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A dimeric heteroleptic five-coordinate zinc(II) complex containing a non-motionally restricted *N*,*N*′-heterocyclic ligand

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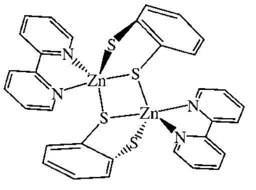
The title compound, bis(μ-1,2-benzenethiolato)-1:2κ^3S,S':S';-2:1κ^3S,S':S'-bis[(2,2′-bipyridine-κ^2N,N')zinc(II)], [$Zn_2(\mu$-$C_6H_4S_2)_2(C_{10}H_8N_2)_2$], crystallizes with the dinuclear molecule located on a center of symmetry. The coordination geometry about the Zn atom is a modestly distorted trigonal bipyramid, with the axial ligating atoms at an angle of 170.81 (4)° and the angles in the equatorial plane in the range 112.94 (4)–129.95 (4)°. Weak π-stacking interactions between bipyridine ligands on adjacent molecules [interplanar spacing = 3.315 (3) Å] and a possible weak intermolecular C—H⋯S hydrogen bond (H⋯S = 2.84 Å) are seen in the crystal.

Comment

There have been numerous investigations of heteroleptic d^{10} complexes involving Zn^{II} or Cd^{II} compounds that employ *N*,*N*′-heterocycles and either two monothiolate ligands or one dithiolate ligand (Koester, 1975; Crosby *et al.*, 1985; Kutal, 1990). These highly colored and luminescent compounds exhibit strong absorptions in the visible region of the spectrum, which have been assigned as a metal-mediated ligand-to-ligand charge-transfer (LLCT) transition (Muresan & Muresan, 1979; Fernandez & Kisch, 1984; Highland & Crosby, 1985; Truesdell & Crosby, 1985; Highland *et al.*, 1986; Reddy *et al.*, 1992; Galin *et al.*, 1993; Gronlund *et al.*, 1995; Zemskova *et al.*, 1998). It has been reported that mononuclear tetrahedral complexes of Zn^{II} are generally obtained when the motionally restricted benzenedithiolate (bdt) ligand is used with *N*,*N*′-heterocycles that are more sterically hindered (Yam *et al.*, 1999; Lowther *et al.*, 2001). When non-substituted *N*,*N*′-heterocyclic ligands are employed with the bdt ligand, unusual multinuclear complexes are observed with both the zinc(II) and the cadmium(II) systems (Gronlund *et al.*, 1995; Halvorsen *et al.*, 1995; Wang *et al.*, 2000; Lowther *et al.*, 2001; Hatch *et al.*, 2003). The geometry of these complexes has been reported to depend on the planarity of the ligands used. We report here that the addition of 1,2-benzenedithiol (bdt) and 2,2′-bipyridine (bipy) to zinc(II) acetate dihydrate in hot ethanol/dimethylformamide forms the dinuclear title complex [Zn(bdt)(bipy)]$_2$, (I).



(I)

Complex (I) has crystallographically imposed centrosymmetry (Fig. 1), with the Zn^{II} atom exhibiting a modestly distorted trigonal-bipyramidal coordinate geometry. The major distortions involve the N1—Zn—N2 and S1—Zn—S2 angles (see Table 1) and result from the geometrical constraints of the bipy and bdt ligands. Also of note is the N1—Zn—S1 angle, which deviates from linearity by only ~10°. This geometry contrasts with that of the closely related complex [Cd(bdt)(ophen)]$_2$ (ophen is 1,10-phenanthroline), in which the corresponding angle is 154.40 (4)° (Lowther *et al.*, 2001). In the latter complex, the angles between the formally equatorial substituents corresponding to the S2—Zn—N2, S2—Zn—S1′ and N2—Zn—S1′ angles in (I) are, respectively, 140.00 (4), 121.74 (2) and 97.09 (4)°, so that the coordination sphere of the cadmium complex is considerably more distorted from trigonal bipyramidal than is that of (I). The mean planes of the two halves of the bipy ligand in (I) are inclined at an angle of 12.80 (8)°, and the ring containing atom N2 shows a weak π-stacking interaction with the counterpart ring at $(1 - x, -y, 1 - z)$. These rings are parallel, separated by 3.315 (3) Å. Also present is a possible weak C—H⋯S hydrogen bond between atom H2 and atom S2 in the asymmetric unit located at $(2 - x, 1 - y, 1 - z)$ [H⋯S = 2.84 Å, C⋯S = 3.637 (2) Å and C—H⋯S = 143°]. These values can be compared with the values (H⋯S = 2.63 Å, C⋯S = 3.53 Å

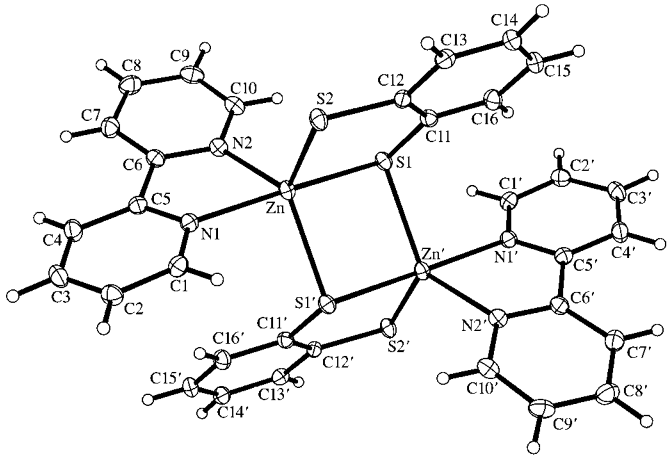


Figure 1
A perspective view of (I). Primed atoms are related to the non-primed atoms by the crystallographic center $(-x, -y, 2 - z)$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii for clarity.

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and C—H···S = 158°) attributed to a C—H···S hydrogen bond between a solvent chloroform molecule and (η^4-Me$_8$taa)GeS (Me$_8$taa is the octamethyldibenzotetraaza-[14]annulene dianion; Kuchta & Parkin, 1994; Steiner, 1998).

Experimental

Zinc acetate dihydrate (219.5 mg, 1 mmol; Fisher Scientific) was dissolved in hot ethanol (10 ml) and a room-temperature solution of 1,2-benzenedithiol (142.2 mg, 1 mmol; Aldrich) in ethanol (5 ml) was added dropwise with stirring. The resulting white precipitate was dissolved by dropwise addition of dimethylformamide, followed by dropwise addition of 2,2-bipyridine (bipy) (156.2 mg, 1 mmol; Aldrich) dissolved in hot ethanol (10 ml). The resulting deep-yellow solution was refluxed for 10 min and allowed to cool slowly for a period of 24 h. The orange crystalline solid that formed was collected by vacuum filtration and dried *in vacuo* (yield 70.9%). Analysis calculated for $C_{32}H_{24}N_4S_4Zn_2$: C 53.11, H 3.34, N 7.74%; found: C 52.8, H 3.1, N 7.6%.

Crystal data

$[Zn_2(C_6H_4S_2)_2(C_{10}H_8N_2)_2]$
$M_r = 723.54$
Monoclinic, $P2_1/n$
$a = 10.859$ (1) Å
$b = 9.523$ (1) Å
$c = 13.910$ (1) Å
$\beta = 93.18$ (1)°
$V = 1436.2$ (2) Å^3
$Z = 2$
$D_x = 1.673$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7279 reflections
$\theta = 2.3$–28.3°
$\mu = 1.99$ mm^{-1}
$T = 100$ (2) K
Plate, yellow
0.31 × 0.20 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.577$, $T_{\max} = 0.796$
12 291 measured reflections
3355 independent reflections
3154 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.7°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.065$
$S = 1.06$
3355 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.9504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.91$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zn—N2	2.1436 (15)	Zn—S1	2.4504 (5)
Zn—N1	2.1857 (14)	Zn—S1^i	2.4634 (5)
Zn—S2	2.2929 (5)	S1—Zn^i	2.4634 (5)
N2—Zn—N1	74.91 (5)	N2—Zn—S1^i	129.95 (4)
N2—Zn—S2	112.99 (4)	N1—Zn—S1^i	89.99 (4)
N1—Zn—S2	98.24 (4)	S2—Zn—S1^i	116.317 (17)
N2—Zn—S1	98.93 (4)	S1—Zn—S1^i	88.896 (15)
N1—Zn—S1	170.81 (4)	Zn—S1—Zn^i	91.104 (15)
S2—Zn—S1	90.420 (16)		

Symmetry code: (i) $-x, -y, 2 - z$.

H atoms were included in calculated positions (C—H = 0.95 Å) as riding contributions, with isotropic displacement parameters 1.2 times those of the attached C atoms. The largest residual density peak is located 0.82 Å from the Zn atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1434). Services for accessing these data are described at the back of the journal.

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