

Di- μ -acetato-bis[(2-acetylpyridine
thiosemicarbazonato)zinc(II)]Emmanuel Ngwang Nfor,^{a,b*} Wei Liu,^a Jing-Lin Zuo,^a
Xiao-Zeng You^{a*} and Offiong Efanga Offiong^b^aState Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China, and ^bDepartment of Chemistry, University of Calabar, PMB 1115, Calabar, Cross River State, Nigeria
Correspondence e-mail: nforemma@yahoo.com, xyz@netra.nju.edu.cn

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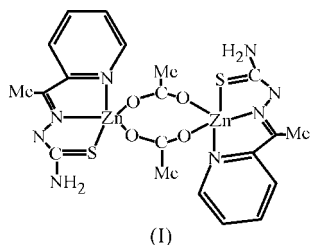
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The title compound, $[\text{Zn}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_8\text{H}_9\text{N}_4\text{S})_2]$, is a centrosymmetric dinuclear molecule with two acetate bridging ligands in a *syn-syn* arrangement. The Zn^{II} atom is five-coordinated in a trigonal-bipyramidal configuration by three thiosemicarbazone atoms (two N and one S) and by an O atom of each of the two acetate groups.

Comment

Metal complexes of Schiff bases synthesized by the condensation of 2-acetylpyridine and thiosemicarbazides, semicarbazides and other amines (Nomiya *et al.*, 2001; West *et al.*, 1993; Wang *et al.*, 2004) have received much attention owing to their antimicrobial, cytotoxic and antioxidant activities (Reddy *et al.*, 1999; Tarafder *et al.*, 2001). However, only a few studies of the synthesis, spectroscopic characterization and antimicrobial activities of such compounds with the Schiff base derived from 2-acetylpyridine and thiosemicarbazide have been reported to date (Kasuga *et al.*, 2003; Kovala-Demertzi *et al.*, 2001).



Zinc(II) complexes with thiosemicarbazone ligands have been reported to have antitumour activities and to exhibit effects in *in vitro* cell proliferation and differentiation. However, few studies of the antimicrobial activities of zinc(II) complexes have been reported to date (Bermejo *et al.*, 1997; Offiong & Martelli, 1993). Divalent zinc(II) complexes are influenced significantly by the reaction conditions, such as the solvent, pH, stoichiometry and reaction temperature (Ferrari *et al.*, 1992; Casas *et al.*, 2000). Furthermore, d^{10} metal poly-

nuclear complexes, including those containing zinc, have been found to be thermally stable and to possess photoluminescence properties, a feature that has contributed immensely to the search for new materials (Weidenbruch *et al.*, 1989; Kunkely & Vogler, 1990; Bertonacello *et al.*, 1992; Wang *et al.*, 2003; Sang & Xu, 2005). As far as we are aware, no crystal structure of a dinuclear Zn^{II} complex of 2-acetylpyridine thiosemicarbazone has been published to date. We report here the synthesis and crystal structure of the title complex, (I).

Complex (I) is an acetate-bridged dinuclear Zn^{II} compound (Fig. 1) which has inversion symmetry. The coordination geometry around the Zn atom is trigonal bipyramidal, based on geometric parameter calculations: $\tau = (\beta - \alpha)/60$ gives $\tau = 0.55$, taking $\text{O1}^i - \text{Zn1} - \text{N2}$ [$121.36(16)^\circ$; symmetry code: (i) $-x + 1, -y + 1, -z + 1$] as β and $\text{O2} - \text{Zn1} - \text{N1}$ [$88.41(14)^\circ$] as α (Addison *et al.*, 1984). The calculated τ value and the geometry of the complex are in agreement with those of dinuclear zinc(II) acetate complexes with similar thiosemicarbazone derivatives reported previously (Garcia *et al.*, 2002; Bresolin *et al.*, 1997). Compound (I) (Fig. 1), which crystallizes as a centrosymmetric dinuclear molecule with the two acetate bridging ligands in a *syn-syn* arrangement, is five-coordinate, with both Zn atoms coordinated by three thiosemicarbazone atoms and by an O atom of each of the two acetate groups. The $\text{Zn} \cdots \text{Zn}$ distance of $3.749(16) \text{ \AA}$ is long enough to rule out any metal-metal bonding.

As in other 2-pyridylthiosemicarbazones (Garcia *et al.*, 2002; Bermejo *et al.*, 2004), the $\text{Zn} - \text{N}_{\text{im}}$, $\text{Zn} - \text{N}_{\text{py}}$ and $\text{Zn} - \text{S}$ bond lengths in (I) (Table 1) increase in that order. The $\text{Zn} - \text{O}$ bond distances are very similar [$\text{Zn} - \text{O1}^i = 2.014(4) \text{ \AA}$ and $\text{Zn} - \text{O2} = 2.010(3) \text{ \AA}$], showing the non-staggered nature of the bridging acetate ion (Ainscough *et al.*, 1987). The $\text{Zn1} - \text{S1}$ bond [$2.3247(16) \text{ \AA}$] is much longer than the other bonds, indicating that the $\text{Zn} - \text{S}$ bond is weaker compared with the others; this is in agreement with bond distances reported for other complexes of zinc(II) with similar thiosemicarbazones (Bresolin *et al.*, 1997). The bridging acetate groups are nearly

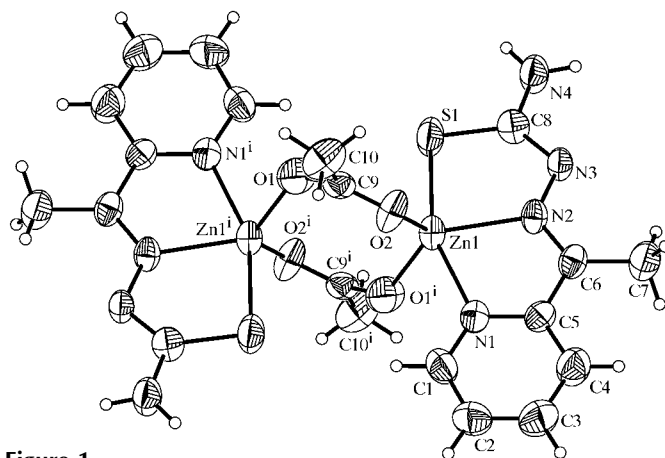


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$].

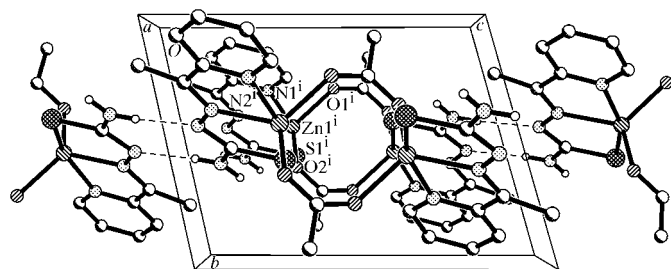


Figure 2
The packing of (I) in the crystal structure. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

linear and show bent coordination modes with the metal atoms [O1—C9—O2 = 126.0 (5)°, Zn1—O2—C9 = 125.3 (3)° and Zn—O1—C9ⁱ = 132.1 (3)°], which is very similar to a dinuclear zinc thiosemicarbazone reported previously (Garcia *et al.*, 2002).

The N2—Zn1—N1 (N2ⁱ—Zn1ⁱ—N1ⁱ) bond angle [75.63 (16)°] of the five-membered chelate ring is much smaller than 90°, a result of the strain created by the five-membered chelate rings Zn1/N1/C5/C6/N2 and Zn1ⁱ/N1ⁱ/C5ⁱ/C6ⁱ/N2ⁱ (You & Zhu, 2005). The C6=C2 bond length [1.294 (5) Å] conforms to the normal value of 1.32 Å for a double bond, while the C8—N3 bond length [1.333 (6) Å] conforms to the normal value of 1.37 Å for a single bond (Allen *et al.*, 1987). As one can observe, the Zn—N bond distances involving azomethine N atoms (N2 and N2ⁱ) and pyridyl N atoms (N1 and N1ⁱ) are almost the same length, at 2.128 (4) and 2.125 (4) Å, respectively, which suggests a charge delocalization over the entire ligand. This is considered important in thiosemicarbazones, especially those containing an aryl group (Palenik *et al.*, 1974; Campbell, 1975).

In the crystal structure of (I) (Fig. 2), intermolecular hydrogen-bond contacts N4—H4B···O2ⁱⁱ [3.073 (5) Å] and N4—H4A···N3ⁱⁱⁱ [3.138 (6) Å] are observed [Table 2; symmetry code: (ii) $x - 1, y, z$; (iii) $-x, 1 - y, -z$]. There are fewer intermolecular hydrogen bonds in (I) than in other complexes of 2-acetylpyridine thiosemicarbazones because of the absence of solvent molecules. The distances and angle for the interaction with the coordinated O atom are comparable with the intermolecular N—H···O attraction in a dinuclear acetate-bridged zinc complex with a similar thiosemicarbazone (Garcia *et al.*, 2002), but without the N4—H4A···N3ⁱⁱⁱ interaction observed in the present case. The molecules of (I) are stacked along the *a* axis (Fig. 2) and are linked by short intermolecular hydrogen bonding between atoms O2 and N3.

Experimental

The 2-acetylpyridine thiosemicarbazone (APytsc) Schiff base was prepared according to the method of Offiong & Martelli (1993). Single crystals of the title complex suitable for X-ray diffraction analysis were obtained by the reaction of Zn(CH₃COO)₂·4H₂O with APytsc in a 1:1 molar ratio in an aqueous acetonitrile (1:3, 12 ml) solution, stirred at room temperature for 10 min, followed by slow evaporation of the solvents at room temperature over a period of two weeks.

Crystal data

[Zn₂(C₂H₃O₂)₂(C₈H₉N₄S)₂]
M_r = 635.33
 Triclinic, *P* $\bar{1}$
a = 7.3690 (16) Å
b = 8.4128 (18) Å
c = 10.716 (2) Å
 α = 76.124 (4)°
 β = 88.754 (4)°
 γ = 70.758 (4)°
V = 607.7 (2) Å³

Z = 1
D_x = 1.736 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2125 reflections
 θ = 0–25°
 μ = 2.19 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.20 × 0.14 × 0.08 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
T_{min} = 0.699, *T_{max}* = 0.839
 3048 measured reflections

2093 independent reflections
 1603 reflections with *I* > 2σ(*I*)
R_{int} = 0.055
 θ_{max} = 25.0°
h = -8 → 8
k = -10 → 9
l = -10 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
wR (*F*²) = 0.091
S = 0.99
 2093 reflections
 166 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0035P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.49 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.44 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C5—N1	1.343 (6)	N2—Zn1	2.128 (4)
C6—N2	1.294 (5)	O2—Zn1	2.010 (3)
C8—N3	1.333 (6)	O1 ⁱ —Zn1	2.014 (4)
N1—Zn1	2.125 (4)	S1—Zn1	2.3247 (16)
N1—C5—C6	115.8 (4)	O2—Zn1—O1 ⁱ	118.95 (17)
N2—C6—C5	115.2 (5)	O2—Zn1—N1	88.41 (14)
O2—C9—O1	126.0 (5)	O1 ⁱ —Zn1—N1	86.60 (15)
C1—N1—Zn1	125.2 (4)	O2—Zn1—N2	115.90 (16)
C5—N1—Zn1	115.4 (3)	O1 ⁱ —Zn1—N2	121.36 (16)
C6—N2—N3	119.7 (4)	N1—Zn1—N2	75.63 (16)
C6—N2—Zn1	117.6 (4)	O2—Zn1—S1	106.67 (11)
N3—N2—Zn1	122.5 (3)	O1 ⁱ —Zn1—S1	101.36 (12)
C9—O2—Zn1	125.3 (3)	N1—Zn1—S1	156.09 (13)
C9—O1—Zn1 ⁱ	132.1 (3)	N2—Zn1—S1	81.04 (11)
C8—S1—Zn1	96.67 (18)		

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

Table 2

Hydrogen-bond geometry (Å, °).

<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>
N4—H4B···O2 ⁱⁱ	0.86	2.34	3.073 (5)	144
N4—H4A···N3 ⁱⁱⁱ	0.86	2.29	3.138 (6)	168

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

H atoms attached to C atoms were placed in calculated positions, with aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å, and were allowed to ride on their parent atoms. Methyl groups were allowed to rotate around their C—C axes. All H atoms were assigned *U_{iso}*(H) values of xU_{eq} (parent), with *x* = 1.2 for aromatic and water H atoms, and *x* = 1.5 for methyl H atoms.

Data collection: SMART (Bruker, 2002); cell refinement: SMART; data reduction: SAINT (Bruker, 2002); program(s) used to solve structure: SHELXTL (Bruker, 2002); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1282). Services for accessing these data are described at the back of the journal.

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