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Structural study of a zinc(II) complex with acetone 3-hexamethyleneiminylthiosemicarbazone

Alfonso Castiñeiras[a], Douglas X. West[b,*]

[a]Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain
[b]Department of Chemistry, 351700, University of Washington, Seattle, WA 98195-1700, USA

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Abstract

The crystal structure of a zinc complex with acetone 3-hexamethyleneiminylthiosemicarbazone has been determined and contains two anionic thiosemicarbazone ligands prepared from acetone. Bis(acetone 3-hexamethyleneiminylthiosemicarbazone)zinc(II), [Zn(Acehexim)$_2$], crystallizes monoclinic, $P2_1/c$, $a = 8.406(3)$, $b = 13.518(5)$, $c = 22.136(3)$ Å, $\beta = 100.61(3)$, $V = 2472.3(12)$ Å^3, $Z = 4$. The distortion from tetrahedral symmetry, while substantial, is less than found for other 4-coordinate zinc complexes with bulkier thiosemicarbazone ligands. The largest angle, S–Zn–S, is 126.44(14)° and the smallest angle, 87.1(3)°, is the average of the chelating N–Zn–S angles. The angle between the mean planes of the two chelate rings is 79.41(21)°. Disorder within the hexamethyleneiminyl rings, which is common for this function, causes a larger than desired *R*-value.

Keywords: Crystal structure; Acetone thiosemicarbazone; Zinc complex; Hexamethyleneimine

1. Introduction

Salicylaldehyde and 2-hydroxyacetophenone N(4)-substituted thiosemicarbazones, as well as heterocyclic thiosemicarbazones, have been the subject of extensive investigation [1] because of their ability to strongly coordinate metal ions as tridentate ligands and their wide spectrum of biological applications [2]. Thiosemicarbazones limited to bidentate coordination have been less studied even though there are examples of biologically important thiosemicarbazones, such as thiacetazone (*p*-acetamido-benzaldehyde thiosemicarbazone), used in the clinical treatment of tuberculosis [3,4]. Metal complexes of potentially bidentate N(4)-substituted thiosemicarbazones have received even less attention [5–7]. Because of their many potential pharmaceutical uses, it is important to continue to prepare and characterize new thiosemicarbazones and their metal complexes. In particular, N(4)-substitution has been shown to affect the activity of thiosemicarbazones and their metal complexes [8]. Here we report a structural study of bis(acetone 3-hexamethyleneiminylthiosemicarbazone)zinc(II), [Zn(Acehexim)$_2$]; the thiosemicarbazone, HAcehexim, is shown in Fig. 1.

2. Experimental

3-Hexamethyleneiminylthiosemicarbazide was prepared as described previously [9]. Equal molar

* Corresponding author. Tel.: +1-206-616-4213; fax: +1-206-685-8665.
E-mail address: westdx@chem.washington.edu (D.X. West).

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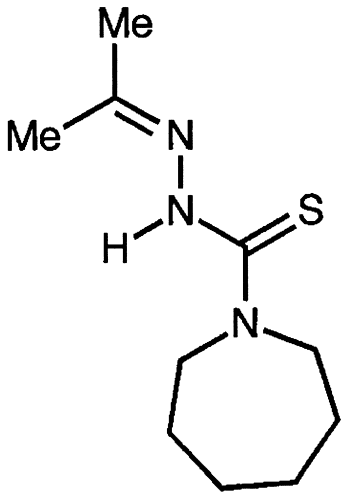

Fig. 1. Drawing of acetone hexamethyleneiminylthiosemicarbazone, HAcehexim.

amounts of 3-hexamethyleneiminylthiosemicarbazide and acetone (0.005 mol) in ethanol (30 ml) with two drops of concentrated H_2SO_4 added, was stirred with gentle warming for 12 h. The solvent was gradually removed on a warm plate (35°), and a white, hygroscopic solid separated, which was filtered and dried. Freshly prepared acetone 3-hexamethyleneiminyl thiosemicarbazone, 0.020 mol, was boiled under reflux in 95% ethanol with 0.010 mol of zinc acetate for more than two hours. The yellow solid, which formed on slow cooling and evaporation of solvent, was filtered, washed with diethyl ether and dried at 35° on a warm plate.

A crystal of [Zn(Acehexim)$_2$], grown from anhydrous EtOH, was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $19.317 < \theta < 45.160°$ with an Enraf Nonius CAD4 automatic diffractometer. Data were collected using Cu Kα radiation ($\lambda = 1.54184$ Å), employing the ω scan technique and correcting for Lorentz and polarization effects. The structure was solved by direct methods [10] that revealed the position of all non-hydrogen atoms and refined by a full-matrix least-squares procedure on F^2 using anisotropic displacement parameters [11]. All hydrogens were located in their calculated positions (C–H 0.93–0.97 Å) and refined using a riding model. Atomic scattering factors are from the 'International Tables for X-ray Crystallography' [12] and molecular graphics are from PLATON98 [13]. A summary of crystal and intensity collection data for [Zn(Acehexim)$_2$] is given in Table 1.

Table 1
Crystal data and structure refinement for bis(acetone 3-hexamethyleneiminyl-thiosemicarbazonato)zinc(II)

Empirical formula	$C_{20}H_{36}N_6S_2Zn$
Color, habit	Yellow, plate
Formula weight	490.04
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
a (Å)	8.406(3)
b (Å)	13.518(5)
c (Å)	22.136(3)
β (°)	100.61(3)
Volume, (Å^3)	2472.3(12)
Z	4
Density (mg m^{-3})	1.317
Absorption coefficient (mm^{-1})	3.089
Crystal size (mm)	$0.35 \times 0.15 \times 0.05$
θ range for data collection (°)	3.85–66.91
Index ranges	$-9 \le h \le 10$
	$-16 \le k \le 0$
	$-26 \le l \le 0$
Reflections collected	4495
Unique reflections	4374 [$R_{int} = 0.0421$]
Absorption correction	Ψ-scan
Max./min. transmission	0.8609/0.776
Data/parameters	4374/266
Goodness-of-Fit on F^2	0.971
Final R indices [$I > 2\sigma$(I)]	R_1=0.0884 $wR_2 = 0.2573$
R indices (all data)	$R_1 = 0.2362$ $wR_2 = 0.3401$
Largest difference peak/hole (e Å^{-3})	0.642 and −0.412

3. Results and discussion

Selected bond distances and angles for [Zn(Acehexim)$_2$] are listed in Table 2 and its rms mean plane data in Table 3. Atomic coordinates and equivalent isotropic displacement coefficients are included in the deposited material (CCDC#154561), as are a complete list of bond distances and angles. An ORTEP drawing with the numbering system is shown in Fig. 2. The relatively high R-value is due to the hexamethyleneiminyl rings, which have been previously reported to show disorder, particularly the

Table 2
Selected bond distances (Å) and angles (°) for bis(acetone 3-hexamethyleneiminylthiosemicarbazonato)zinc(II)

Bond	[Zn(Acehexim)$_2$]	Bond	[Zn(Acehexim)$_2$]
Zn–N12	2.044(9)	Zn–N22	2.068(10)
Zn–S1	2.263(3)	Zn–S2	2.248(3)
S1–C11	1.721(12)	S2–C21	1.690(16)
N12–C18	1.280(14)	N22–C28	1.262(13)
N12–N13	1.385(12)	N22–N23	1.411(12)
N13–C11	1.349(14)	N23–C21	1.352(15)
N14–C11	1.368(13)	N24–C21	1.367(13)
Angle	[Zn(Acehexim)$_2$]	Angle	[Zn(Acehexim)$_2$]
N12–Zn–N22	108.4(4)	S2–Zn–S1	126.44(14)
N22–Zn–S2	87.7(3)	N22–Zn–S1	124.2(3)
N12–Zn–S2	126.3(3)	N12–Zn–S1	86.5(3)
C11–S1–Zn	94.4(4)	C21–S2–Zn	93.8(4)
C18–N12–Zn	128.3(9)	C28–N22–Zn	127.9(9)
N13–N12–Zn	115.7(8)	N23–N22–Zn	115.7(7)
C18–N12–N13	115.8(11)	C28–N22–N23	116.4(10)
N12–N13–C11	115.7(10)	N22–N23–C21	113.2(9)
N13–C11–N14	113.8(10)	N23–C21–N24	112.3(13)
N13–C11–S1	126.3(9)	N23–C21–S2	129.1(9)
N14–C11–S1	119.9(9)	N24–C21–S2	118.6(11)

γ-carbons [14,15]. On loss of the N2H hydrogen, anionic Acehexim coordinates as a bidentate ligand via the imine nitrogen and thiolato sulfur atoms resulting in a 4-coordinate, distorted tetrahedral arrangement about zinc. The NS chelation results in the smallest angles, N12–Zn–S1, 86.5(3)° and N22–Zn–S2, 87.7(3)°, the angle N22–Zn–N12 is 108.4(4)° and the other three coordinate angles around zinc are greater than 120°. The Zn–S bonds are longer than the Zn–N distances as expected, and although the two Zn–S distances are different, as are the Zn–N distances, the differences are within three times the combined values of their estimated standard deviations. The bond distances and angles of the thiosemicarbazone moieties also differ, but not significantly. The N12–C18 (and N22–C28) distance, 1.280(14) Å (and 1.262(13) Å), is consistent with a double bond and is considerably shorter than N13–C11 (and N23–C21), 1.349(14) Å (and 1.352(15) Å), which formally becomes a double bond in the coordinated anion. The C–S distances, 1.721(12) and 1.690(16) Å, are between the values normally associated with C=S and C–S bonds. The chelate rings, Table 3, are reasonably planar with rms values of 0.0674 and 0.0302 Å, and the angle between the two planes, 79.41(0.21)°, provides another measure of the distortion from tetrahedral symmetry.

Table 3
Root mean square plane deviations and angles (°) between planes for [Zn(Acehexim)$_2$]

Plane	Rms dev.	angle with previous plane
N12–C18–C19–C20	0.0131	–
S1–C11–N13–N12–Zn	0.0674	5.59(0.82)
S2–C21–N23–N22–Zn	0.0302	79.41(0.21)
N22–C28–C29–C30	0.0005	5.04(0.88)

An early report of a cobalt(II) complex of acetone thiosemicarbazone, [Co(HAce4DH)$_2$Cl]Cl, involves the neutral ligands coordinating N,S based on spectral data [16]. When the preparative metal salt is CoI_2, 4-coordinate [Co(HAce4DH)$_2$I$_2$] is isolated with HAce4DH coordinating as a monodentate ligand via the thione sulfur. The crystal structure of a nickel(II) complex, [Ni(HAce4DH)$_2$(NO$_3$)]NO$_3$, has been reported [17] and the related [Ni(Ace4DH)$_2$], that did not have its crystal structure reported, has been prepared by reaction of the bis(thiosemicarbazido)-nickel(II) complex with acetone [18]. It was later shown that hydrolysis of coordinated acetone thiosemicarbazone gave acetone and coordinated thiosemicarbazide with 31% conversion resulting in

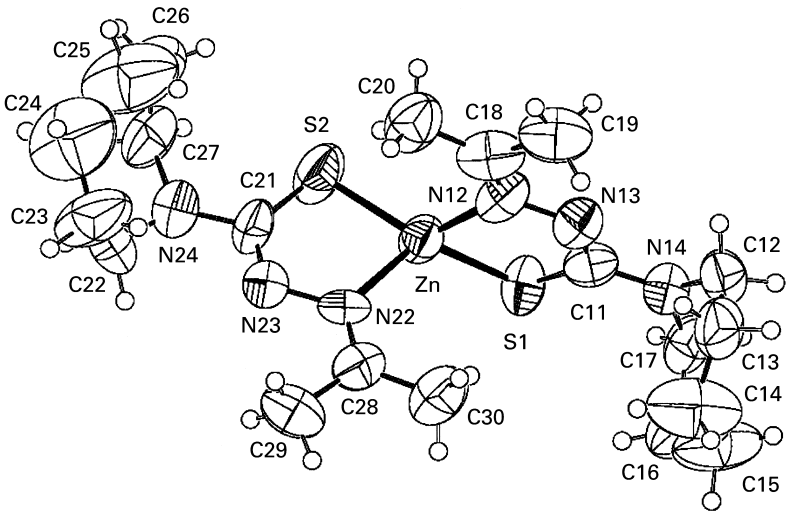

Fig. 2. ORTEP drawing of bis(acetone hexamethyleneiminylthiosemicarbazonato)-zinc(II), [Zn(Acehexim)$_2$] with atom numbering scheme and displacement ellipsoids at 50% probability level.

20 h compared to 19% conversion in 10 d for free acetone thiosemicarbazone [19]. The highest conversion rate was obtained with nickel(II) complexes, and there is a reduction in the rate of hydrolysis with increasing bulkiness of the preparative ketone. Aromatic thiosemicarbazones, particularly with electron withdrawing substituents, are much less susceptible to hydrolysis [19]. Recently, a 6-coordinate tin(IV) complex involving two HAce4DH ligands coordinated via the thione sulfur, but not the imine nitrogen, has been reported [20]. Thus, to our knowledge, there has not been a structure reported of a

Table 4
Bond distances (Å) of zinc complexes with anionic thiosemicarbazone ligands

Compound	Zn–N	Zn–S	C = N	N–N	N–C(S)	C–S	C(S)– N
[Zn(Acehexim)$_2$][a]	2.056(10)	2.255(3)	1.271(14)	1.398(12)	1.351(15)	1.705(16)	1.368(13)
[Zn(2,6Achexim)]$_2$[b]	2.052(5)	2.357(2)	1.303(10)	1.368(9)	1.348(12)	1.730(7)	1.347(11)
[Zn(Amhexim)OAc]$_2$[c]	2.038(3)	2.3724(11)	1.295(4)	1.383(4)	1.307(5)	1.754(4)	1.365(5)
[Zn(2,6Ac4DM)]$_2$[d]	1.989(6)	2.338(3)	1.338(9)	1.409(8)	1.325(10)	1.742(9)	1.330(11)
[Zn(Ac4DH)]$_2$[e]	2.07(1)	2.322(3)					
[Zn(Pgpip)]$_2$[f]	2.177(3)[g]	2.3216(11)	1.300(5)	1.356(4)	1.338(5)	1.745(4)	1.345(5)
	2.160(3)[h]	2.4078(11)	1.311(5)	1.394(4)	1.366(5)	1.714(4)	1.350(5)

[a] Average of two ligands, this work.
[b] 2,6Achexim is the dianion of 2,6-diacetylpyrdine bis(3-hexamethylene-iminylthiosemicarbazone) and distances are the average of the two tetrahedral centers in the binuclear complex [15].
[c] Amhexim is the anion of 2-pyridineformamide 3-hexamethyleneiminylthiosemicarbazone, which coordinates as tridentate ligand to the 5-coordinate zinc centers in this binuclear complex, distances are the average of the centers [22].
[d] 2,6Ac4DM is the dianion of 2,6-diacetylpyridine bis{N(4)-dimethylthiosemicarbazone} and the binuclear complex has 6-coordinate and 4-coordinate zinc, distances are listed for the 4-coordinate zinc [23].
[e] 2,6Ac4DH is the dianion of 2,6-diacetylpyridine bis(thiosemicarbazone) and the binuclear complex has 6-coordinate and 4-coordinate zinc, distances are listed for the 4-coordinate zinc, other data not give in article, [24].
[f] Pgpip is the dianion of 1-phenylglyoxal bis(3-piperidylthiosemicarbazone) and the binuclear complex has two 5-coordinate zinc centers [25].
[g] Aldehyde arm.
[h] Ketone arm.

Table 5
Bond angles (°) of zinc complexes with anionic thiosemicarbazone ligands (see footnotes for Table 4)

Compound	C–N–N	N–N–C	N–C–S	N–C–N	S–C–N	Zn–N–N	Zn–S–C
[Zn(Acehexim)$_2$]	116.1(11)	114.5(10)	127.7(9)	113.0(13)	119.3(11)	115.7(8)	94.1(4)
[Zn(2,6Achexim)]$_2$	115.5(3)	114.6(6)	126.0(6)	115.1(6)	119.0(6)	121.3(5)	94.8(3)
[Zn(Amhexim)OAc]$_2$	116.2(3)	113.7(3)	126.0(3)	116.3(3)	117.6(3)	123.1(2)	94.89(13)
[Zn(2,6Ac4DM)]$_2$	113.3(6)	119.7(7)	121.5(7)	119.4(8)	119.0(6)	117.1(5)	95.1(13)
[Zn(Pgpip)]$_2$	115.7(3)	114.2(3)	125.0(3)	115.9(4)	119.0(3)	123.9(3)	97.3(2)
	118.5(3)	110.5(3)	124.3(1)	115.3(4)	120.3(3)	122.6(3)	93.1(1)

Compound	N–Zn–S	N–Zn–N	S–Zn–S
[Zn(Acehexim)$_2$]	87.1(3)	108.4(4)	126.44(14)
[Zn(2,6Achexim)]$_2$	83.2(2)	159.2(2)	114.6(1)
[Zn(2,6Ac4DM)]$_2$	84.9(2)	135.2(4)	120.30(6)
[Zn(Ac4DH)]$_2$	83.8(4)	140.8(4)	118.3(2)

complex involving an anionic acetone thiosemicarbazone ligand with bidentate N,S coordination.

This past year the structure of acetone N(4)-methylthiosemicarbazone was reported [21], and while the N(4)H has extensive intra- and intermolecular hydrogen bonding interactions, the hydrazine hydrogen common to HAcehexim is not involved in any hydrogen bonding. Therefore, since HAcehexim, the neutral thiosemicarbazone, has not been previously reported, and [Zn(Acehexim)$_2$] is its first complex to have a structure reported, it is instructive to compare bond distances and angles with other zinc complexes of thiosemicarbazones, and particularly those with the hexamethyleneiminyl substituent. Table 4 contains bond distances and Table 5 contains bond angles of some recently studied zinc thiosemicarbazone complexes. The most similar compound to [Zn(Acehexim)$_2$] is [Zn(2,6Achexim)]$_2$, which is a binuclear complex with two 4-coordinate zinc centers coordinated N_2S_2 by thiosemicarbazone moieties from two different dianions of 2,6-diacetylpyridine bis(hexamethyleneiminylthiosemicarbazone) [16]. The structures of other compounds listed in Tables 4 and 5 are described in the footnotes of Table 4. The most striking difference for [Zn(Acehexim)$_2$] is the Zn–S bond distance, which is significantly shorter than for the other zinc complexes, which is presumably due to a reduced steric requirement for the Acehexim ligand. The N12–Zn–S1 angle is also substantially lower than that found for the other complexes listed in Table 5 and the Zn–N12–N13 angle is also significantly lower. The zinc stereochemistry in [Zn(Acehexim)$_2$], although significantly distorted from tetrahedral symmetry due to differences in Zn–N and Zn–S bond distances, is less distorted than the previously studied zinc complexes. However, there is considerable similarity between the bond distances and angles within the thiosemicarbazone moiety among these complexes.

4. Supplementary material

Crystallographic data for the structure reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-154561. Copies of the data can be obtained free of charge on application from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk).

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