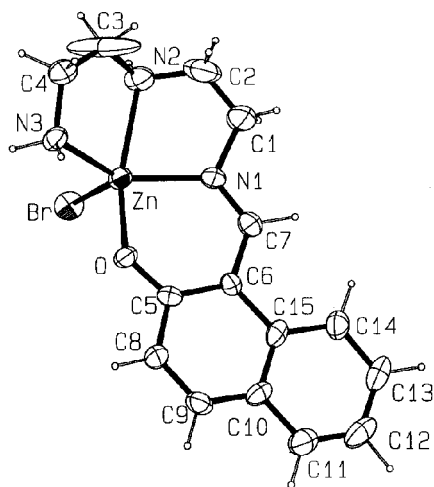


FIG. 1  
View of molecule with atom numbering. Thermal ellipsoids are scaled to 50% probability

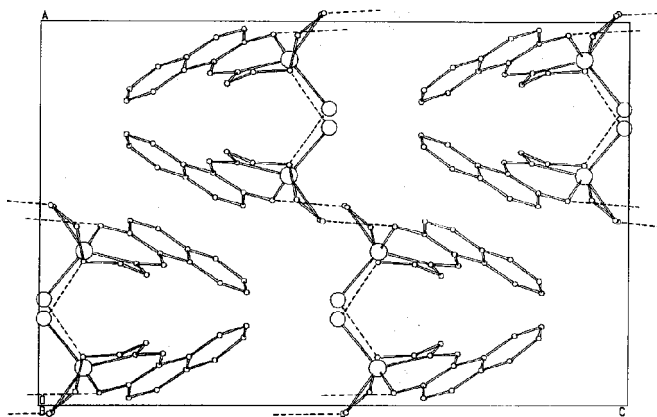


FIG. 2  
Crystal packing. Dashed lines indicate hydrogen bonds

TABLE III

Bond distances (Å), angles (°) and hydrogen bond contact. Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $1/2 - x, 1/2 + y, z$ . E.s.d's in parentheses

Atoms	Distances	Atoms	Distances
Br–Zn	2.425(1)	C5–C6	1.422(12)
Zn–O	2.022(5)	C5–C8	1.436(11)
Zn–N1	2.020(7)	C6–C7	1.433(11)
Zn–N2	2.212(7)	C6–C15	1.476(12)
Zn–N3	2.089(6)	C8–C9	1.353(12)
O–C5	1.288(10)	C9–C10	1.381(12)
N1–C1	1.448(12)	C10–C11	1.418(13)
N1–C7	1.302(10)	C10–C15	1.405(12)
N2–C2	1.379(17)	C11–C12	1.345(15)
N2–C3	1.392(17)	C12–C13	1.383(16)
N3–C4	1.452(12)	C13–C14	1.377(14)
C1–C2	1.334(18)	C14–C15	1.416(12)
C3–C4	1.316(18)		
Atoms	Angles	Atoms	Angles
Br–Zn–N3	109.1(2)	N3–C4–C3	117.4(9)
Br–Zn–N2	100.4(2)	O–C5–C8	117.9(7)
Br–Zn–N1	117.0(2)	O–C5–C6	124.4(7)
Br–Zn–O	104.4(2)	C6–C5–C8	117.7(7)
N2–Zn–N3	80.7(3)	C5–C6–C15	119.3(7)
N1–Zn–N3	132.1(3)	C5–C6–C7	121.4(7)
N1–Zn–N2	79.0(3)	C7–C6–C15	119.3(7)
O–Zn–N3	94.3(2)	N1–C7–C6	126.1(8)
O–Zn–N2	155.0(3)	C5–C8–C9	121.2(8)
O–Zn–N1	86.6(2)	C8–C9–C10	123.2(8)
Zn–O–C5	128.4(5)	C9–C10–C15	119.4(8)
Zn–N1–C7	127.1(5)	C9–C10–C11	123.4(8)
Zn–N1–C1	114.7(6)	C11–C10–C15	117.2(8)
C1–N1–C7	118.1(8)	C(10)–C(11)–C(12)	123.2(9)
Zn–N2–C3	105.4(6)	C11–C12–C13	120.2(10)
Zn–N2–C2	106.8(7)	C12–C13–C14	119.0(9)
C2–N2–C3	114.0(10)	C13–C14–C15	122.0(9)
Zn–N3–C4	110.8(5)	C10–C15–C14	118.5(8)
N1–C1–C2	113.8(10)	C6–C15–C14	122.5(8)
N2–C2–C1	121.3(11)	C6–C15–C10	119.0(7)
N2–C3–C4	124.9(10)		
Hydrogen bonds	Lengths	Hydrogen bonds	Lengths
N3...O <sup>i</sup>	3.003(8)	N2...Br <sup>ii</sup>	3.516(8)
H2N3...O <sup>i</sup>	2.031(8)	HN2...Br <sup>ii</sup>	2.656(7)
N3–H2N3...O <sup>i</sup>	163.5(6)	N2–HN2...Br <sup>ii</sup>	144.0(6)

conformation with unusually small value of N2–C3–C4–N3 torsion angle,  $3(2)^\circ$ . The shape of the chelate ring is also reflected in the deviations of C3 and C4 atoms from the Zn,N2,N3 plane which are 0.17(2) and 0.15(1) Å, respectively. Deviations of C1 and C2 from the Zn,N1,N2 plane are  $-0.09(1)$  and 0.18(2) Å, respectively, which indicate a flat half-chair conformation of the Zn,N1,C1,C2,N2 chelate ring. The value of the N1–C1–C2–N2 torsion angle,  $-25(2)^\circ$ , is also smaller than the majority of these values in related compounds. Six-membered pseudoaromatic ring Zn,O,C5,C6,C7,N1 assumes a half-boat conformation with Zn atom 0.503(2) Å above the best plane of the other five atoms. The last plane is only slightly tilted with the plane of C5,C6,C8,C9,C10, and C15 atoms of the adjacent aromatic ring, the dihedral angle being  $3.4(3)^\circ$ . The value of the dihedral angle between best planes of two aromatic rings is  $3.2(2)^\circ$ .

The most surprising feature of the ligand structure is extremely short C–C bond distances in the five-membered chelate rings, namely 1.33(2) Å and 1.32(1) Å for C1–C2 and C3–C4 bond, respectively, which are the shortest C–C bonds in the whole structure. This short distances are apparently a consequence of intense thermal vibrations of C2 and C3 atoms. The same reason explains rather large values of N2–C2–C1 and N2–C3–C4 angles,  $121(1)^\circ$  and  $125(1)^\circ$ , respectively.

Only weak hydrogen bonds were found in the structure, namely N3–H2N3...O<sup>i</sup> ( $-x, -y, -z$ ) and N2–HN2...Br<sup>ii</sup> ( $1/2 - x, 1/2 + y, z$ ); the donor–acceptor distances are 3.003(8) and 3.516(8) Å, respectively.

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