IRANIAN SOCIETY of CRYSTALLOGRAPHY and MINERALOGY

Vol.21, No. 1, Spring 1392/2013

Pages 1 to 4

IRANIAN JOURNAL of CRYSTALLOGRAPHY and MINERALOGY

# Synthesis and crystal structure of Zinc (II) Complex $[Zn(25\text{-}MBTSC)_2I_2]$

**A. Dehno Khalaji[1*], K. Fejfarova[2], M. Dusek [2]**

*1- Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran*
*2- Institute of Physics of the ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic*

(Received: 1/11/2011, in revised form: 10/3/2012)

**Abstract:** Zinc (II) complex, $[Zn(25\text{-}MBTSC)_2I_2]$ (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 ºC. 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 $\eta^1$-S bonding mode to the zinc center.

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

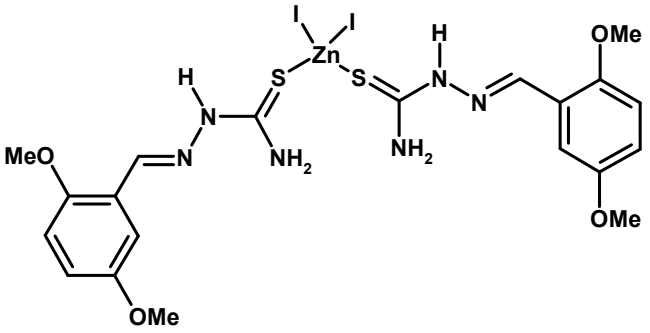
## Introduction

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 $\eta^1$-S bonding mode with Cu(I) and Ag(I) ions [8,9]. Only a few reports exist on the $\eta^1$-S bonding mode of thiosemicarbazone ligands with Zn (II) ion [10, 11].

We describe here another example of this mode, zinc(II) complex $[Zn(25\text{-}MBTSC)_2I_2]$ (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-MBTSCwas prepared following the standard procedure [12].




Scheme 1 The Zn(II) complex $[Zn(25\text{-}MBTSC)_2I_2]$ (1).

* Corresponding author, Tel: (0171) 2245882, Fax: (0171) 2245964, Email: alidkhalaji@yahoo.com

**Preparation of [Zn(25-MBTSC)$_2$I$_2$] (1)**

To a stirring solution of the 25-MBTSC ligand (0.096 g, 0.4 mmol, in 5 ml of ethanol) was added $ZnI_2$ (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 25ºC for several days without disturbance yielding suitable crystals of 1 that subsequently were filtered off and washed with $Et_2O$. The yield was 66%. Anal. Calcd. for $C_{20}H_{26}I_2N_6O_4S_2Zn$: 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 CuKα 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 $F^2$. 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)$_2$I$_2$] (1).

| Parameter | Value |
|---|---|
| Formula weight | 797.8 |
| Crystal system, Space group | Triclinic, P-ī |
| 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 > 3σI | 3622 |
| R ($F^2 > 2\sigma(F^2)$) | 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)$_2$I$_2$] (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) |
| | | | |
| I1Zn1I2 | 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 $[Zn(25\text{-}MBTSC)_2I_2]$ (1) is based on a monomeric where Zn(II) is bonded to two iodide ions (Zn1-I1 = 2.6081(10) and Zn1-I2 = 2.5702(11) Å) and two sulfur atoms from the 25-MBTSC ligands (Zn1-S1 = 2.3439(16) and 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 102.53-113.18º. In this complex, two classical intramolecular hydrogen bonds of the type N2H2···S1 and N5H5···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 $[Zn(25\text{-}MBTSC)_2I_2]$ (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-ī and one symmetry independent molecule $C_{20}H_{26}I_2N_6O_4S_2Zn$. The thiosemicarazone ligand 25-MBTSC acts as a monodentate ligand and coordinates via one S atoms in $\eta^1$-S bonding mode to the zinc center

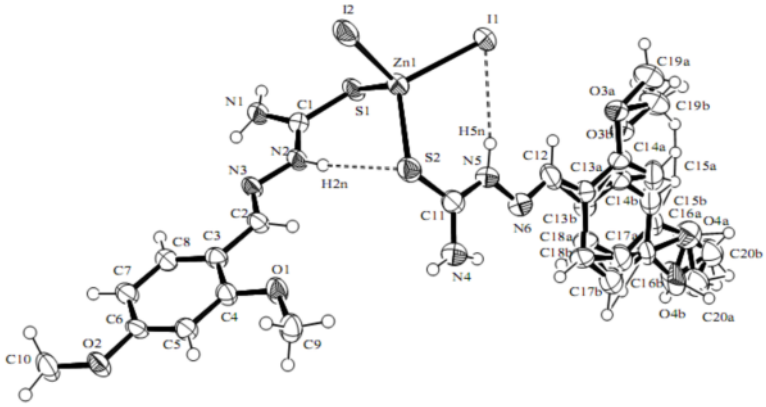



**Fig 1.** Molecular structure of $[Zn(25\text{-}MBTSC)_2I_2]$ (1). Displacement ellipsoids are drawn at 50% probability level.

**Table 3** Hydrogen-bond geometry (Å, °) of $[Zn(25\text{-}MBTSC)_2I_2]$ (1)

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

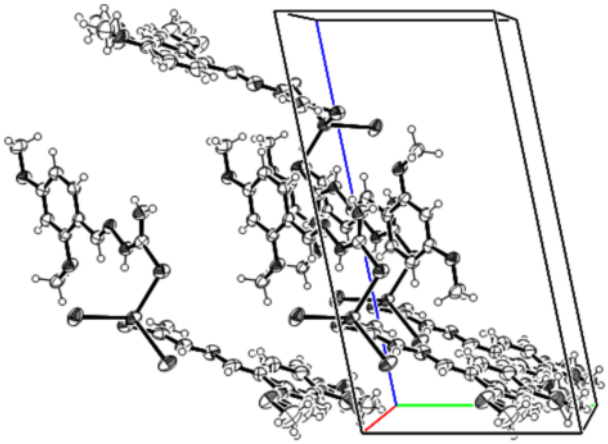


**Fig 2** Packing diagram for $[Zn(25\text{-}MBTSC)_2I_2]$ (1).

**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.

**Acknowledgments**

We acknowledge the Golestan University (GU) for partial support of this work, the institutional research plan No. AVOZ10100521 of the Institute of Physics and the project Praemium Academiae of the Academy of Sciences of the Czech Republic.

**References**

[1] Lobana T.S., Sharma R., Butcher R.J., *"Synthesis, spectroscopy and structures of halogen and sulfur-bridged dinuclear silver(I) complexes with $N^1$-substituted thiophene-2-carbaldehyde thiosemicarbazone"*, Polyhedron 28 (2009) 1103-1110.

[2] Krishna P.M., Reddy K.H., *"Synthesis, single crystal structure and DNA cleavage studies on first $^4$N-ethyl substituted three coordinate copper(I) complex of thiosemicarbazone"*, Inorg. Chim. Acta 362 (2009) 4185.

[3] Lopez-Torres E., Mendiola M.A., *"Mercury complexes with the ligand benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone"*, Inorg. Chim. Acta 363 (2010) 1275-1283.

[4] Chumakov Y.M., Samus N.M., Bocelli G., Suponitskii K.Y., Tsapkov V.I., Gulya A.P., *"Crystal structures of 3-phenylpropenal thiosemicarbazone and its nickel(II) and zinc `chelates"*, Russ. J. Coord. Chem. 32 (2006) 14-20.

[5] Jouad E. M., Allain M., Khan M.A., Bouet G.M., *"Structural and spectral studies of nickel(II), copper(II) and cadmium(II) complexes of 3-furaldehyde thiosemicarbazone"*, Polyhedron 24 (2005) 327-332.

[6] Burrows A.D., Harrington R.W., Mahon M.F., *"Hydrogen bond directed crystal engineering of nickel complexes: the crystal structure of cis-bis(4-ethylthiosemicarbazide)nickel(II) terephthalate and the influence of metal geometry on supramolecular structure"*, CrystEngComm. (2000) 12-16.

[7] Lobana T.S., Sharma R., Bawa G., Khanna S., *"Bonding and structure trends of thisemicarbazone derivatives of metals-An overview"*, Coord. Chem. Rev. 253 (2009) 977-1055.

[8] Lobana T.S., Khanna S., Castineiras A., *"Sulfur bridging by acetophenone thiosemicarbazone in $[Ag(\mu\text{-dppm})_2(\mu\text{-SR})Ag(ONO_2)](NO_3)$ dimer with a new $\{Ag_2(\mu\text{-P,P})_2(\mu\text{-SR})\}$ core"*, Inorg. Chem. Commun. 10 (2007) 13071310.

[9] Lobana T.S., Khanna S., Sharma R., Hundal G., Sultana R., Chaudhary M., Butcher R.J., Castineiras A., *"Versatility of thiosemicarbazones in the construction of monomers, dimmers and hydrogen-bonded networks of silver(I) complexes"*, Cryst. Growth Des. 8 (2008) 1203.

[10] Bermejo E., Castineiras A., Perez T., Carballo R., Hiller W., *"Synthesis and structural characterization of metal complexes of 2-formylpyrrole-$^4$N-ethylthiosemicarbazone ($4EL_1$) and 2-acetylpyrrole-$^4$N-ethylthiosemicarbazone ($4EL_2$) Z."*, Anorg. Allg. Chem. 627 (2001) 2377-2385.

[11] Alomar K., Landreau A., Kempf M., Khan M.A., Allain M., Bouet G., *"Synthesis, crystal structure, characterization of zinc(II), cadmium(II) complexes with 3-thiophene aldehyde thiosemicarbazone (3TTSCH). Biological activities of 3TTSCH and its complexes"*, J. Inorg. Biochem. 104 (2010) 397-404.

[12] Khalaji A.D., Grivani G., Jalali Akerdi S., Gotoh K., Ishida H., Mighani H., *"Synthesis, spectroscopic characterization, crystal structures, and theoretical studies of (E)-2-(2,4-dimethoxybenzylidene)thiosemicarbazone and (E)-2-(2,5-dimethoxybenzylidene)thiosemicarbazone"*, Struct. Chem. 21 (2010) 995-1003.

[13] Burla M.C., Camalli M, Carrozzini B, Cascarano G, Giacovazzo C, Polidori G, Spagna R, SIR2002 : the program, J. Appl. Cryst. 36 (2003) 1103.

[14] Petricek V., Dusek M., Palatinus L., Jana2006., *"Structure Determination Software Programs"*, Praha (Czech Republic): Institute of Physics, 2008.

[15] Farrugia L.J., *"ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI)"*, J. Appl. Cryst. 30 (1997) 565.