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Thiosemicarbazone (E)-2(1-(2-Hydroxyphenyl) Hydrazine)-1-Carbothioamide: Spectroscopic Studies, Xray Diffractometer Characterization and Antioxydant Test

Bogou Ndiaye[1], Thierno Moussa Seck[2], Aîssatou Aliou Gaye[2], Blaise Kama[3], Waly Diallo[1]*, Cheikh Abdoul Khadir Diop[1], Erwann Jeanneau[4]

[1]Laboratoire de Chimie Minérale et Analytique, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal
[2]Laboratoire de Chimie de Coordination Organique, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal
[3]Département de Chimie, Université Alioune Diop de Bambey, Diourbel, Senegal
[4]Institut des Matériaux Jean Rouxel de Nantes, Nantes, France
Email: *waly.diallo@ucad.edu.sn

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Abstract

In the present work, a new semithiocarbazone ligand $C_3NH_4CONHNC(CH_3)C_6H_4OH$ H_4L^2 have been isolated and characterized by single-crystal X-ray diffraction. Compound H_4L^2 crystallizes in the monoclinic system space group P21/n with a = 10.9328(9), b = 8.1700(6), c = 13.8095(11) Å, β = 93.7591(14)˚, V = 3671.57(9) Å^3, Z = 16, Z' = 2. Semithiocarbazone connected through NH···O and OH···O hydrogen bonds. In the crystal, the structure is organized in layer-like arrangements. Structural characterizations were completed by infrared and ^1H, $^{13}C\{^1H\}$ spectroscopy and elemental analysis which corroborate the X-ray elucidations. In another case, this organic compound is submitted to antioxidant test. The test has been done by using Akhtar *et al.* methods [1] with some modifications. The tests are done with different concentration of solutions between 100 to 500 μM. The values of per cent of inhibition (5.18% - 25.90%) of the solution containing semithiocarbazone organic compound show a real difference compared to the values of the reference TROLOX. These results show that our organic ligand $C_3NH_4CONHNC(CH_3)C_6H_4OH$ is a good antioxidant compound.

Keywords

Semicarbazone, Monoclinic, Spectroscopic, Antioxydant Tests

1. Introduction

The derived family compound hydrazones, thiosemicarbazones are more and more known in chemistry. Many compounds have been published by many research groups. In biological and medical fields, many activity tests have been done and results reported in the literature [2]-[6]. Semithiocarbazone are also used to synthesize metal complexes with transitions of lanthanides metals which generate a large diversity of the crystal structures [7]-[12]. These complexes have many physical properties such as magnetism [13]-[15], fluorescence [5] [16] [17] or catalysis [18]-[20]. They are used as corrosion inhibitors [21] or as complexing agents for the removal of heavy metals from wastewater [22]. In the present work, we report the synthesis of two new Schiff-based thiosemicarbazone ligands $C_3NH_4CONHNC(CH_3)C_6H_4OH$ H_4L^2), their characterization by infrared and NMR spectroscopic methods and the resolution of their chemical structures by single-crystal X-ray diffraction. This synthetic organic compound is also submitted to antioxidant test to study the biologic activity.

2. Materials and 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) are converted to the scale downfield from TMS as reference.

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

Single yellow block-shaped crystals of (E)-2-(1-(2-hydroxyphenyl) ethylidene) hydrazine-1-carbothiamide compound were used as supplied. A suitable crystal with dimensions $0.35 \times 0.26 \times 0.17$ mm^3 was selected and mounted on a MITIGEN holder oil on a XtaLAB Synergy, Dualflex, HyPix-Arc 100 diffractometer.

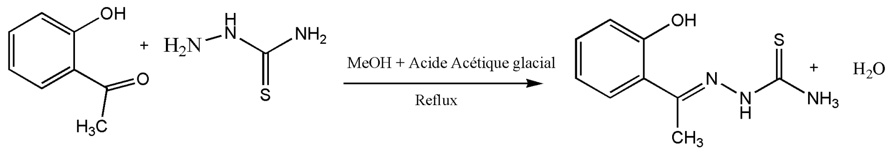
The antioxidant activity of H_4L^2 has been measured by using Akhtar *et al.* method [1] with some modifications. 3.8 ml of methanolic solution of DPPH (1,1-diphenyl-2-picrilhydrazyl) radicals as acceptor(40 mg/L) in 200 μL of H_4L^2 in different concentrations. The mixed solution is incubated in obscurity during thirty minutes and the value of absorbance is read at 517 nm in UV-Visible Lambda 365 de Perkin-Elmer spectrometer. The percent of inhibition has been calculated by using the mathematic equation.

$$\% \text{ Inhibition} = \frac{\text{Absorbance}_{\text{control}} - \text{Absorbance}_{\text{sample}}}{\text{Absorbance}_{\text{control}}}$$

Synthesis of thiosemicarbazone ligand H_4L^2

2 g (0.0219 mol) of thiosemicarbaldehyde and a methanol solution containing

2.981 g (0.0219 mol) of 2-hydroxy acetophenone were introduced into a balloon of 100 mL capacity containing 20 mL of methanol. A few drops of glacial acetic acid were added. The mixture was made in reflux for four hours. A white solid was obtained which was recovered by filtration, washed with cold methanol (30 mL) and diethyl ether (20 mL). In Scheme 1 is showed the process of synthesis of thiosemicarbazone ligand H_4L^2.



Scheme 1. The process of preparation of the thiosemicarbazone molecular.

Process of slow solvent crystallization of H_4L^2

0.195 g (0.1 mmol) of H_4L^2 dissolved in 20 mL of methanol solvent are mixed with 0.199 g (0.1 mmol) of SnM_3Cl dissolved in 20 mL of methanol solvent. The mixture is made in reflux during two hours. A limpid colorless solution is obtained which is made in slow solvent evaporation. One week after, suitable yellow crystals are obtained available to Xray characterization and marron unsuitable crystals which was re-submitted to recrystallization. Elemental analysis confirms that these yellow crystals are corresponded of organic compound of H_4L^2. Melting temperature Mt > 260˚C. Yield = 80.5%.

Spectroscopic Data

IR data (cm^{-1}): 3404 $\nu(NH_2)$; 3280 ν(O-H); 3134 ν(N-H), 2953 ν(C-H), 1587 ν(C=N) imine, 1519-1441 ν(C=C)Ar, 1271; ν(Car-Ophenolic), 1235 ν(C=S), 1050 ν(N-N), 733 δ(C=S). **^{1}H NMR data** (dmso-d6, δ(ppm): 6.89 (2H, mult, H-Ar); 7.21 (1H, mult, H-Ar); 7.52 (1H, mult, H-Ar); 7.88 (2H, S, N-NH_2); 7.92 (1H, S, H-OPh); 10.54 (1H, S, NH). **^{13}C NMR data** (dmso-d6, δ(ppm)): 178.05 (C=S); 148.26 (C=N); 146.34 (C-Ophenolic) (C); 132.1 (CAr); 129.73 (CAr); 120.52 (CAr); 118.52 (CAr); 116.31 (CAr), 11.7 (CH_3).

Determination of structure

The crystal was kept at a steady T = 293(2) K during data collection. The structure was solved with the ShelXT 2018/2 [23] solution program using dual methods and by using Olex2 1.5-ac5-024 [24] as the graphical interface. The model was refined with ShelXL 2018/3 [24] using full matrix least squares minimisation on F^2. Crystal Data. $C_9H_{11}N_3OS$, M_r = 209.27, monoclinic, $P2_1/n$ (No. 14), a = 8.14940(10) Å, b = 9.31130(10) Å, c = 13.2475(2) Å, b = 100.5230(10)˚, $\alpha = \beta = 90$˚, V = 988.33(2) Å^3, T = 293(2) K, Z = 4, Z' = 1, m(MoK_a) = 0.297, 22311 reflections measured, 2580 un i (R_{int} = 0.0220) which were used in all calculations. The final wR_2 was 0.0820 (all data) and R_1 was 0.0304 (I ≥ 2 s(I)).

CCDC 2332641 *contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via* https://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

The data of elemental analysis: [%Calc: C = 51.65, H = 5.30, N = 20.08, S = 15.32: %Found: C = 51.47, H = 5.25, N = 19.96, S = 15.22] are corroborated with $C_3NH_4CONHNC(CH_3)C_6H_4OH$ as formular.

Spectroscopic characterization results

The infrared spectrum (**Figure 1**) reveals that the formation of H_4L^2 is characterized by the presence of phenolic ν(O-H), imine group ν(C=N) imine and ν(C=S) at 3280 cm^{-1}, 1587 cm^{-1} 1235 cm^{-1} et 733 cm^{-1} respectively [25]. The absence of ν(S-H) in the IR spectrum at 2500 cm^{-1} shows that a thione function is formed. NMR spectroscopic characterization reveals many informations. In the ^1H NMR, for example, the two signals as singular at 10.54 ppm and 7.92 ppm are corresponding of NH and OH protons of hydrazon and phenol groups respectively. The aromatic protons appear between 6.89 ppm and 7.52 ppm as multiplate. In the ^{13}C NMR spectrum, appear three signals at 178.05 ppm, 148.26 ppm and 146.34 ppm which are attribute to carbon atoms of thione group (C=S), imine (C=N) group and phenolic C-O. The aromatic carbon atoms signals appear as multiplate between 132.1 ppm and 116.31 ppm [26].

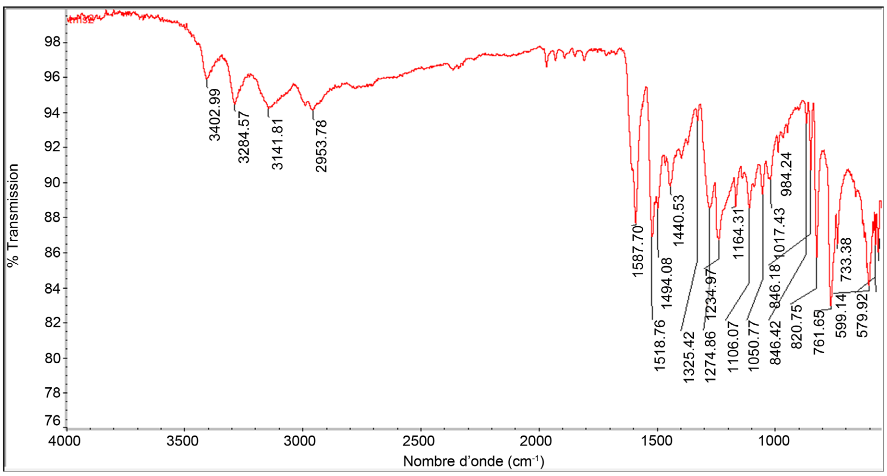


Figure 1. Infrared spectrum of (E)-2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiamide compound.

Xray diffractometer characterization results

The organic ligand crystallizes in monoclinic space group $P2_1/n$. The crystal parameters are given in **Table 1** and, length bonds and angles values in **Table 2**. The asymmetric unit (**Figure 2**) is consist of one 2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiamidemolecule which adopt an E configuration in C2=N2 bond. This molecule contains one intramolecular NH---O hydrogen bond which comes from the hydrogen atom of OH group and the nitrogen atom of CN group. In this structure, sulfur S1 atom of thione group and nitrogen N2 atom of azomethine group are in trans conformation compared to N3-C1 [N2-N3-C1-S1 = 178.9(3)˚]. Then nitrogen atoms N1 and N2 are in Cis conformation compared to N3-C1 bond [N2-N3-

C1-N1 = −8.06(15)˚]. The value of C1-S1 length bond [1.6980(11) Å] shows that H_4L^2 is in thione form in solid state [17]. This thione for mis confirmed by length bonds of N-C [N3-N2 = 1.3911(13) Å, N3-C1 = 1.3412(14) Å, N2-C2 = 1.2993(14)-N3 [1.374(4) Å] which values corroborated with N-C simple bonds [27]. The crystalline mesh (**Figure 3**) is constituted of four organic molecules linked by NH···O intermolecular hydrogen bonds [N1-H(1A)···O2 = 2.9921(13)] and N1-H(1A)···O2 = 3.3577(10) [28]. These secondary interactions between molecules ensure the stability of crystallin network of H_4L^2 compound.

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

Chemical formula	$C_9H_{11}N_3OS$
*M*r	209.27
Crystal shape/color	Block, yellow
Crystal system, space group	Monoclinic, $P2_1/n$
Crystal size (mm)	0.35 × 0.26 × 0.17
a (Å)	8.1494(1)
b (Å)	9.3113(1)
c (Å)	13.2475(2)
β (˚)	100.523(1)
V (Å3)	988.33(2)
Z	4
*D*calc (g·cm^{-3})	1.406
λ (MoK*α*) (Å)	0.71073
T (K)	293
μ (mm^{-1})	0.30
Index ranges	$-11 \leq h \leq 10$, $-12 \leq k \leq 13$, $-18 \leq l \leq 18$
F (000)	440
θ range (˚)	5.5 - 29.8
No. of measured reflections	22311
No. of independent reflections	2580
No. of observed [$I > 2\sigma(I)$] reflections	2401
*R*int	0.022
$R [F2 > 2\sigma(F^2)]$	0.030
$wR (F^2)$	0.082
Goodness-of-fit (Gof) on F^2	1.08

Continued

No. of parameters	129
No. of restraints	0
Δρmax, Δρmin (e Å^{-3})	0.44, −0.37
CCDC number	2,332,641

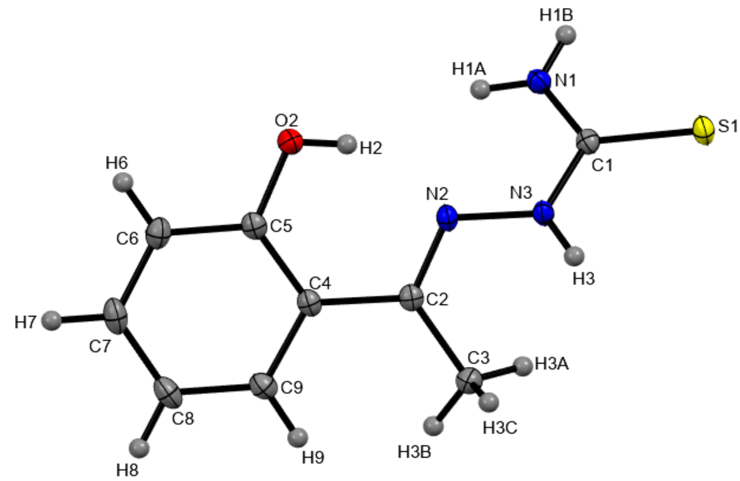
Table 2. Select bonds lengths values (Å) and angles values (˚).

Bonds	lengths		
S1-C1	1.6980(11)	C4-C2-C3	121.33(10)
O2-H2	0.8200	C9-C4-C5	117.21(10)
O2-C5	1.3602(13)	C8-C7-H7	119.9
N1-H1A	0.8600	C6-C7-H7	119.9
N1-H1B	0.8600	H1A-N1-H1B	120.0
N1-C1	1.3344(14)	C1-N1-H1A	120.0
N3-H3	0.8600	C1-N1-H1B	120.0
N3-N2	1.3911(13)	N2-C2-C3	122.49(10)
N3-C1	1.3412(14)	N2-C2-C4	116.18(10)
N2-C2	1.2993(14)	N1-C1-S1	122.17(8)
C3-C2	1.5023(15)	N1-C1-N3	118.25(10)
C3-H3C	0.9600	N3-C1-S1	119.57(8)

Hydrogen-bond geometry (Å, ˚)

D-H···A	D-H	H···A	D···A	D-H···A
O2-H2···N2	0.82	1.83	2.5524(13)	146
N1-H1A···S1i	0.86	2.70	3.3577(10)	134
N1-H1B···O2ii	0.86	2.32	2.9921(13)	135
O2-H2···N2	0.82	1.83	2.5524(13)	146
N1-H1A···S1i	0.86	2.70	3.3577(10)	134
N1-H1B···O2ii	0.86	2.32	2.9921(13)	135
N3-H3···S1iii	0.86	2.60	3.3766(10)	151
C3-H3C···S1iii	0.96	2.89	3.6306(12)	135
N3-H3···S1iii	0.86	2.60	3.3766(10)	151
C3-H3C···S1iii	0.96	2.89	3.6306(12)	135

Symmetry codes: i) −x + 1/2, y − 1/2, −z + 1/2; ii) −x + 1/2, y + 1/2, −z + 1/2; iii) −x + 1, −y + 2, −z + 1.



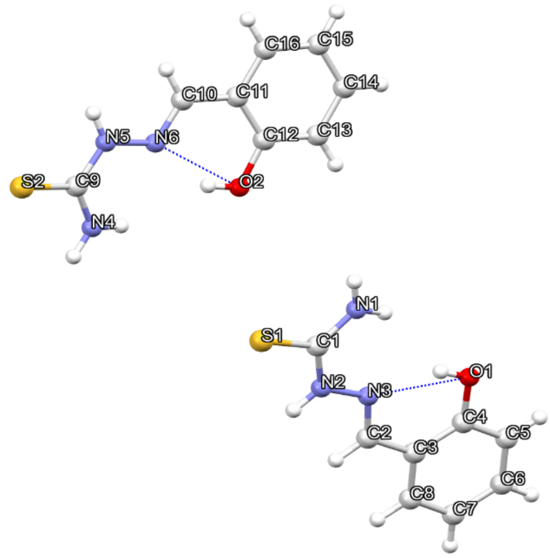
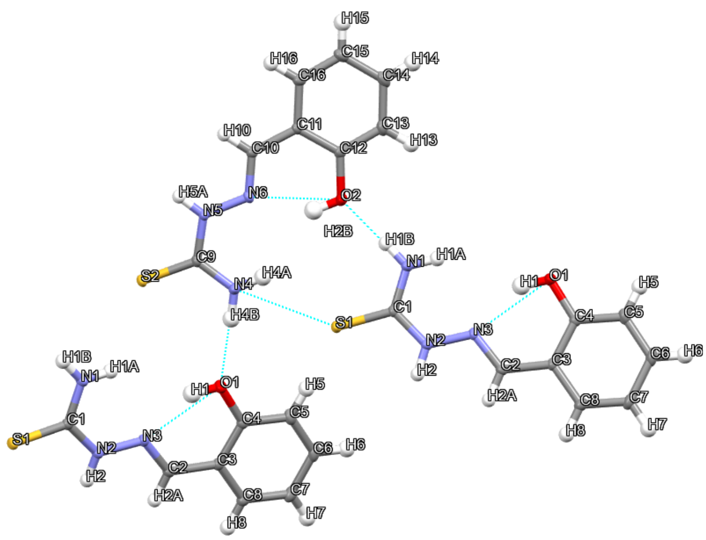


Figure 2. Asymmetric unit of crystal structure of (E)-2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiamide.



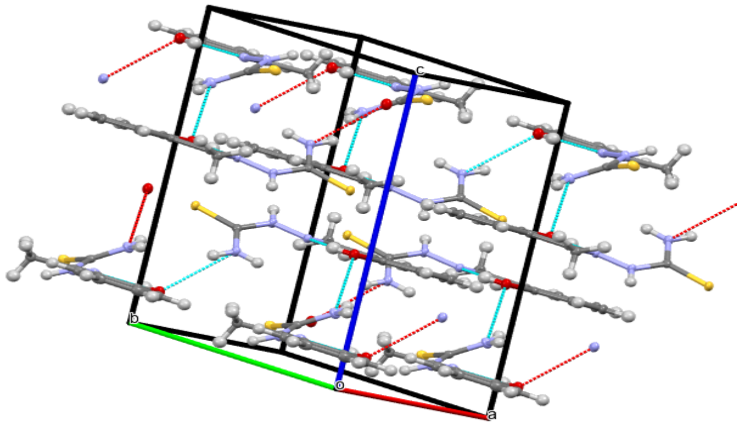


Figure 3. Crystal lattice of (E)-2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiamide with intermolecular hydrogen bonds.

4. Antioxidants Test Results

Antioxidant properties are actually a chemical process that eliminates free radicals in the molecule. To trigger this process, hydrogen must be supplied to the free radicals when they are reduced to non-reactive species. This addition of hydrogen atom would remove the strange electronic characteristic responsible for radical reactivity. The hydrogen reactive using DPPH (1,1-diphenyl-2-picrilhydrazyl) radicals as acceptor, showed that a significant association could be found between the concentration of novel molecule and percentage of inhibition. The anti-oxydant activity of H_4L^2 has been evaluated by using DPPH radical method [1]. This method is used as well for biological or organic compounds as inorganic compounds. Figure 4 shows the evolution of antioxydant activity for H_4L^2 in solution for different concentrations compared to TROLOX solution. The inhibition of DPPH radical increases with the concentration of the organic ligand solution. The inhibition due to H_4L^2 varied from 5.18% - 25.90% which values are different from the inhibition due to the TROLOX (7.82% - 39.10%) between 100 to 500 µM solution. These results are corroborated with those which have published in the thiosemicarbazone derivative [29] Schiff base 2-(2-imino-1-methylimidazolidin-4-ylidene) hydrazinecarbothioamide.

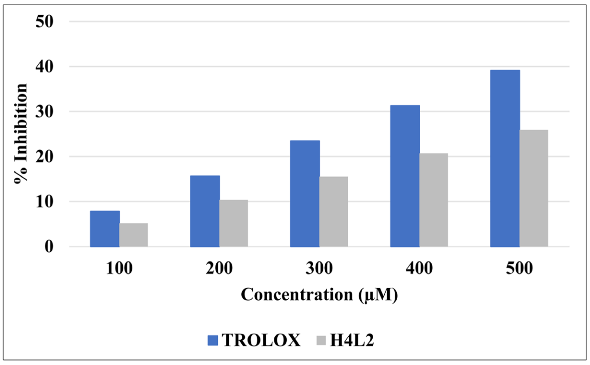


Figure 4. Evolution of antioxidant activity for H_4L^2 in solution for different concentrations compared to TROLOX solution.

5. Conclusion

Reactions between Thiosemicarbaldehyde and 2-hydroxy acetophenone, were studied, leading to the isolation as single-crystal of Thiosemicarbazone (E)-2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiamide. Organic monomers are linked via secondary contacts leading to the formation of layer-like arrangements. The characterization of H_4L^2 was completed by the measurement of spectroscopic data. The antioxidant activity test gives interesting results. Inbiological activity vue, the results of the antioxydant test permeit to conclude that this organic ligand can be used to biological field.

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Conflicts of Interest

State that the authors have no conflict of interest.

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