

Synthesis and crystal structure of Zinc (II) Complex $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$

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Abstract: Zinc (II) complex, $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1), where (25-MBTSC = (E)-2-(2,5-dimethoxybenzaldehyde) thiosemicarbazone, has been synthesized from the reaction of ZnI_2 with 25-MBTSC in methanol as solvent at 25 °C. It was characterized by elemental analysis (CHN) and is confirmed by single-crystal X-ray diffraction analysis. The complex 1 crystallizes in a triclinic system, with space group $P\bar{1}$, having one symmetry-independent Zn^{2+} ion coordinated in a distorted tetrahedral geometry by two S atoms of the 25-MBTSC ligand and by two I atoms. The thiosemicarbazone ligand 25-MBTSC acts as a monodentate ligand and coordinates via one S atom in η^1 -S bonding mode to the zinc center.

Keywords: Zinc (II); crystal structure; triclinic; distorted tetrahedral.

Introduction

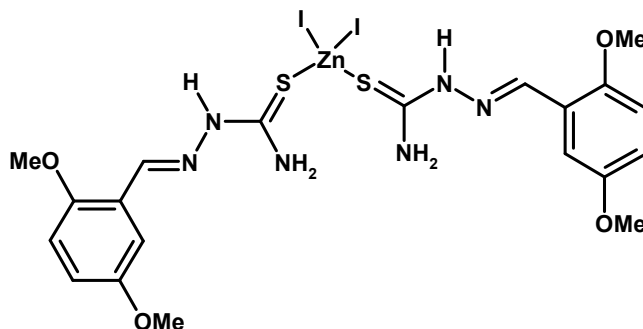
Thiosemicarbazone N, S donor ligands and their transition metal complexes have been studied because of their interesting chemical and structural properties [1-3]. Thiosemicarbazones have a propensity to react with a wide range of transition metal ions [1-5]. They can bind to a metal ion via a variety of coordination modes in their neutral and anionic forms [1-5]. They usually act as chelating N, S ligands with transition metal ions such as Zn(II), Hg(II), Ni(II), Co(II), Cu(II) and Cd(II), bonding through the sulfur and hydrazine nitrogen atoms [6,7] and as η^1 -S bonding mode with Cu(I) and Ag(I) ions [8,9]. Only a few reports exist on

the η^1 -S bonding mode of thiosemicarbazone ligands with Zn (II) ion [10, 11].

We describe here another example of this mode, zinc(II) complex $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1) obtained from (2,5-dimethoxybenzaldehyde) thiosemicarbazone (25-MBTSC) as a ligand.

Experimental

All reagents and solvents for synthesis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. The thiosemicarbazone ligand 25-MBTSC was prepared following the standard procedure [12].



Scheme 1 The Zn(II) complex $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1).

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Preparation of [Zn(25-MBTSC)₂I₂] (1)

To a stirring solution of the 25-MBTSC ligand (0.096 g, 0.4 mmol, in 5 ml of ethanol) was added ZnI₂ (0.064 g, 0.2 mmol) in 10 ml of ethanol and the mixture was stirred for 10 min at room temperature. It was left at 25°C for several days without disturbance yielding suitable crystals of 1 that subsequently were filtered off and washed with Et₂O. The yield was 66%. Anal. Calcd. for C₂₀H₂₆I₂N₆O₄S₂Zn: C, 30.11; H, 3.28; N, 10.53%. Found, %: C, 29.95; H, 3.36; N, 10.40.

X-ray structure determination

A single crystal of compound 1 with the dimensions 0.23 × 0.16 × 0.09 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at 150 K with four-circle CCD diffractometer (Gemini of Oxford diffraction, Ltd.), using mirrors collimated CuK α radiation (λ = 1.54184 Å, graphite monochromator and area detector Atlas). The crystal structure was solved by direct methods with the SIR2002 program [13]

and refined with the Jana 2006 program package [14] by the full-matrix least-squares technique on F². The molecular structure plots were prepared by ORTEP III for Windows [15]. One of 2,5-dimethoxyphenyl groups is disordered, and its atoms are divided into two sites [occupancy ratio: 0.556(7)] Hydrogen atoms in non-disordered part were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. Positions of hydrogen atoms bounded to nitrogen were refined using a distance restraint. The other H atoms were fixed in the ideal geometry, allowing only rotation of methyl groups. All hydrogen atoms were refined with thermal displacement coefficient U_{iso} (H) set to 1.5 U_{eq} (C) for the methyl groups and to 1.2 U_{eq} (C,N) for the other hydrogens. Crystallographic data and details of the data collection and structure refinements are summarized in Table 1. Bond distances and angles are listed in Table 2.

Table 1 Crystal data for [Zn(25-MBTSC)₂I₂] (1).

Parameter	Value
Formula weight	797.8
Crystal system, Space group	Triclinic, P-1
T, K	120
a, Å	8.7141(4)
b, Å	9.2077(4)
c, Å	18.1901(8)
α , deg	101.664(4)
β , deg	93.574(3)
γ , deg	99.041(4)
V, Å ³	1404.92(11)
Z	2
μ , mm ⁻¹	20.14
Measured reflections	20637
Independent reflections	4319
R _{int}	0.055
S	1.71
Number of parameters	365
Reflections with I > 3 σ I	3622
R (F ² > 2 σ (F ²))	0.043
wR (F ²)	0.109
T _{min} , T _{max}	0.104, 0.35
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ ⁻³)	-0.63, 1.49

Table 2 Selected bond distances (Å) and angles (deg) for [Zn(25-MBTSC)₂I₂] (1).

I1-Zn1	2.6081(10)	I2-Zn1	2.5702(11)
Zn1-S1	2.3439(16)	Zn1-S2	2.3840(17)
S1-C1	1.727(7)	S2-C11	1.708(8)
N1-C1	1.311(7)	N2-N3	1.386(8)
N2-C1	1.327(7)	N3-C2	1.288(7)
N4-C11	1.342(9)	N5-N6	1.392(9)
N5-C11	1.325(9)	N6-C12	1.297(10)
C2-C3	1.457(9)	C12-C13	1.307(18)
I1ZnI2	111.44(3)	S1-Zn1S2	111.87(6)
I1Zn1S2	113.18(5)	I1Zn1S1	105.46(5)
I2Zn1S1	112.58(6)	I2Zn1S2	102.53(6)
Zn1S1C1	106.5(2)	Zn1S2C11	107.7(2)
S1C1N2	119.6(4)	S2C11N5	122.1(5)
N4-C11-N5	117.0(7)	N6C12C13	127.1(9)
N3N2C1	121.1(5)	N2N3C2	111.9(5)
N6N5C11	120.0(5)	N5N6C12	114.0(6)
S1C1N1	120.5(5)	N1C1N2	119.9(6)
N3C2C3	124.1(6)	S2C11N4	120.9(6)

Results and Discussion

The molecular structure of $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1) is based on a monomeric where Zn(II) is bonded to two iodide ions ($\text{Zn1-I1} = 2.6081(10)$ and $\text{Zn1-I2} = 2.5702(11)$ Å) and two sulfur atoms from the 25-MBTSC ligands ($\text{Zn1-S1} = 2.3439(16)$ and $\text{Zn1-S2} = 2.3840(17)$ Å), as shown in Figure 1. The coordination geometry around zinc can be described as a distorted tetrahedral [9]. The bond angles in the tetrahedron are close to those of a perfect tetrahedron, and are found to be in the range 102.53 - 113.18° . In this complex, two classical intramolecular hydrogen bonds of the type $\text{N2H2}\cdots\text{S1}$ and $\text{N5H5}\cdots\text{I1}$ are formed between H-atoms of the ligand and the S and I atoms

coordinated to zinc ion (Fig. 1, Table 3). The molecular packing is given in Fig. 2.

Conclusions

The new thiosemicarbazone zinc (II) complex $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1) was synthesized and characterized by elemental analyses. Single crystals were successfully grown from solution by slow evaporation technique at 298 K. The single crystal X-ray diffraction revealed a triclinic structure with space group $P\bar{1}$ and one symmetry independent molecule $\text{C}_{20}\text{H}_{26}\text{I}_2\text{N}_6\text{O}_4\text{S}_2\text{Zn}$. The thiosemicarbazone ligand 25-MBTSC acts as a monodentate ligand and coordinates via one S atoms in η^1 -S bonding mode to the zinc center

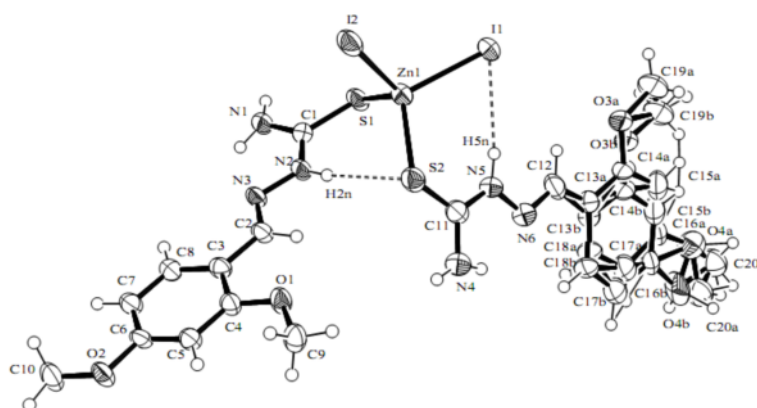


Fig 1. Molecular structure of $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1). Displacement ellipsoids are drawn at 50% probability level.

Table 3 Hydrogen-bond geometry (Å, °) of $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1)

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
N5—H5n \cdots I1	0.878	2.710	3.578(3)	170.42
N2—H2n \cdots S2	0.863	2.549	3.402(4)	170.07

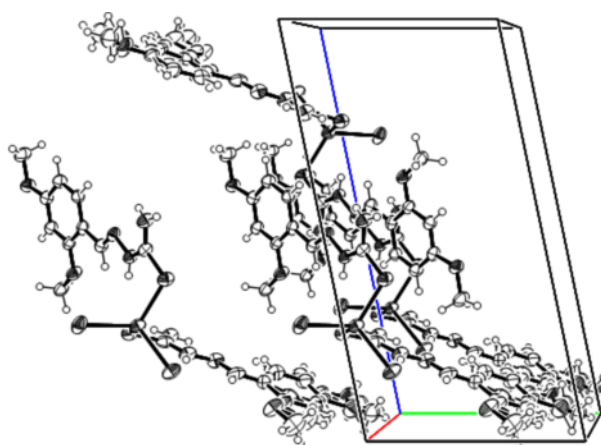


Fig 2 Packing diagram for $[\text{Zn}(\text{25-MBTSC})_2\text{I}_2]$ (1).

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 861425. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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