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Bis[μ-2-benz(oxa/thia)zolyl-2-phenolato-κ^3*N*,*O*:*O*]bis{bis[2-benz(oxa/thia)zolyl-2-phenolato-κ^2*N*,*O*]zinc(II)}

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In the crystal structure of the title compound, $[Zn_2(C_{13}H_4NO_{1.67}S_{0.33})_4]$, the ring O atom in the benz(oxa/thia)zolyl-2-phenolate anions is disordered with respect to the S atom. The anions chelate to the Zn atom; the phenoxy O atom of two of them is also bridged to an adjacent molecule so that the geometry of the Zn atom in the centrosymmetric dimer is a trigonal bipyramid.

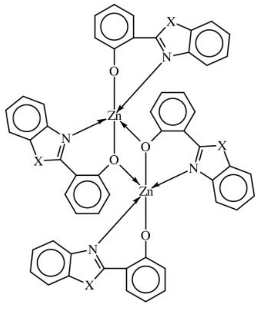
Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.115
Data-to-parameter ratio = 13.8

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

Comment

Bis(2-benzthiazolyl-2-phenolato)zinc is an excellent electroluminescent compound that can be used in light-emitting diodes; its crystal structure has been recently determined in order to relate the observed properties with the three-dimensional arrangement of atoms in the solid state (Yu *et al.*, 2003). The deprotonated organic reagent chelates to a number of metal atoms, and the structure of several 2-benzthiazolyl-2-phenolates have been reported; the anion binds through the phenoxy O and the thiazolyl N atoms to furnish a six-membered chelate ring. The structure of the reagent has been known for more than 30 years (Stenson, 1970). This compound and the oxazolyl analog are commercially available; however, the structure of 2-benzoxazolyl-2-phenol has not been determined and an aluminium derivative, $(C_{13}H_8NO_2)_4(OH_2)Al_2$, appears to have been crystallographically verified (Hoveyda *et al.*, 1993). That of the 4-methyl-substituted complex with Mn^{III} has also been reported (Asada *et al.*, 1999).



(I)

We had thought of synthesizing the mixed-ligand zinc complex, $(C_{13}H_8NO_2)(C_{13}H_8NOS)Zn$, in order to examine its electronic structure, but the mixed system we obtained was a compound in which the O and S atoms in both chelating groups are statistically disordered. The refinement yielded a formula that approximated a 2:1 ratio of O to S in each anion, so that the compound can be alternatively regarded as the cocrystal $[(C_{13}H_8NO_2)_2Zn]_2\cdot[(C_{13}H_8NOS)_2Zn]$, (I). The compound exists as a dimer (Fig. 1), and the anions chelate to the Zn atom; the O atom of one of them is linked to the Zn atom of another molecule across a centre of symmetry, rendering the metal atom five-coordinate in a *trans*-trigonal bipyramidal environment. The bond dimensions involving the Zn atom are similar to those (Yu *et al.*, 2003) found in $(C_{13}H_8NOS)_2Zn$, but the two compounds are not isomorphous.

Experimental

Zinc acetate dihydrate (0.11 g, 0.5 mmol), 2-(benzthiazol-2-yl)phenol (0.11 g, 0.5 mmol) (Acros), 2-(benzoxazol-2-yl)phenol (0.11 g, 0.5 mol) (Aldrich), water (10 ml) were placed in a 23 ml Teflon-lined stainless steel Parr bomb. The bomb was heated at 443 K for 96 h, after which it was cooled to room temperature at 5 K h^{-1} to give crystals. Elemental analysis calculated for $C_{52}H_{32}N_4O_{6.67}S_{1.33}Zn_2$: C 62.90, H 3.25, N 5.64%; found: C 62.51, H 3.32, N 5.57%. Measurements performed on several specimens all gave the same structure, *i.e.* the cocrystal; neither bis(2-benzoxazolyl-2-phenolato)zinc nor bis(2-benzthiazolyl-2-phenolato)zinc could be found among the crystals.

Crystal data

$[Zn_2(C_{13}H_4NO_{1.67}S_{0.33})_4]$
M_r = 992.96
Triclinic, $P\overline{1}$
a = 9.5356 (7) Å
b = 9.6262 (7) Å
c = 11.6413 (8) Å
α = 81.701 (1)°
β = 82.397 (1)°
γ = 85.453 (1)°
V = 1046.1 (1) Å^3
Z = 1
D_x = 1.576 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3074 reflections
θ = 2.6–24.6°
μ = 1.28 mm^{-1}
T = 293 (2) K
Block, green–yellow
0.23 × 0.10 × 0.09 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.749, T_{max} = 0.888
8361 measured reflections
4180 independent reflections
3423 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 26.3°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.115
S = 0.99
4180 reflections
304 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O3	2.090 (2)	Zn1—N1	2.119 (3)
Zn1—O3^i	2.002 (2)	Zn1—N2	2.068 (3)
Zn1—O4	1.967 (2)		
O3—Zn1—O3^i	77.4 (1)	O3^i—Zn1—N1	118.2 (1)
O3—Zn1—O4	174.7 (1)	O3^i—Zn1—N2	119.2 (1)
O3—Zn1—N1	82.9 (1)	O4—Zn1—N1	94.9 (1)
O3—Zn1—N2	97.1 (1)	O4—Zn1—N2	88.2 (1)
O3^i—Zn1—O4	99.5 (1)	N1—Zn1—N2	121.0 (1)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The title crystal is a cocrystal having the formulation $(C_6H_4NCX–C_6H_4O)_2Zn$ where $X = (O_x, S_{1-x})$; for both independent $C_6H_4NCX–C_6H_4O$ anions, the O atom is disordered with respect to the S atom although the C atoms connected to them are not disordered. As such, when the pair of S—C distances was restrained to a fixed value, the corresponding pair of O—C distances was instead restrained to equal each other. The S—C distance was satisfactorily restrained to 1.750 (5) Å; the use of a small deviation led to four distances that were somewhat similar to each other. The resulting bond dimensions in the group are considered to be reasonable when compared with the bond dimensions found in the parent 2-benzthiazolyl-2-phenol (Aydin *et al.*, 1999; Stenson, 1970), as well as those found in bis(2-benzthiazolyl-2-phenolato)zinc (Yu *et al.*, 2003). The O—C distances were retrained to be approximately equal. The resulting bond dimensions of the benzoxazolyl unit are also regarded as being acceptable when compared with those found in, for example, 5-chloro-2-(4-*tert*-butylphenyl)benzoxazole (Mrozek *et al.*, 1999); the structure of the parent substituted phenol is not known and the bond dimensions for the closely related 2-phenylbenzoxazole (Rao & Murthy, 1966) are unavailable. The displacement parameters of the disordered atoms in each group were constrained to be equal to each other; additionally, the displacement parameters were restrained to be approximately isotropic. As the occupancy factors of both S atoms refined to almost 0.33, the value of X in the $C_6H_4NCX–C_6H_4O$ entities was then assumed to be 2/3, *i.e.* $X = \frac{1}{3}S + \frac{2}{3}O$. The formula from the refinement is in excellent agreement with the elemental analysis. H atoms were placed at calculated positions in the riding-model approximation (C—H = 0.93 Å) with their displacement parameters tied to those of the parent atoms; $U_{iso}(H) = 1.2U_{eq}(C)$.

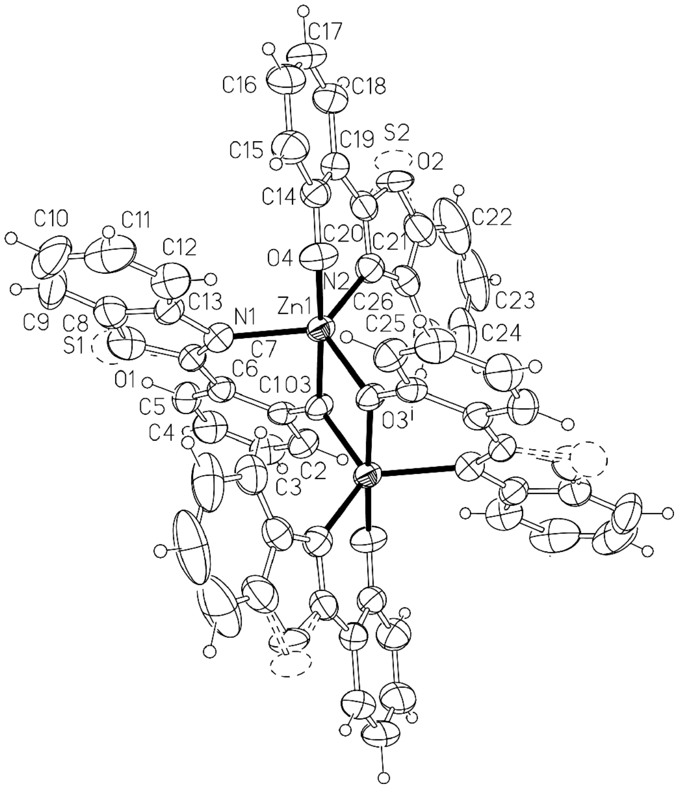


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Minor component S atoms are shown as dashed ellipses.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

*ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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