

A novel 8-carboxyindeno[1,2-*b*]-quinoxalin-11-one thiosemicarbazone zinc(II) Schiff base complex

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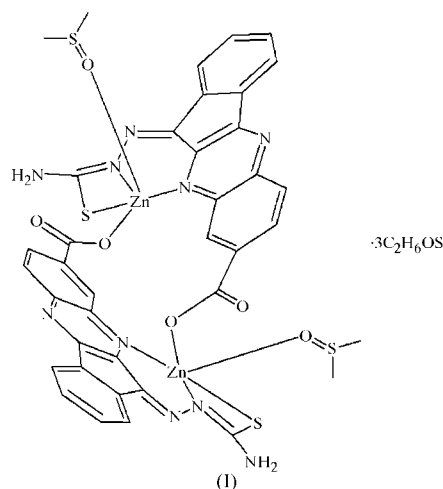
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In the novel title binuclear zinc(II) Schiff base complex, bis-(μ -11-thiosemicarbazonoindeno[1,2-*b*]quinoxaline-8-carboxylato)bis[(dimethyl sulfoxide)zinc(II)] dimethyl sulfoxide trisolvate, $[\text{Zn}_2(\text{C}_{17}\text{H}_9\text{N}_5\text{O}_2\text{S})_2(\text{C}_2\text{H}_6\text{OS})_2] \cdot 3\text{C}_2\text{H}_6\text{OS}$, each Zn^{II} atom is five-coordinated and situated in a distorted square-pyramidal environment, coordinated by two L^{2-} ligands and one dimethyl sulfoxide molecule. Each L^{2-} ligand, which coordinates to two Zn^{II} atoms, has two parts. One part, acting in a tridentate chelating mode, coordinates to one Zn^{II} atom through two N atoms and one S atom, while another part coordinates to another Zn^{II} atom through a monodentate carboxylate group. The whole complex has a dimeric structure. The coordination mode of the nearly planar L^{2-} ligand is quite different from the most common mode for Schiff bases.

Comment

Due to their photoelectromagnetic characteristics and physiologically important bactericidal and cancer-fighting activities, the hydrazone class of Schiff bases and their complexes have always 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 biocatalytic activity (Singh *et al.*, 1978). Belonging to an important class of nitrogen-containing heterocyclic rings, indeno[1,2-*b*]quinoxalin-11-one derivatives have always been closely watched (Javad *et al.*, 2005), but there are few studies of the syntheses of these Schiff bases; to date, only two papers have been found in the literature (Rao, Kumar & Rao, 1984; Rao, Rao & Girisham, 1984) and there are no single-crystal structure reports on either ligands or complexes. In the present work, the title 8-carboxyindeno[1,2-*b*]quinoxalin-11-one thiosemicarbazone Schiff base zinc(II) complex, $[\text{Zn}_2\text{L}_2(\text{C}_2\text{H}_6\text{OS})_2] \cdot 3\text{C}_2\text{H}_6\text{OS}$, (I) (L is the 8-carboxyindeno[1,2-*b*]quinoxalin-11-one thiosemicarbazone anion), has been synthesized and its crystal structure determined.



To the best of our knowledge, this is the first report of the crystal structure of an indeno[1,2-*b*]quinoxalin-11-one Schiff base derivative. This ligand has many interesting characteristics. Firstly, this type of thiosemicarbazide Schiff base has a large conformational diversity, so that *cis-trans* isomerism is observed (always configured differently in the free state and complex) (Mathew & Palenik, 1971; Restivo & Palenik, 1970; Gabe *et al.*, 1969). Secondly, within the H_2L ligand, multiple N atoms, one S atom and one carboxyl group may participate in coordination to produce additional structural diversity. Thirdly, in the previously reported Schiff base structures, the ligands are typically synthesized from the carbonyl groups outside the aromatic rings, while in the present ligand, the Schiff base was synthesized directly from the carbonyl group in the aromatic ring. This type of Schiff base has rarely been reported (Liu *et al.*, 1999, 2000). 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.

The title complex, (I), in which the molecular structure unit is identical to the asymmetric unit, is a dimer composed of two $\text{Zn}^{\text{II}}\text{-L}$ units and five DMSO (dimethyl sulfoxide) molecules, three of which are solvent molecules not participating in coordination. Each Zn^{II} is five-coordinate (Fig. 1), involving one S and two N atoms from one L^{2-} ligand, one O atom from the carboxyl group of the other L^{2-} ligand and one O atom from DMSO. The coordination mode of each Zn^{II} atom in the coordination dimer is the same. For example, for atom Zn1, the bond angles formed between Zn1 and coordination atoms N2, N4, S1, O3 and O5 are in the range 63.62 (15)–153.25 (14)°. The Zn atom is displaced by 0.320 (3) Å towards atom O5 of the DMSO, from the mean plane of basal atoms N4, N2, S1 and O3 of L^{2-} . Thus, the central Zn1 atom is best described as having distorted square-pyramidal (not trigonal-bipyramidal) geometry (Table 1). Each L^{2-} ligand provides two N atoms, one from the quinoxaline ring and another from the thiosemicarbazone, along with one S atom, thus coordinating to one Zn^{II} atom in a tridentate mode, and provides one O atom of the carboxylate group to coordinate to the other

Zn^{II} atom in a monodentate mode. Each L^{2-} ligand links two Zn^{II} atoms, and each Zn^{II} atom connects two L^{2-} ligands, so as to form a binuclear Zn^{II} coordination dimer.

As demonstrated by the relevant literature, the coordination modes of thiosemicarbazide Schiff base ligands are richly diverse. Although thiosemicarbazide Schiff bases are often of *cis* geometry in the free state, they convert into *trans* configurations on complex formation (Gabe *et al.*, 1969; Liu *et al.*, 1999, 2000; Mathew & Palenik, 1971; Restivo & Palenik, 1970). However, the coordination mode of L^{2-} is very different from these. Taking one L^{2-} ligand in (I) as an example, atom N2 is in the *cis* (not *trans*) position with respect to atom N4 in the quinoxaline ring. Moreover, it is atom N2 and not N3 that coordinates to Zn^{II}. The reason is probably that the Schiff base H_2L is synthesized directly from the carbonyl groups in the indeno-quinoxaline aromatic ring. To the best of our knowledge, this coordination mode has not been reported previously.

The C2–N3 bond length is 1.299 (7) Å, which demonstrates that this is a double bond and that compound (I) exists

in the imide form. The C1–S1 bond length is 1.692 (7) Å, which agrees very well with the values found in related compounds (Liu *et al.*, 1999), being intermediate between 1.82 Å for a C–S single bond and 1.56 Å for a C=S double bond. The corresponding C1–N1, C1–N2 and N2–N3 distances [1.308 (8), 1.371 (8) 1.350 (7) Å, respectively] are indicative of some double-bond character, which is similar to related compounds (Liu *et al.*, 1999, 2000).

When forming the complex, N2 loses a H atom from the tautomeric thiol form and the ligand coordinates with Zn^{II} in the form of an anion. The anionic carboxylate group on another L^{2-} ligand coordinates to Zn^{II} to balance the electric charge of whole complex. Except for the carboxylate group, the other non-H atoms (C1–C16, N1–N4 and S1) within ligand L^{2-} are in the same plane (the mean deviation of the atoms from the least-squares plane is 0.0631 Å). The Zn^{II} atom is also in this plane [the distance of Zn^{II} from the least-squares plane is 0.0004 (1) Å]. Within this coordination dimer, the dihedral angle between the two least-squares planes of the L^{2-} ligands is 70.64 (6)°. Atom N5 at another potential coordinating position of the quinoxaline ring does not participate in coordination, and so only a simple coordination compound forms rather than a coordination polymer. The cause is probably the steric hindrance of two neighbouring H atoms (H7 and H13) in L^{2-} , for if atom N5 were to coordinate to a metal ion, atoms H7 and H13 would occupy the metal coordination sites. This would make it difficult for the metal ion to form a stable complex and link to another L^{2-} ligand.

The packing of complex (I) is shown in Fig. 2. The intermolecular interactions are mainly mediated by the hydrogen bonds N1–H1A···O4ⁱ and N6–H6A···O2ⁱⁱ (Table 2). In this way, a one-dimensional supermolecular chain is formed along the $[\bar{1}11]$ direction. Note that there are also hydrogen bonds (N1–H1B···O8ⁱ and N6–H6B···O9ⁱⁱⁱ) between the L^{2-} ligand and the DMSO solvent molecules.

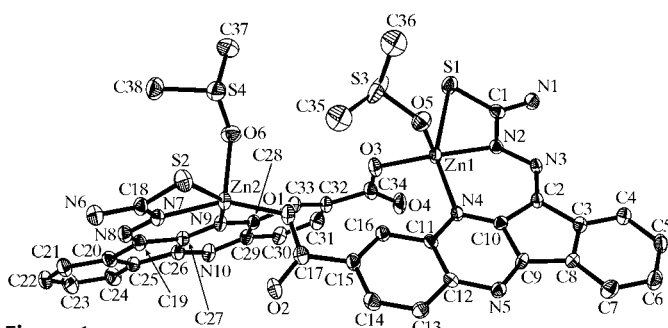


Figure 1

A view of the title complex, (I), showing the atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level. Only the major orientation of the disordered DMSO molecule is shown. H atoms and the DMSO solvent molecules have been omitted for clarity.

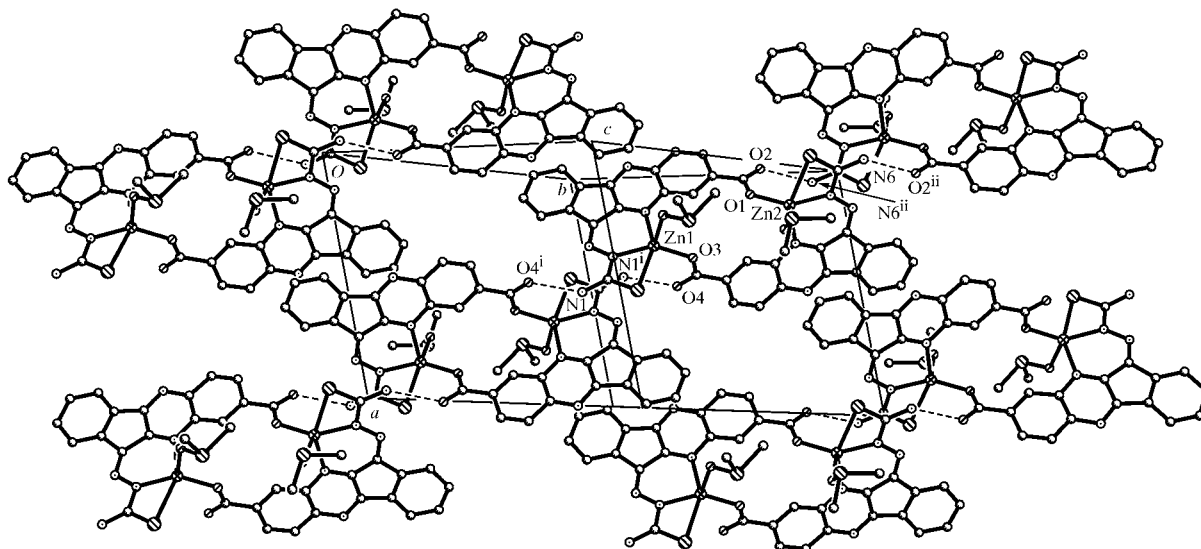


Figure 2

A packing view of (I), showing the N–H···O hydrogen-bonded one-dimensional chain among the complex molecules, extending along $[\bar{1}11]$. Hydrogen bonds are shown as dashed lines. DMSO solvent molecules have been omitted for clarity. [Symmetry codes: (i) $1 - x \ 1 - y \ 1 - z$; (ii) $-x \ 2 - y \ 2 - z$.]

Experimental

All reagents were purchased from Aldrich and used without further purification. The ligand *L* was synthesized according to the method of Rao, Kumar & Rao (1984). Ligand *L* (0.698 g, 0.002 mol) was dissolved in DMSO (20 ml) and then Zn(OAc)₂·2H₂O (0.220 g, 0.001 mol) was added. After heating at 343 K for 20 min, the mixture was allowed to cool and evaporate naturally. After a few days, red crystalline lumps formed (yield 0.48 g, ca 80% based on Zn). Analysis found: C 43.10, H 3.89, N 11.62, S 18.81%; C₄₄H₄₈N₁₀O₉S₇Zn₂ requires: C 43.42, H 3.95, N 11.51, S 18.42%.

Crystal data

[Zn ₂ (C ₁₇ H ₉ N ₅ O ₂ S) ₂ (C ₂ H ₆ OS) ₂]- 3C ₂ H ₆ OS	$\gamma = 79.533 (5)^\circ$
$M_r = 1216.08$	$V = 2650.6 (12) \text{ \AA}^3$
Triclinic, <i>P</i> $\bar{1}$	$Z = 2$
$a = 11.716 (3) \text{ \AA}$	$D_x = 1.524 \text{ Mg m}^{-3}$
$b = 15.063 (4) \text{ \AA}$	Mo <i>K</i> α radiation
$c = 15.837 (4) \text{ \AA}$	$\mu = 1.25 \text{ mm}^{-1}$
$\alpha = 76.490 (5)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 80.577 (5)^\circ$	Block, dark red
	$0.14 \times 0.13 \times 0.06 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	14815 measured reflections
φ and ω scans	9680 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	5453 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.856$, $T_{\max} = 0.928$	$R_{\text{int}} = 0.046$
	$\theta_{\text{max}} = 25.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.0896P)^2]$
$wR(F^2) = 0.188$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} = 0.002$
9680 reflections	$\Delta\rho_{\text{max}} = 0.97 \text{ e \AA}^{-3}$
666 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zn1—O3	1.941 (4)	Zn2—O1	1.935 (4)
Zn1—N2	1.976 (5)	Zn2—N7	1.980 (5)
Zn1—O5	2.045 (5)	Zn2—O6	2.066 (5)
Zn1—N4	2.151 (5)	Zn2—N9	2.157 (5)
Zn1—S1	2.736 (2)	Zn2—S2	2.735 (2)
O3—Zn1—N2	146.2 (2)	O1—Zn2—N7	146.2 (2)
O3—Zn1—O5	97.4 (2)	O1—Zn2—O6	100.3 (2)
N2—Zn1—O5	112.9 (2)	N7—Zn2—O6	110.7 (2)
O3—Zn1—N4	105.88 (19)	O1—Zn2—N9	103.75 (19)
N2—Zn1—N4	89.77 (19)	N7—Zn2—N9	89.0 (2)
O5—Zn1—N4	89.41 (19)	O6—Zn2—N9	91.7 (2)
O3—Zn1—S1	98.57 (14)	O1—Zn2—S2	101.09 (14)
N2—Zn1—S1	63.62 (15)	N7—Zn2—S2	63.33 (15)
O5—Zn1—S1	98.18 (14)	O6—Zn2—S2	95.92 (14)
N4—Zn1—S1	153.25 (14)	N9—Zn2—S2	152.26 (14)

The DMSO molecule that coordinates to Zn1 is disordered over a major and a minor orientation of the S and C atoms, with refined occupancies of 0.599 (18) and 0.401 (18) that were ultimately fixed at

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O4 ⁱ	0.86	2.10	2.922 (7)	161
N1—H1B...O8 ⁱ	0.86	2.10	2.950 (7)	168
N6—H6A...O2 ⁱⁱ	0.86	2.10	2.912 (7)	157
N6—H6B...O9 ⁱⁱⁱ	0.86	2.02	2.863 (8)	166

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 2, -z + 2$; (iii) $-x, -y + 1, -z + 2$.

0.6 and 0.4. Standard DFIX restraints were used for the dimensions of the disordered DMSO. The C atoms of the minor orientation were refined with an overall U_{iso} value. All other non-H atoms were refined anisotropically. The S atom in one DMSO solvent molecule is disordered, with refined occupancies of 0.772 (6) and 0.228 (6) that were subsequently fixed at 0.8 and 0.2. The maximum positive peak in the final difference electron-density map is located 1.05 \AA from atom S3' and 1.14 \AA from atom S3. H atoms were generated geometrically and refined as riding atoms, with C—H = 0.93 (CH) or 0.96 \AA (CH₃) and N—H = 0.86 \AA (NH₂), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ for CH and NH₂, or $1.5U_{\text{eq}}(\text{C})$ for CH₃. The H atoms attached to the disordered DMSO molecules were not located.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus (Sheldrick, 1990); software used to prepare material for publication: SHELXTL-Plus.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3031). Services for accessing these data are described at the back of the journal.

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