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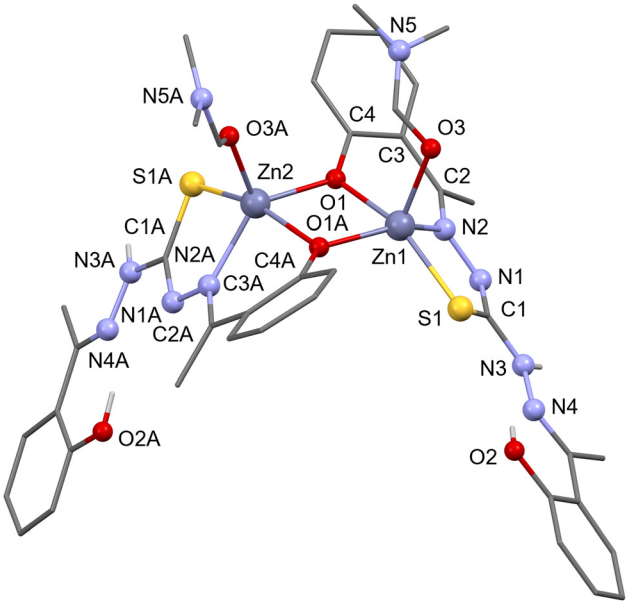
Crystal structure of bis(μ_2-1,5-bis[(*E*)-1-(2-hydroxyphenyl)ethylidene] thiocarbonohydrazide)-bis(dimethylformamide)-dizinc(II) dimethylformamide solvate, $C_{40}H_{46}N_{10}O_6S_2Zn_2 \cdot C_3H_7NO$



https://doi.org/10.1515/ncrs-2025-0284
Received June 24, 2025; accepted August 21, 2025;
published online September 3, 2025

Abstract

$C_{40}H_{46}N_{10}O_6S_2Zn_2 \cdot C_3H_7NO$, orthorhombic, *Pbca* (no. 61), a = 15.2562(4) Å, b = 20.5310(6) Å, c = 29.7848(6) Å, V = 9329.3(4) Å^3, Z = 8, $R_{gt}(F)$ = 0.0576, w$R_{ref}(F^2)$ = 0.0870, T = 180 K.

CCDC no.: 2481580

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Table 1: Data collection and handling.

Crystal:	Clear light colourless prism
Size:	0.29 × 0.15 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.18 mm^{-1}
Diffractometer, scan mode:	Bruker APEX2, φ and ω scans
θ_{max}, completeness:	29.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	42005, 11020, 0.074
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6508
$N(param)_{refined}$:	632
Programs:	Bruker,[1] SIR2014,[2] SHELX,[3] Mercury,[4] WinGX[5]

The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

Synthesis of ligand (H_2 L): A mixture of thiocarbohydrazide (0.4 g) and *o*-hydroxyacetophenone (0.92 ml) in ethanol was heated under reflux for 3 h in the presence of one drop of concentrated hydrochloric acid. The reaction mixture was allowed to cool overnight. The white precipitate was filtered off and purified by recrystallization from absolute ethanol. Pale-yellow powder-like substance was obtained (yield 0.72 g, 67.4 %). **Synthesis of complex $[Zn_2(\mu\text{–L})_2(DMF)_2]\cdot DMF$:** To a hot solution of zinc(II) acetate dihydrate (0.25 mmol; 54.8 mg) in dimethylformamide was added the hot solution of L (0.5 mmol, 112 mg). After 5 days the mixture was filtered, yielding yellow-orange crystals (yield: 0.194 g, 95.44 %).

2 Experimental details

Dimethylformamide (DMF) bonded to Zn1 was refined by applying rigid-body restraint (RIGU) on the atoms O3, C18,

and N5. Oxygen and carbon atoms of the DMF ligand bonded to Zn2 are disordered. To model the disorder, SIMU and SADI restraints were used. Occupancies of O3A, C18A/O3B,C18B were refined to 0.65/0.35. Hydrogen atoms bonded to O were located in difference Fourier map. Remaining hydrogen atoms were placed at calculated positions. All hydrogen atoms were refined using riding model.

3 Comment

Thiocarbohydrazones are important in various biological processes, including catalytic reactions[6] and anticancer activity.[7] We reported previously the crystal structure of the title ligand 1,5-bis[(*E*)-1-(2-hydroxyphenyl)ethylidene] thiocarbonohydrazide (H_2L) as a dimethylsulfoxide solvate.[8] Due to versatile coordination capabilities thiocarbohydrazones can form complexes of varying nuclearity.[9] In many cases biological activity of thiocarbohydrazones is influenced by their variable coordination modes towards metal atoms.[10] The crystal structures of the title ligand H_2L coordinated to Mo[11] and Sn[12,13] have been reported previously. Here, we report the synthesis and crystal structure of the Zn(II) complex with the H_2L.

The asymmetric unit consist of dimeric Zn(II) complex molecule and dimethylformamide solvent. The figure depicts the complex molecule and atom labeling scheme. Due to clarity hydrogen atoms bonded to C and some C labels have been omitted from the Figure. Both metal atoms are five-coordinated in a distorted square-pyramidal environment. The base of the square-pyramid for both zinc atoms is formed by the sulfur, imine nitrogen and two bridging phenolate oxygen atoms. The vertices of the coordination polyhedra are occupied by the dimethylformamide (DMF). The Addison distortion index τ[14] is 0.25 for Zn1 and 0.43 for Zn2. DMF ligand bonded to Zn1 is disordered. Only one of the disordered DMF positions is shown in the Figure and is considered for the calculation of Adisson distortion index. Comparison of the bond lengths in ligand L with the uncoordinated molecule H_2L[15] indicate lengthening of the bonds involving coordinated atoms (C1A–S1A = 1.73/1.74 Å, N2A–N1A = 1.40/1.39 Å, vs. C–N = 1.68 Å, N–N = 1.37 Å in uncoordinated ligand). In both ligands L, the hydroxy group is hydrogen bonded to a double bonded N atom, generating a six-membered ring. Geometry of these interactions is O2–H52···N4 = 1.88(4) Å/148(5)° and O2A–H51···N4A = 1.80(4) Å/142(4)°. Same interaction is observed in this ligand in the crystal structures where it is uncoordinated[16] or coordinated.[11–13] The complex molecules are arranged into chains directed along the a-axis. This arrangement is associated with intermolecular C–H···π interaction (C13A–H19···O2^{i} = 2.46 Å/156°); (symmetry code: $i = 1/2 + x, 1/2 - y, 1 - z$). There are no other significant intermolecular contacts between the molecules in the chain. The DMF solvent is situated between the molecular chains and bonded to complex molecule through the hydrogen bond, N3A–H53···O4 = 2.24(4) Å/177(4)°. The solvent molecule is not involved in significant intermolecular contacts between the molecular chains.

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