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RESEARCH ARTICLE

SPECTROSCOPIC STUDIES IR, ^{1}H, ^{13}C NMR AND XRAY DIFFRACTOMETER CHARACTERIZATION OF A NEW THIOSEMICARBAZONE ORGANIC LIGAND (E)-(2-(1-(2-HYDROXYPHENYL)ETHYLEN)HYDRAZIN-1-CARBOTHIOAMID

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Abstract

A new thiosemithiocarbazone ligand $C_6H_4(OH)CHN(NH)S(NH_2)$ named H_4L^1 have been isolated and characterized by single-crystal X-ray diffraction. H_4L^1 compound crystallizes in the monoclinic system, space group C2/c with a = 28.1975(4) Å, b = 6.71768(10) Å, c = 19.4249(3) Å, β = 94.6290(17)°, V = 1737.84(14) Å3 and Z = 4. The asymmetric unit of $H_4L^1$is consisted ofa dimeric structure of two molecules of $C_6H_4(OH)CHN(NH)S(NH_2)$. Each monomer contains one intramolecular OH---N[NH(4)----O'(3) =2.553A] hydrogen bond which comes from the hydrogen atom of OH group and the nitrogen atom of CN group and NH---S[N(4)H(4A)----S(1)=2.699A] intermolar hydrogen bond, acetic acid type, interacting electrostatically with two semicarbazone ligands. In supramolecular vue, organic ligands are linked via S(H,H)O bifurcated hydrogen bonds or NH---O hydrogen bonds. Structural characterization were completed by elemental analysis,infrared and 1H, 13C{1H} spectroscopies and which corroborate the X-ray elucidations.

Introduction:-

Thiosemicarbazones are compounds family which derived from hydrazones that are very well known in chemistry. Many works around these compounds have been reported in the literature interesting such as their easy synthesis methods and their stereochemistry, their biological activities, their ability to complex many metal elements, their spectral characteristics and the diversity of the crystal structures they generate [1- 6]. These Schiff bases are generally obtained by condensation reaction of thiosemicarbazones with aldehyde or ketones under mild conditions in excellent yields. Sometimes a slight heating and the addition of a few drops of glacial acetic acid are necessary for the selectivity of the reaction [7, 8].

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Thiosemicarbazones also have various applications in analytical chemistry [9, 10]. They are used as corrosion inhibitors or as complexing agents for the removal of heavy metals from wastewater [11, 12]. In the present work, we report the synthesis of a new Schiff-based thiosemicarbazone ligands (H_4L^1), their characterization by infrared and NMR spectroscopic methods and the resolution of their chemical structures by single-crystal X-ray diffraction.

Experimental methods

All the chemical products and solvents are used without any purification. Thiocarbazide molecule, 2-hydroxacétophénone, cadmium dichloride dihydrated were acquired from Sigma Aldrich Chemicals and used without any further purification.

Infrared spectra were recorded on FTIR Spectrum Two of Perkin Elmer. ^1H, $^{13}C\{1H\}$ spectra were recorded on Bruker Avance 250 MHz spectrometer in DMSO-d6. Chemical shift (δ, ppm) is converted to the scale downfield from TMS as reference.

Elemental analyses wereperformed at the Institut de Chimie Moléculaire, Université de Bourgogne Franche- Comté, Dijon, France

Synthesis du ligand H_4L^1

2g (0.0219 mol) of thiosemicarbaldehyd are dissolved in a flask containing 20 mL of methanol solvent is mixed with 10 mL of methanolic solution of 2.6805 g (0.0219 mol) of 2-hydoxybenzaldehyd. The mixture has been refluxed during two hours. A yellow precipitate has been obtained. This precipitate was recovered by filtration, washed with diethyl ether and dried in vacuum. The precipitate is corresponded of H_4L^1 (confirmed by elemental analysis).

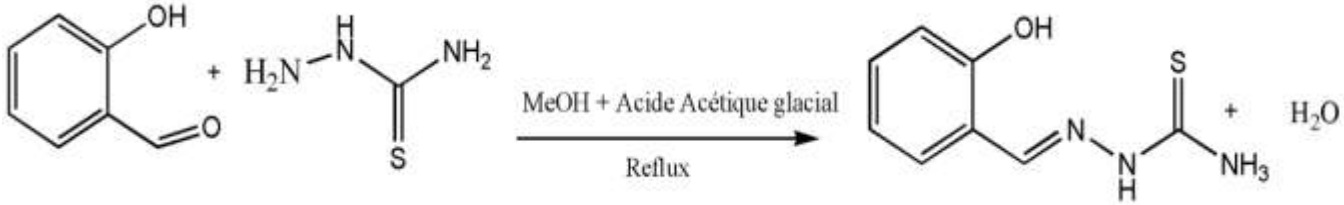


Figure 1: Synthesis process of the thiosemicarbazone molecular

Processus of crystallization

The first object was to synthetize complexes of coordination between the organic ligand thiosemicarbazone and a MX_2 (M=Cd, Zn, Co; X=Cl, Br) molecules.

At first, 0.1g (0.5 mmol) of white powder of H_4L^1 dissolved in 20 mL of methanol solvent is mixed with 0.155g (0.5mmol) of $CdCl_2.H_2O$ dissolved in 20 mL of methanol solvent. The mixture is made in reflux during two hours. An unclear yellow solution is obtained, filtered to obtain a limpid solution and a weak quantity of white precipitate. The yellow filtrate is made to slow solvent evaporation. One week after, grey crystals are obtained suitable to X ray characterization. The elemental analysis confirm that these crystals are corresponded of H_4L^1 organic ligand and the instant precipitate is corresponded of dihydrated initial metal precursor.

Spectroscopic IR and NMR data

The compound H_4L^1 is soluble in many organic solvents: dimethylsulfoxyd (DMSO), dimethylformamide (DMF), acetonitrile and hot distilled water. Melting temperature Mt > 260 °C. yield= 86.3 %. Elemental analysis: Calculated C=49.21; H=4.65; N=21.52; Found C=49.30; H=4.71; N=21.30. IR data (υ, cm^{-1}): 3437 (NH_2); 3311 (O-H); 3171 (N-H); 2986 (C_{Ar}-H) ; 1601 (C=N) ; 1536-1462 (C_{Ar}= C_{Ar}); 1263 (C_{Ar}-Ophenolic) ; 1201 (C=S) ; 1060 (N-N), 747 δ(C=S). RMN ^{1}H data (dmso-d6, δ en ppm) : 6.88 (2H, m, H-aromatic,) ; 7.25 (1H, m, H-aromatic) ; 7.9 (2H, S, NH_2) ; 8.09 (1H, m, H-aromatic) ; 8.38 (1H, S, 1H, HC=N) ; 9.86 (1H, S, OHphenolic,), 11.23 (1H, S, NH). RMN ^{13}C (dmso-d6, δ en ppm) : 178.16 (C=S) ; 156.86 (C-Ophenolic) ; 140.12 (C=N) ; 131.51 (C_{Ar}) ; 127.23 (C_{Ar}) ; 120.81 (C_{Ar}) ; 119.71 (C_{Ar}) ; 116/31 (C_{Ar}).

X ray structure determination

Single colorless block-shaped crystals of H_4L^1 recrystallized after recrystallization. A suitable crystal with dimensions 0.47 × 0.32 × 0.26 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a XtaLAB Synergy, Dualflex, HyPix-Arc 100 diffractometer. The crystal was kept at a steady T = 100.0(4) K during data collection. The structure was solved with the Superflip [13] solution program using iterative methods and by

using Olex2 1.5-ac5-024 [14] as the graphical interface. The model was refined with ShelXL 2018/3 [15] using full matrix least squares minimisation on F^2. Crystal Data. $C_8H_9N_3OS$, M_r = 195.24, monoclinic, C2/c (No. 15), a = 28.1975(4) Å, b = 6.71768(10) Å, c = 19.4249(3) Å, b = 93.7591(14)°, a = g = 90°, V = 3671.57(9) Å^3, T = 100.0(4) K, Z = 16, Z' = 2, m(Mo K_a) = 0.314, 4821 reflections measured, 4821 unique (R_{int} = .) which were used in all calculations. The final wR_2 was 0.1252 (all data) and R_1 was 0.0427 (I≥2 s(I)). All crystallographic data, selected bonds distances and angles are presented in (table 1 and 2).

Table 1. Crystallographic data and refinement parameter for the compounds (1).

Chemical formula	C8H9N3OS
Mr	195.24
Crystal shape/color	Block, colorless
Crystal system, space group	Monoclinic, C2/c
Crystal size (mm)	0.47 × 0.32 × 0.26
a (Å)	28.1975 (4)
b (Å)	6.71768 (10)
c (Å)	19.4249 (3)
β (°)	93.7591 (14)
V (Å3)	3671.57 (9)
Z	16
Dcalc (g.cm^{-3})	1.413
Wavelength (Å)	0.71073
T (K)	100
μ (mm^{-1})	0.31
Index ranges	-39 ≤ h ≤ 38, 0 ≤ k≤ 9, 0≤ l≤ 26
F(000)	1632
range (°)	5.7–30.0
No. of measuredreflections	4821
No. of independentreflections	4821
No. of observed [I>2σ(I) DTRFG reflections	4552
R[F2> 2σ(F^2)]	0.043
wR(F^2)	0.125
Goodness-of-fitt (Gof) on F^2	1,38
No. of parameters	238
No. of restraints	0
Δρmax, Δρmin (e Å^{-3})	0.60, −0.38
CCDC number	2332641

Table 2 . Selected bond distances [Å] and angles [deg] for the compound (1)

Select bonds	Values	Select bonds	Values
S1—C1	1.6984 (17)	C11—C12	1.408 (2)
S2—C9	1.6927 (17)	C2—C3	1.454 (2)
O1—C4	1.363 (2)	C3—C4	1.409 (2)
O2—C12	1.365 (2)	C3—C8	1.406 (2)
N1—C1	1.331 (2)	C5—C6	1.389 (3)
N4—C9	1.327 (2)	C5—C6	1.389 (3)
N5—N6	1.3743 (18)	C4—C5	1.393 (2)
N6—C10	1.290 (2)	C11—C16	1.404 (2)
N5—C9	1.350 (2)	C13—C14	1.390 (3)
N2—N3	1.3786 (19)	C12—C13	1.390 (2)

N2—C1	1.344 (2)	C14—C15	1.391 (3)
N3—C2	1.289 (2)	C15—C16	1.386 (2)
O1—H1	0.8400	O2—H2B	0.8400
N1—H1A	0.8800	N4—H4A	0.8800
N1—H1B	0.8800	N4—H4B	0.8800
N2—H2	0.8800	N5—H5A	0.8800
Select angles	Values	Select angles	Values
N6—C10—C11	121.24 (15)	C9—N5—N6	119.91 (13)
C12—C11—C10	122.73 (15)	C10—N6—N5	116.32 (14)
C8—C3—C2	118.80 (15)	N4—C9—S2	122.31 (13)
C16—C11—C10	119.20 (15)	N4—C9—N5	118.14 (15)
C8—C3—C4	118.27 (15)	N5—C9—S2	119.55 (12)
O1—C4—C3	121.13 (15)	O1—C4—C5	118.16 (16)
C13—C12—C11	120.63 (16)	C1—N2—N3	121.01 (14)
C16—C11—C12	118.04 (15)	C2—N3—N2	115.21 (14)
O2—C12—C11	121.53 (15)	N1—C1—S1	121.98 (12)
C13—C14—C15	120.20 (16)	N1—C1—N2	119.16 (15)
C12—C13—C14	120.12 (16)	N2—C1—S1	118.85 (12)
C4—C3—C2	122.92 (15)	N3—C2—C3	122.10 (15)
C5—C4—C3	120.71 (16)	O2—C12—C13	117.84 (15)
C6—C5—C4	119.66 (17)	C5—C6—C7	120.68 (16)
C4—O1—H1	109.5	C7—C8—C3	121.03 (16)

1. Results and discussion

1.1.1. Spectroscopiccharacterization discussion

The chemical function of the H_4L^1thiosemicarbazone molecule is mainly characterized by the presence of many strong vibration bands at 3437 cm^{-1}, 3311 cm^{-1}, 1601 cm^{-1}, 1201 cm^{-1} et 747 cm^{-1} which corresponding of n(NH_2), n(O-H) phenolic, n(C=N) imine et n(C=S) et δ(C=S) respectively [16, 17]. The absence at 2500 cm^{-1} of the vibration n(S-H) is shown that the sulfur atom becomes a thione group.

The ^1H and ^{13}C NMR characterization of H_4L^1 is realized in deterred dimethylsulfoxyd solution. Its spectrum shows a single signal at δ=11.23 ppm which integrated the proton NH of hydrazone -C=N-NH group. The two others single signals in the spectrum at δ=9.68 ppm and δ=8.38 ppm are identified and attributed to phenolic proton ((1H, S, H-OPh) and imine proton (1H, S, H-C=N). The four aromatic protons appeared as multiplet between δ=6.88 ppm and δ=8.09 ppm (4H, m, H-Ar). Finally, the single signal at δ=7.90 ppm which integrate 2H is attributed for the two protons of NH_2 group (2H, S, N-NH_2).

As to ^{13}C NMR spectrum, it reveals five signals. A signal at δ=178.16 ppm is attributed to carbon atom of thione function (C=S). A δ=140.12 ppm and δ=156.86 ppm, the spectrum shows two single signals which are corresponded respectively to carbon atoms of imine function (C=N) and phenolic group (C-O). As to aromatic carbon atoms, there chemical shift appears between 131.15 ppm and 116.31 ppm.

1.1.2. Xray structure discussion

Compound H_4L^1 crystallizes in the monoclinic system, space group C2/c with a = 28.1975(4) Å, b = 6.71768(10) Å, c = 19.4249(3) Å, β = 94.6290(17)°, V = 1737.84(14) Å3 and Z = 4. The asymmetric unit in Figure 1 is consisted of a dimeric structure of two isolated molecules of C_6H_4(OH)CHN(NH)S(NH_2). Each monomer contains one intramolecular OH---N hydrogen bond which comes from the hydrogen atom of OH group and the nitrogen atom of CN group. As shown , the structure C_6H_4(OH)CHN(NH)S(NH_2) monomers are linked via NH---O hydrogen bonds [NH(4)----O'(3) =2.553A] of acetic acid type, interacting electrostatically with two semicarbazone ligands.

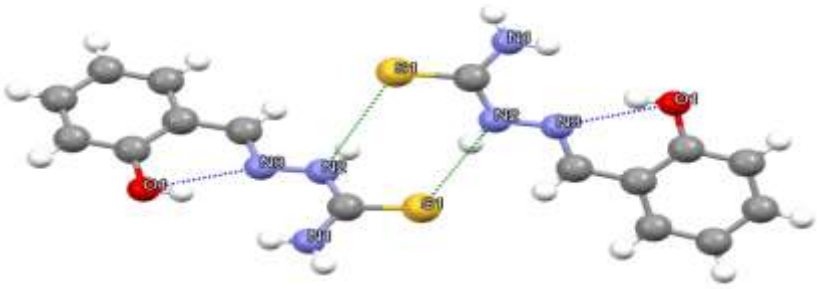
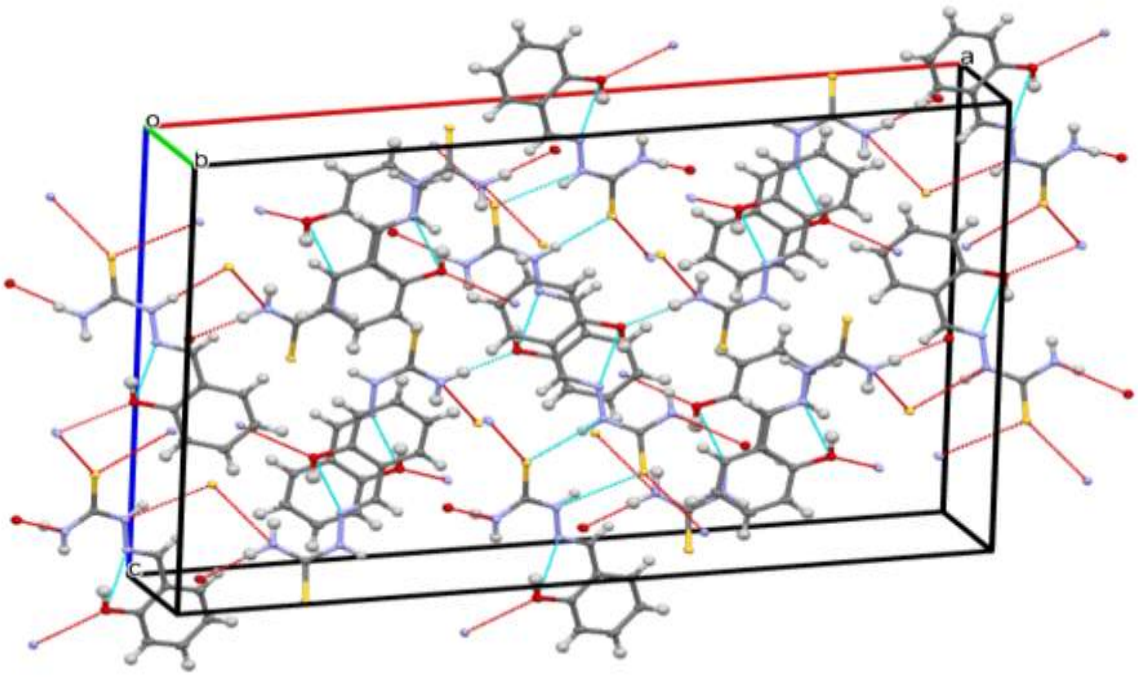


Figure 1:Asymmetric unit of (E)-(2-(1-(2-hydroxyphenyl)ethylen)hydrazin-1-carbothioamid

In supramolecular vue, each thiosemicarbazone molecule is linked to the two neighboring thiocarbazone molecules via three different types of hydrogen bonds. In one case, one organic ligand is linked to a neighboring one via NH---S hydrogen bonds between one hydrogen atom of NH_2 group of the first molecule and the S atom of the other molecule [N(4)H(4A)----S(1)=2.699A].In another case, that first organic molecule is linked to that same neighboring molecule in an O---HN hydrogen bonds coming from oxygen atom of the first molecule and the hydrogen atom of NH2 group of the other molecule [O(2)----HN(1)=2,147A].

In a thirst case, that first thiosemicarbazone is linked to a second neighboring thiosemicarbazone molecule via NH----O between the hydrogen atom of NH_2 group of the first molecule and the oxygen atom of OH group of the second neighboring molecule [N(6)H----O(1)=



2.081A.

Figure 2 :The crystal partial packing for the of (E)-(2-(1-(2-hydroxyphenyl)ethylen)hydrazin-1-carbothioamid

2. Conclusion :

We are presented here the spectroscopic study and Xray diffractometer of a new thiosemocarbazone organic ligand. The structure analysis shows a dimeric asymmetric unit with two acid acetic hydrogen bonds. In supramolecular vue, this organic ligand is a 3D structure with NH----O and NH----S hydrogen bond.

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