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Structural and spectral studies of nickel(II), copper(II) and cadmium(II) complexes of 3-furaldehyde thiosemicarbazone

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Abstract

The synthesis and characterisation of Ni(II), Cu(II) and Cd(II) complexes of 3-furaldehyde thiosemicarbazone (3FTSC) are reported. Elemental analysis, molar conductance and spectral (IR, UV and ¹H NMR) measurements have been used to characterise the complexes. In addition, the structure of the complex [Cu(3FTSC)₂] has been determined by X-ray diffraction methods. In Cu(II) and Ni(II) complexes, the metal ion is coordinated through the sulfur atom and the azomethine nitrogen atom while in the Cd(II) complexes the coordinating atoms are sulfur and furanic oxygen ones.

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1. Introduction

Thiosemicarbazones, their derivatives, as well as their transition metal complexes have aroused considerable interest in the areas of chemistry and biology. These compounds present a wide variety of biological activity such as antitumoral [1–5], fungicidal [6,7], bactericidal [8] or antiviral [3]. They have been used for metals analyses [9], for device applications relative to telecommunications, optical computing, storage and information processing [10].

As part of our continuous research work about synthesis and biological activity, mainly with thiosemicarbazones and semicarbazones deriving from fur-aldehyde and their metal complexes [11–16], we describe in this work a new series of transition metal complexes obtained from 3-furaldehyde thiosemicarbazone 3FTSC (Fig. 1) as ligand and the chlorides and bromides of

Ni(II), Cu(II) and Cd(II). All structures are determined on the basis of elemental analyses and spectroscopic techniques. In addition, the crystal structure of the copper complex [Cu(3FTSC)₂] is described.

2. Experimental

2.1. Reactants

All reactants and solvents were analytical grade. Thiosemicarbazide and 3-furaldehyde were purchased from Merck and Aldrich, respectively. Nickel, copper and cadmium hydrated salts were used as received (Prolabo).

2.2. Preparation of ligand

The 3-furaldehyde thiosemicarbazone was synthesised as previously described [11] by refluxing 3-furaldehyde and thiosemicarbazone (1:1 molar ratio) in absolute ethanol in the presence of pure acetic acid.

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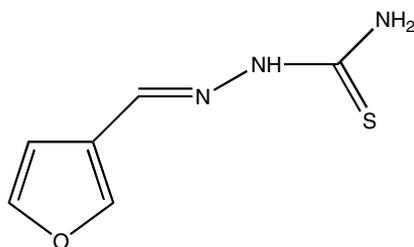


Fig. 1. Chemical structure of 3-furaldehyde thiosemicarbazone (3FTSC).

The mixture was refluxed for 1 h and then cooled, filtered and recrystallised from a mixture of ethanol (75% V/V) and water. Yellow microcrystalline products are obtained. (Elemental Anal. Calc. for $C_6H_7N_3OS$: C, 42.59; H, 4.17; N, 24.83. Found: C, 42.90; H, 4.19; N, 24.70%). M.P. = 154 to 155 °C.

2.3. Preparation of complexes

2.3.1. Bis(3-furaldehydethiosemicarbazone)nickel (II) [$Ni(3FTSC)_2$]

The hexahydrated nickel chloride, $NiCl_2 \cdot 6H_2O$ (2.5×10^{-3} mol, 0.59 g), was dissolved in distilled water. An ethanolic solution of FTSC (5×10^{-3} mol; 0.85 g, 10 mL) was added slowly while stirring. The mixture was refluxed for 3 h. After cooling at room temperature, a green precipitate appeared. It was filtered, washed with small amounts of absolute ethanol and finally dried in vacuum over silicagel. All the compounds were washed and dried in the same way.

2.3.2. Dichloro bis(3-furaldehydethiosemicarbazone) copper (II) [$CuCl_2(3FTSC)_2$]

This complex was prepared from a mixture of ethanolic solution (10 mL) of 3FTSC (0.42 g, 2.5×10^{-3} mol) and $CuCl_2 \cdot 2H_2O$ (1.25×10^{-3} mol) after 1 h reflux.

2.3.3. Bis(3-furaldehydethiosemicarbazone) copper (II) [$Cu(3FTSC)_2$]

When 2×10^{-3} g of complex [$CuCl_2(3FTSC)_2$] was dissolved in ethanol (20 mL), a dark-green crystalline product of formula [$Cu(3FTSC)_2$] was isolated after several days at room temperature. As the crystal structure of this compound was fully solved by X-ray diffraction, its analytical and infrared data are not given in Tables 2 and 4.

2.3.4. Bis(chloro(3-furaldehydethiosemicarbazone) copper (II)) [$CuCl(3FTSC)_2$]

$CuCl_2 \cdot 2H_2O$ (0.24 g, 1.25×10^{-3} mol, 5 mL) was added to 3FTSC (0.21 g, 1.25×10^{-3} mol, 10 mL) in EtOH. The complex is obtained after refluxing EtOH for 1 h.

2.3.5. Bis(bromo(3-furaldehyde thiosemicarbazone) copper (II)) [$CuBr(3FTSC)_2$]

The bromo complex was obtained as the chloro complex starting from 3FTSC (0.21 g, 1.25×10^{-3} mol, 10 mL) and $CuBr_2$ (0.28 g, 1.25×10^{-3} mol, 5 mL).

2.3.6. Dichloro(3-furaldehyde thiosemicarbazone) cadmium (II) [$CdCl_2(3FTSC)_2$]

This complex was prepared from a mixture of ethanolic solution of 3FTSC (0.21 g, 1.25×10^{-3} mol, 5 mL) and $CdCl_2$ (0.23 g, $1 \times 25 \cdot 10^{-3}$ mol, 5 mL) after a 1 h reflux.

2.3.7. Dibromo(3-furaldehyde thiosemicarbazone) cadmium (II) [$CdBr_2(3FTSC)_2$]

$CdBr_2 \cdot 4H_2O$ (0.34 g, 1.25×10^{-3} mol, 5 mL EtOH) was added to 3FTSC (0.21 g, 1.25×10^{-3} mol, 10 mL) in EtOH. The mixture was refluxed for 1 h.

2.4. Measurements

Elemental analysis were carried out by the Service Central d'Analyses (C.N.R.S. Vernaison, France). Melting points were determined with a digital melting point apparatus using a capillary technique. Conductance values were obtained with a Tacussel CD6NG conductometer at 298 K from 10^{-3} mol L^{-1} solutions of complexes in absolute EtOH. The solvent had a conductance of 10^{-8} S cm^2 mol $^{-2}$.

The IR spectra were recorded with a Shimadzu FTIR-8010M spectrometer between 4600 and 400 cm^{-1} (KBr disks) and with a Nicolet FTIR 20F in the range 400–50 cm^{-1} using polyethylene disks (Institut des Matériaux Jean Rouxel, UMR 6502, Nantes, France). Electronic spectra were recorded with a Perkin-Elmer Lambda 19 spectrometer from ethanolic solutions (10^{-3} mol L^{-1}). The 1H NMR spectra were recorded on a Bruker Advance DRX 500 spectrometer in DMSO- D_6 operating at 500 MHz. The chemical shifts, δ , are given in parts per million (relative to TMS) and coupling constants in hertz.

2.5. Crystal data collection and processing

Crystals of [$Cu(3FTSC)_2$] are monoclinic with space group $P2_1/c$. The crystal and instrumental parameters used in the unit-cell determination and data collection are summarised in Table 1. X-ray diffraction data were collected at 293 K on an Enraf Nonius MACH3 four-circles diffractometer ($\lambda_{Mo\ K\alpha} = 0.71073$ Å) equipped with a graphite monochromator (IMMO, UMR, C.N.R.S, 6501 Angers). The structure was solved by direct methods (SIR) using MOLEN package programs [17] and the structure was refined on F by full-matrix least-squares techniques.

Table 1
Crystallographic data for copper complex

Compound	[Cu(3FTSC) ₂]
Formula	C ₁₂ H ₁₂ N ₆ CuO ₂ S ₂
Molecular weight	394
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.871(2)
<i>b</i> (Å)	4.417(1)
<i>c</i> (Å)	17.283(4)
α (°)	90
β (°)	100.08(2)
γ (°)	90
<i>V</i> (Å ³)	741.9(5)
<i>Z</i>	2
Color	dark-green
<i>D</i> _{calc} (g cm ⁻³)	2.07
<i>F</i> (0 0 0)	464
μ (mm ⁻¹)	3.168
<i>hkl</i> limits	−9.9 −4.0 0.16
θ_{\min} , θ_{\max}	2.5, 20
Number of data with <i>I</i> > 3 σ (<i>I</i>)	494
Weighting scheme	4 <i>F</i> _o ² /[$\sigma^2(F_o^2) + (0.06F_o^2)^2$]
Number of variables	82
<i>R</i>	0.045
<i>R</i> _w	0.059

The small size of the crystal did not allow us to obtain enough data and carbon atoms were refined isotropically. Oxygen and nitrogen atoms were refined anisotropically. Hydrogen atoms attached to nitrogen atom (N) were located from Fourier difference synthesis [17]. The remaining hydrogen atoms were located using HYDRO program [17].

3. Results and discussion

The analytical and physical data for the ligand and the metal complexes are listed in Table 2. All the analytical data are in good agreement with the empirical formulae as given in Table 2. The complexes are stable in air. However, the cadmium complexes showed an hygroscopic

character. Their molar conductivities are in a range corresponding to a non-electrolytic nature. These results agreed with measurements of the conductivity carried out with their homologous thiosemicarbazones and semicarbazones [13,18–20]. On heating, all the complexes decomposed and did not present a clear melting point.

3.1. Crystal structure of [Cu(3FTSC)₂]

The main crystal parameters are reported in Table 1. The bond distances and their angles for this crystal are shown in Table 3. Fig. 2 shows a view of the molecule of [Cu(3FTSC)₂] with numbering scheme.

The centrosymmetric structure consists in the neutral molecules Cu(3FTSC)₂, with copper at the centre of symmetry. The coordination results in a square planar configuration, which involves the thiolato sulfur atoms and the imine nitrogen atom N3 of the two ligands in *cis*-configuration.

In the complex, the monodeprotonated bidentate ligand shows a *cis*-configuration for the nitrogen N3 and sulfur S atoms. In the free ligand, however, these

Table 3
Bond lengths (Å) and angles (°) for the free ligand and complex

Bond lengths (Å)		Bond angles (°)	
Cu–S	2.180(3)	S–Cu–N3	85.2(2)
Cu–N3	1.911(6)	Cu–S–C1	96.4(3)
S–C1	1.726(8)	C5–O–C6	105.2(7)
O–C5	1.32(1)	N3–N2–C1	112.2(6)
O–C6	1.36(1)	Cu–N3–N2	121.8(5)
N2–N3	1.39(1)	Cu–N3–C2	125.6(6)
N2–C1	1.30(1)	N2–N3–C2	112.6(6)
N3–C2	1.30(1)	S–C1–N2	123.2(7)
C2–C3	1.45(1)	N3–C2–C3	127.8(8)
C3–C4	1.43(1)	C2–C3–C4	123.5(8)
C3–C6	1.32(1)	C2–C3–C6	132.8(9)
C4–C5	1.33(1)	C4–C3–C6	103.7(8)
		C3–C4–C5	106(1)
		O–C5–C4	111.6(9)
		O–C6–C3	112.9(8)

Table 2
Analytical data

Compound	Color	Yield (%)	M.p (°C)	Elemental analysis found (Calc.)				<i>A</i> (S cm ² mol ⁻¹)
				C (%)	H (%)	X (%)	M (%)	
3FTSC	yellow	43	154–155	42.90 (42.59)	4.19 (4.17)			
[Ni(3FTSC) ₂]	green	20	238 d	36.39 (36.29)	3.14 (3.55)		14.81 (14.78)	0.3
[CuCl ₂ (3FTSC) ₂]	green	19	213 d	30.35 (30.48)	2.82 (2.98)	15.07 (14.99)	13.17 (13.44)	39.5
[(CuCl(3FTSC)) ₂]	green	37	210 d	26.57 (26.87)	2.73 (2.63)	12.58 (13.22)	22.84 (23.69)	9.2
[(CuBr(3FTSC)) ₂]	black	26	223 d	23.10 (23.05)	2.22 (2.26)	25.27 (25.56)	19.41 (20.32)	11.3
[CdCl ₂ (3FTSC)]	clear brown	40	241 d	20.26 (20.44)	2.09 (2.00)	19.63 (20.11)	29.71 (31.89)	7.9
[CdBr ₂ (3FTSC)]	clear brown	65	237 d	16.50 (16.33)	1.60 (1.60)	35.86 (36.20)	24.06 (25.47)	5.2

Table 4
Main IR spectral vibrations (cm^{-1})

	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	Ring Breath.	$\nu(\text{C}-\text{O}-\text{C})$	$\nu(\text{M}-\text{X})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{O})$
3FTSC	3421a, 3290s	837	1587	936	1009	1289				
$[\text{Ni}(\text{3FTSC})_2]$	3439a, 3344s	829	1608		1010	1290		232	390	
$[\text{CuCl}_2(\text{3FTSC})_2]$	3389a, 3260s	800	1610	945	1010	1293	240, 255	440	380	
$[\text{CuCl}(\text{3FTSC})_2]$	3398a	799	1608	948	1015	1289	260	436	390	
$[\text{CuBr}(\text{3FTSC})_2]$	3397a, 3272s	819	1601	944	1014	1289	263	435	388	
$[\text{CdCl}_2(\text{3FTSC})]$	3441a, 3329s	832	1599	942	999	1300	245, 255		381	490
$[\text{CdBr}_2(\text{3FTSC})]$	3449a, 3329s	829	1594	940	1000	1298	247, 258		380	485

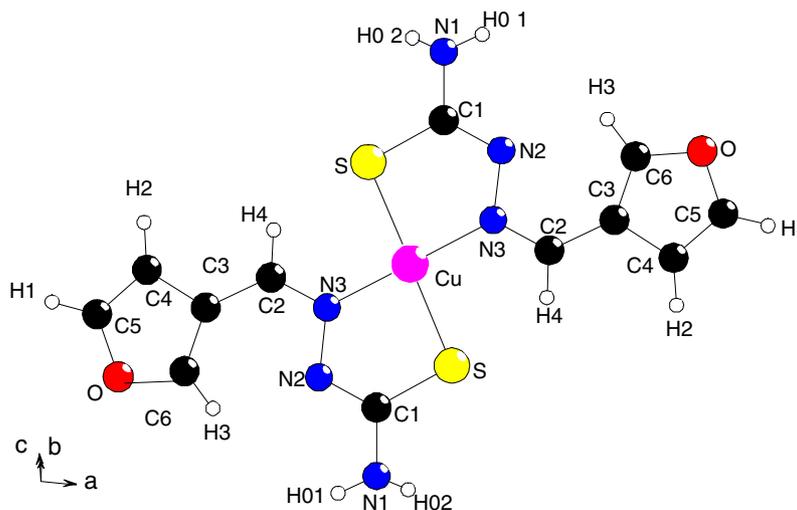


Fig. 2. Perspective view of complex and atom numbering of $[\text{Cu}(\text{3FTSC})_2]$.

centres present a *trans*-configuration [11], indicating that the complexation occurs after a 180° rotation around the C1–N2 bond.

As the ligand is deprotonated on N2 atom, a negative charge appears and is delocalized along the thiosemicarbazone moiety. This fact is confirmed by the difference between the bond distances in the deprotonated ligand of copper complex: S1–C1 = 1.726(8) Å (thiolato form); C1–N2 = 1.30(1) Å and C2–N3 = 1.30(1) Å, and the same bond distances in the free ligand: S1–C1 = 1.690(2) Å (thione form); C1–N2 = 1.338(2) Å and C2–N3 = 1.271(2) Å [11–13].

The configuration of the complex $[\text{Cu}(\text{3FTSC})_2]$ is planar, while the carbon atom, C1, is slightly out of this plane, with 0.12 Å deviation.

It is not very easy to compare the S–Cu and N3–Cu bonds lengths with the distances reported in the literature for the same bonds in thiosemicarbazones copper (II) complexes. Generally, these complexes are formulated as $[\text{CuLX}_2]$ or $[\text{CuLX}]$ (X = halogen, L = ligand) with tridentate ligands, whereas the complex $[\text{Cu}(\text{3FTSC})_2]$ should be written $[\text{CuL}_2]$ with L being a bidentate ligand.

The molecular arrangement in the unit-cell shows that the neutral molecules $\text{Cu}(\text{3FTSC})_2$ in the complex

$[\text{Cu}(\text{3FTSC})_2]$ are stacked, one above the other, so that their main planes are parallel and the copper atoms occupy the apexes and the mid-point of the *c* edges. This is shown by the projection of the structure on the plane (0 1 0) presented in Fig. 3.

The packing is governed by hydrogen bonds between the hydrogen H1 of the amino group N1 and the oxygen atom in furanic ring. This hydrogen bond shows a bond distance of 2.45 Å and a bond angle of 147° . The coordinates of N1 and O are, respectively, $(2 - x, 0.5 + y, 1.5 - z)$ and $(1 - x, 1 - y, 1 - z)$.

3.2. Infrared spectra

Selected vibration bands of 3FTSC and of its metal complexes are given in Table 4.

The vibration $\nu(\text{C}=\text{S})$ in the spectrum of the ligand shows a band around 837 cm^{-1} [11]. This band is shifted to lower wavenumbers in all the complexes [21,22]. On the other hand, the bands in the region $3421\text{--}3290 \text{ cm}^{-1}$ attributed to symmetrical and asymmetrical stretching modes $\nu(\text{NH}_2)$ in the spectra of the ligand, undergo a change in the spectra of the complexes. This is explained by the coordination of sulfur from the C=S (NH₂) group as reported earlier [23]. In addition, this

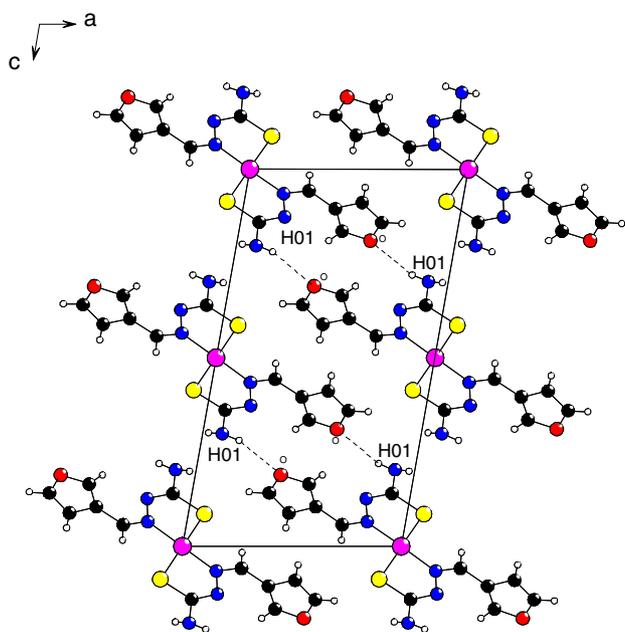


Fig. 3. Packing arrangement and hydrogen bonding in $[\text{Cu}(\text{3FTSC})_2]$ X-ray structure.

coordination is confirmed by the presence in all complexes of a new band at $380\text{--}390\text{ cm}^{-1}$ [5,24], relative to $\nu(\text{M-S})$ vibration.

In the ligand spectra, the strong band observed at 1587 cm^{-1} is assigned to $(\text{C}=\text{N})$ stretching vibration [11]. This band shifts to higher wavenumbers in the spectra of all metal complexes, indicating the coordination of nitrogen of the azomethine group to the central metal atoms [21,23]. In the case of the cadmium complex, this shift is very feeble. The presence of a new band in the region $430\text{--}440\text{ cm}^{-1}$ due to $\nu(\text{M-N})$ is an other indication of the involvement of nitrogen of the azomethine group in the coordination [5,24]. However, we did not observe any shifts of frequency of the $\nu(\text{Cd-N})$ vibration for the complexes of $\text{Cd}(\text{II})$. On the opposite side, we noted a significant displacement of the frequency of the ring breathing and $\nu(\text{C-O-C})$ vibrations, and this shows that the coordination occurs through the furanic oxygen atom (instead of the azomethine nitrogen) [25]. This coordination is also supported by the appearance of the $\nu(\text{Cd-O})$ vibration for $[\text{CdCl}_2(\text{3FTSC})]$ and $[\text{CdBr}_2(\text{3FTSC})]$ at 490 and 485 cm^{-1} , respectively [18,19,25,26].

In the literature, the bands appearing between 160 and 300 cm^{-1} are allotted to the vibration of the M-X bonds, where $\text{M} = \text{metal}$ and $\text{X} = \text{Cl}$ or Br [18,26–29]. In our case, the $\nu(\text{M-X})$ frequencies appearing between 240 and 260 cm^{-1} (Table 4) are in good agreement with the reported values in the literature.

Generally, the infrared spectra of copper complexes such as $[\text{CuCl}_2(\text{L})_2]$ or $[\text{CuCl}_2(\text{L})]$ present two bands between 240 and 280 cm^{-1} , due to $\nu(\text{Cu-Cl})$ vibration

[27,28]. Billing et al. [30] showed that, when copper(II) complexes present only one vibration band in this range, their structures show halogenide bridges in these compounds. This is observed in the case of the binuclear complexes $[\text{CuCl}(\text{3FTSC})_2]$ and $[\text{CuBr}(\text{3FTSC})_2]$.

3.3. Electronic spectra

The study of the electronic spectra in ethanol allowed us to determine the geometry of the polyhedrons of coordination for copper complexes. The binuclear complexes $[\text{CuCl}(\text{3FTSC})_2]$ and $[\text{CuBr}(\text{3FTSC})_2]$ showed only one band around $13\,700\text{ cm}^{-1}$. This band was also observed in the spectrum of the binuclear complex $[\text{Cu}(\text{TTSC})\text{Cl}]_2$ described by Nair et al. [31], where TTSC is 2-thiophene carboxaldehyde thiosemicarbazone. It is typical of a d–d transition in a square planar environment.

The electronic spectrum of the complex $[\text{CuCl}_2(\text{3FTSC})_2]$ presents an asymmetrical band with a maximum around $15\,410\text{ cm}^{-1}$. According to Raising [32], the asymmetry of this band is a characteristic of octahedral copper (II) compounds, where a lengthening of the bonds located along the $z'Oz$ -axis is often observed. At the outset, this lengthening can lead to an ionic complex with square planar geometry. This fact is confirmed by the high value of the conductivity of $[\text{CuCl}_2(\text{3FTSC})_2]$ (Table 2) and the loss of the two chlorine atoms during the formation of the monocrystals of $[\text{Cu}(\text{3FTSC})_2]$. We conclude that the geometry of this complex is closer to square planar rather than regular octahedral geometry.

3.4. NMR spectra

Theoretically, the complexation by azomethine nitrogen should affect the chemical shift of the $\text{C}=\text{N}$ protons [5]. The recording of spectra ^1H NMR for the cadmium complexes did not show any shift of this signal. This confirms our earlier hypothesis, formulated from infrared data, that the second coordinating atom is the oxygen of the furanic ring for the $\text{Cd}(\text{II})$ complexes. In addition, no signals appeared around 11.4 ppm (field of appearance of the signal of a NH group next to $\text{C}=\text{S}$) and this confirms that the coordination occurs through the thiolato form.

4. Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or at [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk))), and are available on request quoting the deposition numbers CCDC 252861.

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