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[(*S*,*S*)-*N*-(1-{6-[1-(Dimethylamino)ethyl]-pyridin-2-yl}ethyl)-*N*,*N*-dimethylamine-κ^3N]dibromozinc(II)

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The title compound, $[ZnBr_2(C_{13}H_{23}N_3)]$, (3), was readily prepared from the reaction between $ZnBr_2$ and (*S*,*S*)-(1–6-[1-(dimethylamino)ethyl]-2-pyridinylethyl)-*N*,*N*-dimethylamine. (3) exists as a distorted square pyramid and crystallizes with two independent molecules in the asymmetric unit. The apical position of the square pyramid is occupied by one of the Br atoms, with the base of the pyramid consisting of the three N atoms of the ligand and the other Br atom. This is the first reported structure determination of a compound containing the C_2-symmetric molecule (*S*,*S*)-*N*-(1-{6-[1-(dimethylamino)-ethyl]pyridin-2-yl}ethyl)-*N*,*N*-dimethylamine.

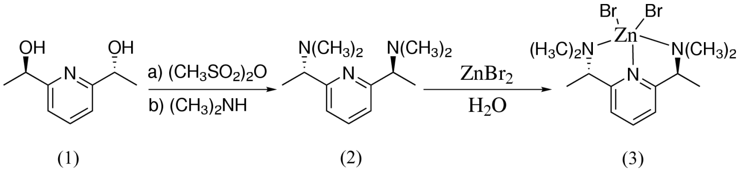
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.009 Å
R factor = 0.051
wR factor = 0.131
Data-to-parameter ratio = 21.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Zinc complexes are important in organic chemistry due to the their central role in many enantioselective reactions (Denmark & Beutner, 2002; Lebel *et al.*, 2003; Soai, 1999) and biological systems (Auld, 2001; Lipscomb & Strater, 1996; Vallee & Auld, 1993). In our ongoing program that aims at developing ligands for molecular recognition of biologically important compounds (Chin *et al.*, 1999; Mancin & Chin, 2002), we wish to report the synthesis and the X-ray analysis of complex (3) from the optically active C_2-symmetric ligand (*S*,*S*)-*N*-(1-{6-[1-(dimethylamino)ethyl]pyridin-2-yl}ethyl)-*N*,*N*-dimethylamine, (2), and zinc(II) bromide.



Ligand (2) was prepared from the readily available chiral diol (*R*,*R*)-(BHEP), (1) (Brown *et al.*, 1997), where BHEP = 2,6-bis(1-hydroxyethyl)pyridine, through its reaction with methanesulfonic anhydride and dimethylamine in acetonitrile (see Scheme). The substitution reaction proceeded through conversion of stereochemistry to afford the (*S*,*S*) enantiomer of ligand (2), which was then complexed with zinc(II) bromide to produce compound (3).

In the crystal structure of (3), there are two molecules, *A* and *B*, in the asymmetric unit (Figs. 1 and 2). The coordination geometry of compound (3) is a distorted square pyramid, with the apical position occupied by a Br atom (Br1). The three N atoms of the ligand and the other Br atom (Br2) occupy the base of the pyramid. The Zn atom is displaced by 0.668 (2) and 0.675 (2) Å in molecules *A* and *B*, respectively, towards atom Br1 from the least-squares plane formed by N1/N2/N3/Br2. The maximum deviations from these planes are for atoms N2*A*

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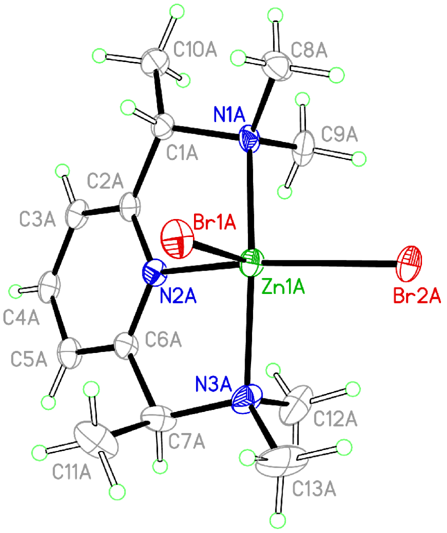

Figure 1
View of molecule *A* of (3), with the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

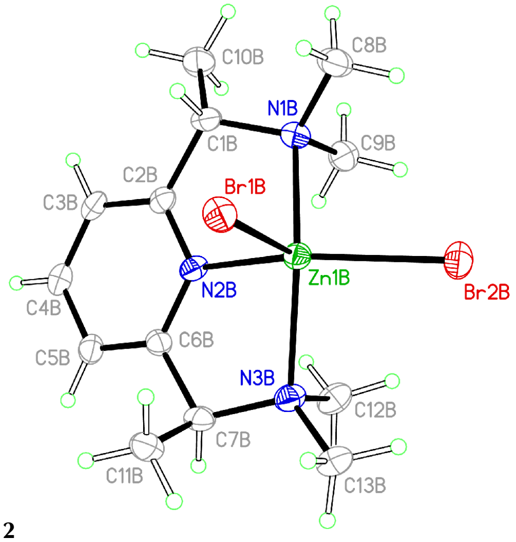

Figure 2
View of molecule *B* of (3), with the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

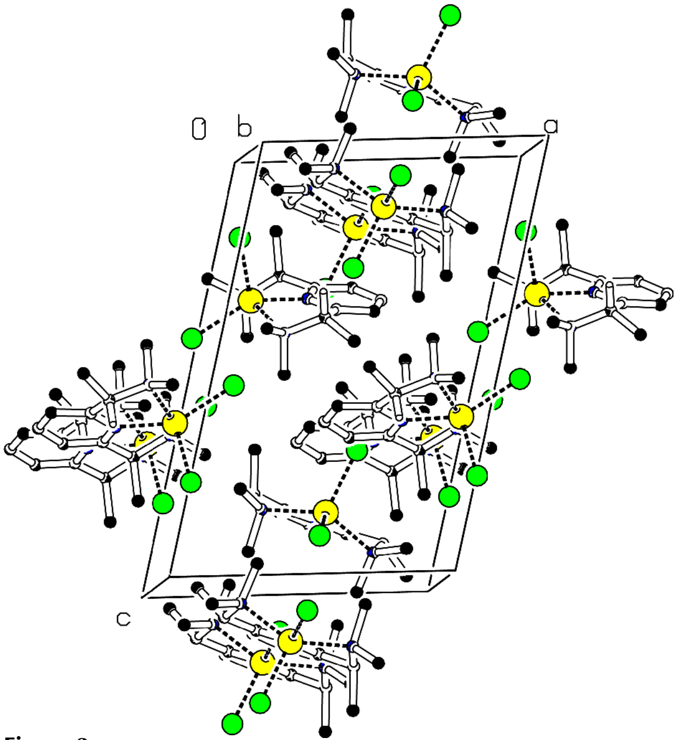

Figure 3
Packing diagram (Spek, 2002) of (3), viewed bown the *b* axis. Colour codes: green Br, yellow Zn, blue N, and black C.

[0.027 (3) Å] and N2*B* [0.103 Å]. An analysis (Cremer & Pople, 1975) of the puckering of the five-membered metallacycle (Zn1/N1/C1/C2/N2), where the C atom (C10) is equatorial to the chelate ring, gives Q_t values of 0.412 (5) and 0.424 (5) Å for molecules *A* and *B*, respectively. The puckering of the five-membered metallacycle (Zn1/N3/C7/C6/N2), where the C atom (C11) is axial to the chelate ring, gives Q_t values of 0.404 (6) and 0.414 (5) Å for molecules *A* and *B*, respectively. The conformations of each five-membered ring in both molecules is 'envelope', with a local pseudo-twofold axis running along N1 and the mid-point of the C2—N2 bond or N3 and the mid-point of the C6—N2 bond (Duax *et al.*, 1976). The angles N2—Zn1—N1 of 76.00 (17) and 75.61 (19)°, and N2—Zn1—N3 of 74.85 (18) and 74.15 (19)° for molecules *A* and *B*, respectively, are considerably smaller than the ideal angle of 90° for a square pyramid. These angles are due to the formation of strained five-membered chelate rings and the distortion in the square pyramid environment around the Zn atom. The Zn—$N_{pyridine}$ bond length in molecules *A* and *B* [average 2.106 (5) Å], is comparable to the corresponding bond lengths in other ligands with pyridine complexed to Zn^{II} (Canary *et al.*, 1998; Comba *et al.*, 2002). The only differences between the two molecules in (3) are the values of some of the angles at the Zn center; the most notable of these are N3*A*—Zn1*A*—Br1*A* of 108.90 (16)° and N3*B*—Zn1*B*—Br1*B* of 113.89 (14)°. These differences, which may be apparent on viewing Figs. 1 and 2, can only be attributable to packing forces.

Experimental

2,6-Bis(1-hydroxyethyl)pyridine, (1) (1.21 g, 7.21 mmol), was dissolved in 40 ml dry acetonitrile. Pyridine (3.00 ml, 37.2 mmol) was added to this solution and the mixture was cooled to 273 K in an ice bath. Methanesulfonic anhydride (3.00 g,16.7 mmol) was added to this mixture under an atmosphere of argon. The clear yellow solution turned cloudy after 5 min. This mixture was stirred at room temperature for an additional 30 min and the precipitate was filtered off. Dimethylamine (20 ml, 40.0 mmol) from a 2 *M* tetrahydrofuran solution was added to the golden brown filtrate and this mixture was stirred at room temperature for 24 h. The precipitate was filtered off and the organic solvents removed under reduced pressure. The remaining residue was partitioned between (30 ml) chloroform and (20 ml) saturated aqueous solution of Na_2CO_3. The aqueous layer was further extracted with (30 ml) chloroform and the two organic extracts were combined, dried over anhydrous sodium sulfate and the solvent evaporated to afford the crude product, (2), as a brown oil. This oil was chromatographed on silica with dichloromethane/methanol (8:2) as eluant to afford the pure product (2) as a yellow oil

(1.31 g, 82%). ^{1}H NMR, 300 MHz ($CDCl_3$): 7.60 (*t*, J = 7.7 Hz, 1H), 7.21 (*d*, J = 7.7 Hz, 2H), 3.48 (*q*, J = 6.6 Hz, 2H), 2.24 (*s*, 12H), 1.36 (*d*, J = 6.6 Hz, 6H). ^{13}C NMR, 100 MHz ($CDCl_3$): δ 162.5, 136.6, 119.8, 67.2, 43.1, 19.1. Zinc(II) bromide (183 mg, 0.813 mmol) in 1.5 ml H_2O was added to (2) (18.0 mg, 81.3 µmol). The precipitate was collected and dissolved in hot ethanol (2.0 ml). Slow evaporation of the ethanol at room temperature afforded crystals of (3) suitable for X-ray analysis.

Crystal data

$[ZnBr_2(C_{13}H_{23}N_3)]$
M_r = 446.53
Monoclinic, $P2_1$
a = 9.9680 (2) Å
b = 11.5077 (2) Å
c = 15.4906 (4) Å
β = 103.712 (1)°
V = 1726.26 (6) Å^3
Z = 4
D_x = 1.718 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24950 reflections
θ = 2.6–27.5°
μ = 6.04 mm^{-1}
T = 150 (1) K
Block, colourless
0.35 × 0.30 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans from κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.131, T_{max} = 0.234
12530 measured reflections
7418 independent reflections
6981 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 27.5°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.131
S = 1.06
7418 reflections
344 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.0739P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0082 (10)
Absolute structure: Flack (1983); 3292 Friedel pairs
Flack parameter = −0.021 (13)

Table 1
Selected geometric parameters (Å, °).

Zn1*A*—N2*A*	2.110 (4)	Zn1*B*—N2*B*	2.101 (5)
Zn1*A*—N1*A*	2.234 (4)	Zn1*B*—N1*B*	2.241 (5)
Zn1*A*—N3*A*	2.241 (6)	Zn1*B*—N3*B*	2.269 (5)
Zn1*A*—Br1*A*	2.4025 (8)	Zn1*B*—Br1*B*	2.4109 (8)
Zn1*A*—Br2*A*	2.4401 (8)	Zn1*B*—Br2*B*	2.4504 (9)
N2*A*—Zn1*A*—N1*A*	76.00 (17)	N2*B*—Zn1*B*—N1*B*	75.61 (19)
N2*A*—Zn1*A*—N3*A*	74.85 (18)	N2*B*—Zn1*B*—N3*B*	74.15 (19)
N1*A*—Zn1*A*—N3*A*	139.05 (18)	N1*B*—Zn1*B*—N3*B*	135.45 (19)
N2*A*—Zn1*A*—Br1*A*	104.93 (12)	N2*B*—Zn1*B*—Br1*B*	100.44 (13)
N1*A*—Zn1*A*—Br1*A*	105.97 (13)	N1*B*—Zn1*B*—Br1*B*	103.14 (13)
N3*A*—Zn1*A*—Br1*A*	108.90 (16)	N3*B*—Zn1*B*—Br1*B*	113.89 (14)
N2*A*—Zn1*A*—Br2*A*	146.82 (12)	N2*B*—Zn1*B*—Br2*B*	149.60 (13)
N1*A*—Zn1*A*—Br2*A*	95.11 (11)	N1*B*—Zn1*B*—Br2*B*	96.46 (14)
N3*A*—Zn1*A*—Br2*A*	93.81 (14)	N3*B*—Zn1*B*—Br2*B*	93.45 (14)
Br1*A*—Zn1*A*—Br2*A*	108.25 (3)	Br1*B*—Zn1*B*—Br2*B*	109.96 (3)

All H atoms bonded to C atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 1.00 Å, and included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of the carrier atom. The deepest hole (−1.64 e Å^{-3}) is 0.79 Å from Br2*A*.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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