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Bis[1-(2-hydroxyethyl)-4,10-diazapyrazolo[4,3-*b*]fluoren-5(1*H*)-one thiosemicarbazonato]zinc(II) dimethylformamide trisolvate monohydrate

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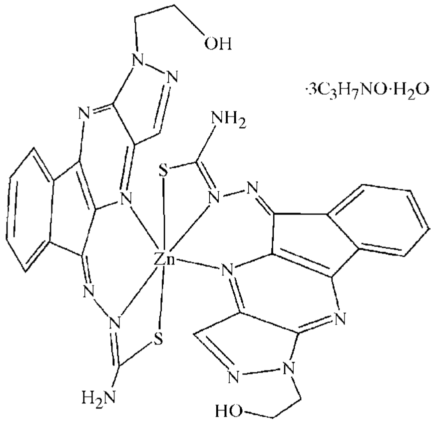
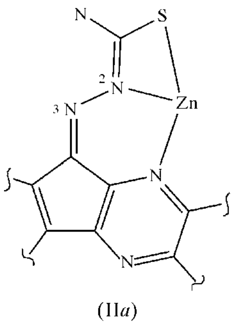
In the title Schiff base complex, $[Zn(C_{15}H_{12}N_7OS)_2]\cdot 3C_3H_7NO\cdot H_2O$, each Zn^{II} atom is six-coordinated in a distorted octahedral environment by two ligands acting in a tridentate chelating mode through two N atoms and one S atom. The coordination mode of the ligand is nearly planar. There are three dimethylformamide molecules and one water molecule solvating the complex. The coordination behavior of the ligand is compared with that of related ligands in similar complexes.

Comment

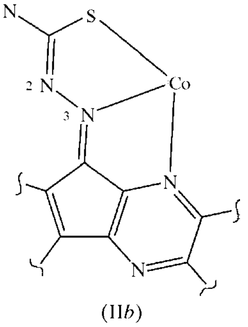
Owing to their photoelectromagnetic characteristics and physiologically important bactericidal and cancer-fighting activities, the hydrazone class of Schiff bases and their complexes have attracted much attention (Reiter *et al.*, 1985; Kovala-Demertzi *et al.*, 1999; Matthews *et al.*, 2001). Among these, the thiosemicarbazide Schiff base and its complexes have been particularly widely studied, because they are not only organic colorants with excellent performance, showing antibacterial and antiviral activities, but also templates for studying biological activity (Singh *et al.*, 1978). The title compound, $[ZnL_2]\cdot 3DMF\cdot H_2O$ [H*L* is 1-(2-hydroxyethyl)-4,10-diazapyrazolo[4,3-*b*]fluoren-5(1*H*)-one thiosemicarbazone and DMF is dimethylformamide], (I), has been synthesized because *L* is not only a novel thiosemicarbazone Schiff base but also a member of an important class of pyrazole-containing ring structures. This type of ligand displays unusual characteristics, including *cis–trans* isomerism in complexes (Che & Wang, 2006; Che *et al.*, 2006). Therefore, we aim to determine the single-crystal structures of examples of this class of compound, in order to understand their coordination mode and structural characteristics, as a guide for further studies. To our knowledge, this is the first report of the synthesis and crystal structure of a complex of this ligand.



(I)



(II*a*)



(II*b*)

Complex (I), in which the molecular structure unit is identical to the asymmetric unit, is composed of one ZnL_2 unit, one water molecule and three DMF molecules, with the solvent molecules not participating in coordination. Within the complex, each Zn^{II} ion is six-coordinated (Fig. 1) by four N and two S atoms from two ligands. The bond angles formed between atom Zn1 and coordination atoms N2, N4, S1, N9, N11 and S2 are in the range 62.63 (8)–110.76 (9)°, while the bond lengths involving atom Zn1 and these coordination atoms are in the range 1.978 (3)–2.739 (1) Å. Thus, the central Zn coordination geometry is best described as a distorted octahedron (Table 1). Each ligand *L*, as a tridentate chelate, provides two N atoms and one S atom to coordinate to Zn^{II}, forming a six-membered and a four-membered ring. As demonstrated by the relevant literature (Mathew & Palenik, 1971; Restivo & Palenik, 1970; Gabe *et al.*, 1969), this type of thiosemicarbazide Schiff base has a large conformational diversity, so that *cis–trans* isomerism is observed. The coordination mode of the present ligand *L* is very different from those of the reported examples. Using one of the independent *L* ligands as an example, atom N2 is in the *cis* (not *trans*) position with respect to N4 on the diazafluorenone ring, and it is N2 (not N3) that coordinates to the Zn^{II} atom. The cause may be that *L* is synthesized directly from the carbonyl group in the aromatic ring, while most Schiff base ligands are synthesized from aldehyde groups and those carbonyl groups that are not in the aromatic ring (Mathew & Palenik, 1971; Restivo & Palenik, 1970; Gabe *et al.*, 1969). There may exist *cis–trans* isomerism for this ligand as well, because this coordination mode is similar to that observed in bis(μ-11-thio-

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semicarbazonoindeno[1,2-*b*]quinoxaline-8-carboxylato)bis-[(dimethyl sulfoxide)zinc(II)] dimethyl sulfoxide trisolvate, (II*a*) (Che *et al.*, 2006), but different from that found in the indeno[1,2-*b*]quinoxalin-11-alkone thiosemicarbazone–cobalt(II) Schiff base complex (Che & Wang, 2006), (II*b*), in which N3 (not N2) coordinates to the metal atom. Although many examples of *cis–trans* isomerism in Schiff base ligands have been observed, the existence of complexes with both isomers of a given ligand are rarely reported. The reason for the *cis–trans* conversion is still unknown.

The C17—N10 bond length in (I) [1.324 (4) Å] indicates a double bond and the compound exists in the imide form. The C16—S1 bond length [1.667 (4) Å] is intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C═S double bond. The C16—N8, C16—N9 and N9—N10 bonds [1.336 (5), 1.360 (4) and 1.348 (4) Å] are indicative of some double-bond character. Except for the hydroxyethyl group, all other non-H atoms (C1–C13, N1–N7 and S1) within *L* are in the same plane (the mean deviation of atoms from the least-squares plane is 0.0180 Å), with the Zn^{II} ion located in the center, 0.181 (1) Å from the plane. The dihedral angle between the least-squares planes of the two ligands is 87.4 (2)°. Atom N5 at another potential coordinating position of the diazafluorenone ring does not participate in coordination, and so only a simple coordination compound forms rather than a coordination polymer. This is presumably due to steric hindrance. Thus, the complex is a simple structure rather than a dimeric structure and the metal center is six-coordinate rather than five-coordinate, which is different from what was previously observed in (II*a*) (Che *et al.*, 2006).

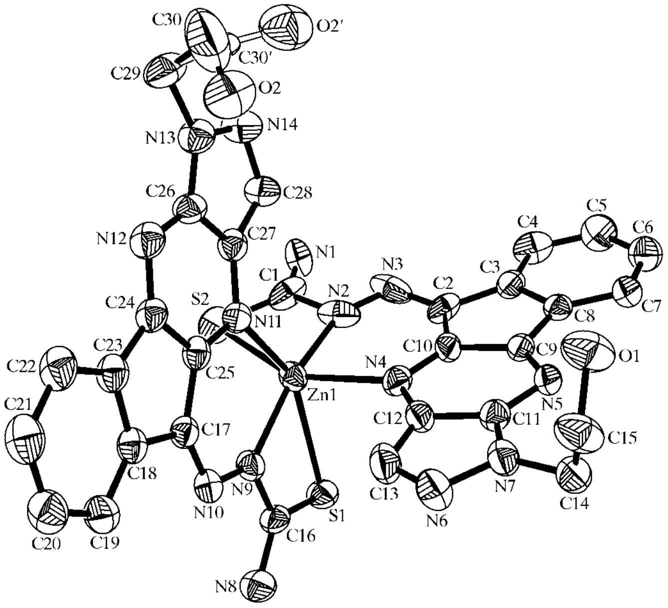

Figure 1
A view of complex (I), showing the atomic labeling scheme. Displacement ellipsoids are shown at the 30% probability level and solvent DMF and water molecules have been omitted for clarity.

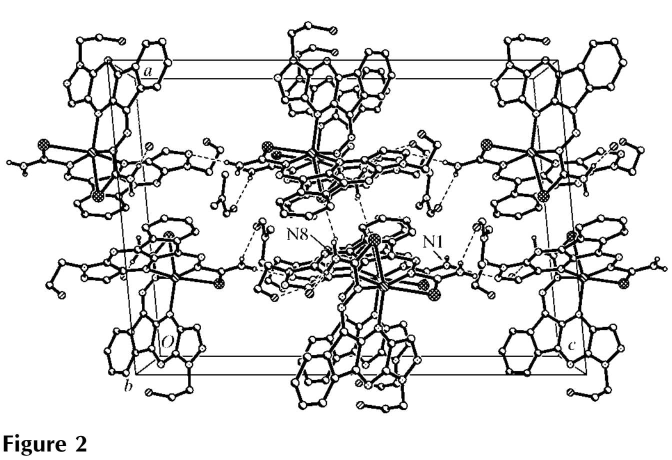

Figure 2
A view of the packing of complex (I) along the *b* axis. Hydrogen bonds are shown as dashed lines and some solvent DMF molecules have been omitted for clarity.

The packing diagram of (I) (Fig. 2) shows that the intermolecular interactions are mainly mediated by hydrogen bonds between NH donors and N, O and S acceptors (Table 2), which lead to the formation of a three-dimensional supermolecular structure. There are also some hydrogen-bonding interactions between the disordered DMF molecules and the hydroxyethyl group, but these are difficult to evaluate with precision because of the disorder.

Experimental

All reagents were purchased from Aldrich and used without further purification. The ligand *L* was synthesized according to a reported method (Che *et al.*, 2006). *L* (0.760 g, 0.002 mol) was dissolved in DMF (20 ml) and $Zn(OAc)_2 \cdot 6H_2O$ (0.237 g, 0.001 mol) was added. After heating at 373 K for 20 min, the mixture was allowed to cool and evaporate naturally. After a few days, red crystalline lumps formed (yield 0.51 g, *ca* 56.6% based on Zn). Analysis found: C 47.30, H 4.71, N 24.12, S 6.71%; $C_{39}H_{47}N_{17}O_6S_2Zn$ requires: C 47.83, H 4.84, N 24.31, S 6.55%.

Crystal data

$[Zn(C_{15}H_{12}N_7OS)_2] \cdot 3C_3H_7NO \cdot H_2O$
$M_r = 979.43$
Monoclinic, $P2_1/c$
$a = 16.530\ (5)$ Å
$b = 12.104\ (5)$ Å
$c = 23.601\ (5)$ Å
$\beta = 95.191\ (5)°$
$V = 4703\ (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.67$ mm^{-1}
$T = 293\ (2)$ K
0.28 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.834$, $T_{max} = 0.877$
28631 measured reflections
11219 independent reflections
5488 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.166$
$S = 1.02$
11219 reflections
659 parameters
221 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

H atoms were positioned geometrically and refined as riding atoms [C—H = 0.93 (CH), 0.96 (CH_3) and 0.97 Å (CH_2), N—H = 0.86 Å, $U_{iso}(H) = 1.2U_{eq}(C,N)$ for CH_2 and NH_2, and $U_{iso}(H) = 1.5U_{eq}(C)$ for

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	1.978 (3)	Zn1—N4	2.284 (3)
Zn1—N9	2.012 (3)	Zn1—S2	2.6581 (12)
Zn1—N11	2.151 (3)	Zn1—S1	2.7394 (12)
N2—Zn1—N11	110.31 (12)	N9—Zn1—S2	110.76 (9)
N9—Zn1—N11	88.19 (11)	N11—Zn1—S2	91.04 (8)
N2—Zn1—N4	86.21 (16)	N2—Zn1—S1	98.68 (9)
N9—Zn1—N4	97.22 (12)	N9—Zn1—S1	62.63 (8)
N11—Zn1—N4	94.34 (10)	N4—Zn1—S1	91.11 (8)
N2—Zn1—S2	65.89 (13)	S2—Zn1—S1	97.64 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8*A*···S1^{i}	0.86	2.50	3.340 (3)	166
N8—H8*B*···O6*W*	0.86	2.32	3.051 (5)	144
N1—H1*B*···N6^{ii}	0.86	2.40	3.258 (6)	172
N1—H1*A*···O4^{iii}	0.86	2.31	3.039 (6)	143

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

CH_3 and CH_2]. One of the three DMF solvent molecules is disordered over two positions with refined occupancies of *ca* 0.79 and 0.21. Atoms O2 and C30 of the hydroxyethyl group of one ligand are disordered with refined occupancies of *ca* 0.51 and 0.49. Standard DFIX and SIMU restraints were used for the dimensions of the disordered DMF molecule and the hydroxyethyl groups. The H atoms of the disordered water molecule and the hydroxy groups were not located. The highest peak in the final difference map is located 0.98 Å from atom N3.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; 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* and local programs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3102). Services for accessing these data are described at the back of the journal.

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