

# Metallic complexes from 2-furaldehyde semicarbazone and 5-methyl-(2-furaldehyde) semicarbazone

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## Summary

The synthesis and characterization of Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Cd<sup>II</sup> complexes with 2-furfuralsemicarbazone (FSC) and 5-methyl 2-furfuralsemicarbazone (MFSC) are reported. These ligands lead to the complexes: [ML<sub>2</sub>X<sub>2</sub>] or [MLX<sub>2</sub>] (L = FSC or MFSC) whose structures were determined using elemental analysis, molar conductivity, magnetic measurements, i.r., far i.r. and electronic spectra as well as by n.m.r. FSC and MFSC act as bidentate ligands in most of the Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Cd<sup>II</sup> complexes. MFSC is a monodentate ligand in [NiBr<sub>2</sub>(MFSC)<sub>4</sub>].

## Introduction

We recently reported the synthesis and characterisation of metallic complexes obtained from 3-(2-furyl) 2-propenal semicarbazone (FASC)<sup>(1)</sup>. We present here the synthesis and structural characterisation of new metallic complexes between, on one hand, cobalt, nickel, copper, zinc and cadmium dihalides and 2-furaldehyde semicarbazone (FSC) and, on the other, 5-methyl-(2-furaldehyde) semicarbazone (MFSC). Their structures are given in Figure 1. We have previously described the complexes deriving from various furan oximes and 3d metal dihalides<sup>(2–3)</sup>. The coordinating properties of some semicarbazones metallic complexes have also been studied<sup>(4–6)</sup>, and many papers have dealt with thiosemicarbazones metal complexes<sup>(7–15)</sup>. The copper complexes of furan oxime derivatives, semicarbazone

and thiosemicarbazone derivatives were found to be potent cytotoxic agents in both murine and human tissue cultured cell lines, as well as in solid tumors<sup>(16–20)</sup>. In this paper, we describe thirteen new complexes obtained from FSC, MFSC and cobalt(II), nickel(II), copper(II) and cadmium(II) chlorides and bromides.

## Experimental

### Synthesis of the ligands

#### 2-Furaldehyde semicarbazone (FSC)

To an aqueous solution (50 cm<sup>3</sup>) of semicarbazidium chloride (11.15 g, 0.1 mol) and AcONa (20 g) was added dropwise an EtOH solution (50 cm<sup>3</sup>) of 2-furaldehyde (9.6 g; 0.1 mol). After 1 h refluxing, FSC precipitated on cooling. It was filtered and finally recrystallized from boiling H<sub>2</sub>O (m.p. 188 °C; yield 85%). The semicarbazone gave satisfactory analysis and spectral properties. Mass spectroscopy exhibited the molecular ion at m/z = 156 and main ion fragments at respectively 136, 93 (McLaferty's rearrangement), 110.

#### 5-Methyl-(2-furaldehyde) semicarbazone (MFSC)

5-Methyl-(2-furaldehyde) semicarbazone was obtained by mixing EtOH (50 cm<sup>3</sup>) solutions of 5-methylfurfural (11 g; 0.1 mol) and semicarbazidium chloride (11.15 g; 0.1 mol). MFSC was recrystallized from boiling H<sub>2</sub>O (m.p. 196 °C; yield 95%) and was dried under reduced pressure at room temperature. The main peaks in mass spectroscopy were at m/z = 167 (molecular ion), 150, 124 and 107.

### Preparation of the complexes

Most of the complexes were prepared in anhydrous EtOH from 0.01 mol of semicarbazone and the corresponding stoichiometric quantity of metal dihalide. After refluxing, the complexes were filtered off, washed with small quantities of anhydrous EtOH and n-pentane, dried and stored under reduced pressure at room temperature, unless otherwise indicated. The purity of the complexes was verified using thin layer chromatography in appropriate apolar solvents at room temperature.

#### Dichloro bis(2-furfural semicarbazone) cobalt(II) (1)

The EtOH solution (35 cm<sup>3</sup>) of FSC was added to CoCl<sub>2</sub>·6H<sub>2</sub>O (1.19 g, 0.005 mol) in EtOH (20 cm<sup>3</sup>) and reflux conditions were maintained for 48 h. After reducing the vol. by 50% under reduced pressure, a pink solid precipitated.

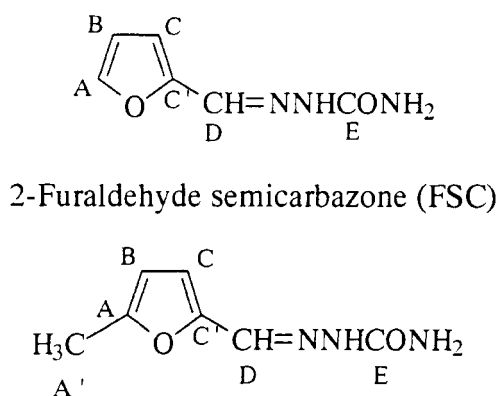


Figure 1. Ligand structures.

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*Dibromo bis(2-furfural semicarbazone) cobalt(II) (2)*

$\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  (1.94 g, 0.005 mol) was dissolved in EtOH (50 cm<sup>3</sup>) and heated to the reflux temperature. An EtOH solution of the ligand (30 cm<sup>3</sup>) was added dropwise. After 8 h refluxing, the vol. was reduced to 20 cm<sup>3</sup> under reduced pressure, until the appearance of a pink solid.

*Dichloro bis(2-furfural semicarbazone) nickel(II) (3)*

FSC (1 g, 0.0065 mol) in EtOH (20 cm<sup>3</sup>) was added slowly to an EtOH (10 cm<sup>3</sup>) solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.78 g, 0.0033 mol). After refluxing for 6 h, a green yellow solid appeared.

*Dichloro bis(2-furfural semicarbazone) copper(II) (4)*

A solution (20 cm<sup>3</sup>) of the semicarbazone (1.53 g, 0.01 mol) was heated up to reflux and a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.7 g, 0.005 mol, 20 cm<sup>3</sup>) was then added dropwise. A green solid appeared instantaneously.

*Dichloro (2-furfural semicarbazone) cadmium(II) (5)*

$\text{CdCl}_2$  (1.83 g, 0.01 mol) in EtOH (20 cm<sup>3</sup>) was heated up to the reflux temperature and the semicarbazone (10 cm<sup>3</sup>) was then added. After 15 min, a white solid appeared.

*Dibromo (2-furfural semicarbazone) cadmium(II) (6)*

This complex was obtained in the same way as the above chloro derivative, starting from FSC (15 cm<sup>3</sup>) and  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (3.44 g; 0.01 mol; 30 cm<sup>3</sup>).

*Dichloro bis(5-methylfurfural semicarbazone) cobalt(II) (7)*

This complex was prepared by adding at 80 °C, a solution of MFSC in butan-1-ol (1 mmol; 25 cm<sup>3</sup>) to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in the same solvent (20 cm<sup>3</sup>). After refluxing for 8 h, a blue compound precipitated.

*Dibromo bis(5-methylfurfural semicarbazone) cobalt(II) (8)*

A butan-1-ol solution (20 cm<sup>3</sup>) of  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  (1.02 g, 0.003 mol) was heated at the reflux temperature and added slowly to the semicarbazone (1 g, 0.006 mol) nBuOH solution (25 cm<sup>3</sup>). The reflux was maintained for 4 h after the addition. A pink solid precipitated.

*Dichloro bis(5-methylfurfural semicarbazone) nickel(II) (9)*

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (2.13 g, 0.009 mol) in EtOH (15 cm<sup>3</sup>) was added dropwise to a solution (10 cm<sup>3</sup>) of MFSC (0.009 mol; 1.5 g) under reflux conditions. A green-yellow solid precipitated instantaneously.

*Dibromo bis(5-methylfurfural semicarbazone) nickel(II) (10)*

To an EtOH (20 cm<sup>3</sup>) solution of MFSC (2.0 g; 0.012 mol) and under refluxing conditions, was added

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1.31 g; 0.006 mol) in EtOH (30 cm<sup>3</sup>). After refluxing for 4 h, a green solid was obtained.

*Dichloro bis(5-methylfurfural semicarbazone) copper(II) (11)*

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.35 g, 0.0025 mol) in EtOH (25 cm<sup>3</sup>) was added slowly to an EtOH solution (10 cm<sup>3</sup>) of MFSC (0.42 g; 0.0025 mol). The complex appeared instantaneously, however the reflux maintained for 1 h.

*Dichloro (5-methylfurfural semicarbazone) cadmium(II) (12)*

Starting from MFSC (1 g, 0.006 mol) in EtOH (20 cm<sup>3</sup>) and  $\text{CdCl}_2$  (1.1 g; 0.006 mol) solutions (30 cm<sup>3</sup>). The complex precipitated during the addition of  $\text{CdCl}_2$  but the refluxing conditions were maintained for 1 h in order to complete the reaction.

*Dichloro bis(5-methylfurfural semicarbazone) cadmium(II) (13)*

It was prepared in the same way as the above chloro derivative with MFSC (30 cm<sup>3</sup>) and  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (1 g, 0.006 mol) in EtOH (25 cm<sup>3</sup>).

*Physical measurements*

Elemental analysis were carried out by the Service Central d'Analyse du C.N.R.S. (Vernaison, France). Melting points were determined with a Büchi Tottoli apparatus. Magnetic measurements were made at 298 K with a magnetic balance Bruker B-SU 10 (Laboratoire de Chimie de Coordination, U.S.T.H.B., Alger, Algeria) calibrated against  $\text{Hg}[\text{Co}(\text{SCN})_4]$  with correction for diamagnetism. Conductance values were obtained using a Tacussel CD6NG conductimeter at 298 K using 10<sup>-3</sup> mol·dm<sup>-3</sup> solutions of complexes in absolute EtOH; the solvent had a conductance of 10<sup>-8</sup> S·cm<sup>2</sup>·mol<sup>-2</sup>; the conductance of NaI (10<sup>-3</sup> mol·dm<sup>-3</sup>) is 33 S·cm<sup>2</sup>·mol<sup>-2</sup>. The i.r. spectra were recorded on a Shimadzu FTIR-8010 M spectrophotometer between 4600 and 400 cm<sup>-1</sup> (KBr discs) and in the 400–50 cm<sup>-1</sup> range using polyethylene discs with a Nicolet FTIR 20 F instrument (Laboratoire de Physique Cristalline, Institut des Matériaux, Nantes, France). Electronic spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer from EtOH or  $\text{CHCl}_3$  solutions (10<sup>-3</sup> mol·dm<sup>-3</sup>). <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were obtained with a Jeol GSX 270 WB (270 MHz) spectrophotometer in D<sub>6</sub>-D.M.S.O. solutions, using TMS as an internal reference (Service commun de R.M.N., Université d'Angers). The mass spectroscopy diagrams were obtained with a GC-MS Delsi-Nermag spectrometer (Laboratoire des Substances d'Origine Naturelle et Analogues Structuraux, Faculté de Pharmacie, Angers).

**Results and discussion***Analytical data*

Analytical data for these thirteen new complexes are reported in Table 1. Three series are obtained:  $[\text{ML}_2\text{X}_2]$ ,

**Table 1.** Analytical data for the complexes

Compound	n°	Colour	Yield (%)	M.p. (°C)	Found (Calcd.) (%)		X	M	$\Lambda$ (S cm <sup>2</sup> · mol <sup>-1</sup> )	$\mu$ (B.M.)
					C	H				
[CoCl <sub>2</sub> (FSC) <sub>2</sub> ]	(1)	pink	30	243	32.7(33.1)	3.2(3.2)	16.5(16.1)	13.6(13.5)	24.8	4.8
[CoBr <sub>2</sub> (FSC) <sub>2</sub> ]	(2)	pink	20	247	27.2(27.5)	2.7(2.7)	29.8(30.2)	11.4(11.3)	31.6	4.7
[NiCl <sub>2</sub> (FSC) <sub>2</sub> ]	(3)	green	61	282	33.3(33.2)	3.4(3.3)	16.1(16.1)	13.2(13.3)	29.7	3.2
[CuCl <sub>2</sub> (FSC) <sub>2</sub> ]	(4)	green	28	163	32.7(32.8)	3.1(3.2)	16.2(15.9)	14.1(14.3)	16.4	2.1
[CdCl <sub>2</sub> (FSC) <sub>2</sub> ]	(5)	white	46	240	21.0(21.4)	2.2(2.1)	21.2(20.8)	33.8(33.8)	9.1	diam.
[CdBr <sub>2</sub> (FSC) <sub>2</sub> ]	(6)	white	37	245	17.5(17.0)	1.7(1.7)	37.1(37.1)	26.6(26.8)	4.3	diam.
[CoCl <sub>2</sub> (MFSC)]	(7)	blue	29	282	28.6(28.4)	3.1(3.1)	23.2(23.6)	18.9(19.9)	15.3	4.9
[CoBr <sub>2</sub> (MFSC) <sub>2</sub> ]	(8)	pink	28	223	30.5(30.5)	3.4(3.3)	28.1(28.6)	10.1(10.7)	23.4	4.0
[NiCl <sub>2</sub> (MFSC) <sub>4</sub> ]	(9)	green	62	203	42.8(42.2)	4.6(4.6)	8.2(8.8)	6.9(7.3)	28.1	3.3
[NiBr <sub>2</sub> (MFSC) <sub>2</sub> ]	(10)	green	39	260	30.1(30.5)	3.7(3.3)	25.7(28.6)	10.2(10.5)	37.1	3.7
[CuCl <sub>2</sub> (MFSC)]	(11)	green	37	185	28.2(28.0)	3.2(3.0)	23.0(23.3)	19.6(21.0)	29.2	2.4
[CdCl <sub>2</sub> (MFSC)]	(12)	yellow	86	202	23.7(23.9)	2.6(2.6)	20.3(19.9)	32.1(32.5)	6.0	diam.
[CdBr <sub>2</sub> (MFSC)]	(13)	white	65	200	26.6(27.7)	3.0(3.0)	27.9(26.1)	19.4(18.8)	8.8	diam.

Conductance of absolute EtOH: 10<sup>-8</sup> S · cm<sup>2</sup> · mol<sup>-1</sup>, conductance of NaI (10<sup>-3</sup> mol · dm<sup>-3</sup> EtOH): 33.3 S · cm<sup>2</sup> · mol<sup>-1</sup>.

[ML<sub>2</sub>]X<sub>2</sub> and [MLX<sub>2</sub>]. The low molar conductances show that most of the complexes are non-ionic species in ethanol<sup>(21)</sup>. All these metallic complexes are stable in air and very slightly soluble in common organic solvents but soluble in dimethylsulfoxide (DMSO), which is typical of oligomeric or polymeric species.

#### Infrared spectra

The i.r. spectra of FSC and MFSC show that the ligands are present only in the keto form because bands higher than 3500 cm<sup>-1</sup> (representative of the hydroxyl form of the enol structure) are absent<sup>(22)</sup>. The spectrum of FSC shows two strong bands at 3475 and 3283 cm<sup>-1</sup> attributed respectively to  $\nu$ (N—H) asymmetric and  $\nu$ (N—H) symmetric vibrations of the terminal NH<sub>2</sub> group<sup>(22)</sup>; these bands appear at 3459 and 3324 cm<sup>-1</sup> respectively in MFSC spectrum. Two medium intensity bands at 3154 and 3080 cm<sup>-1</sup> (3135 and 3100 for MFSC) are attributed to the N—H stretching vibration of the imino group, the band appearing at 1624 cm<sup>-1</sup> (1630 cm<sup>-1</sup> in the case of MFSC) is due to  $\nu$ (C=N), while the other at 949 (FSC) or 963 cm<sup>-1</sup> (MFSC) is assigned to  $\nu$ (N—N). The stretching vibration band of the carbonyl group lies at 1692 (FSC) and 1670 cm<sup>-1</sup> (MFSC).

A comparison of the spectra of FSC with those of its metal complexes (Table 2) allows us to determine the coordinating atoms in all species. In the complexes

[CoCl<sub>2</sub>(FSC)<sub>2</sub>], [CoBr<sub>2</sub>(FSC)<sub>2</sub>], [NiCl<sub>2</sub>(FSC)<sub>2</sub>] and [CuCl<sub>2</sub>(FSC)<sub>2</sub>], FSC acts as a bidentate ligand, through the carboxyl oxygen and the ring oxygen atoms. This bonding mode is supported by the following observations: the shift of  $\nu$ (C=O) to lower wavenumbers; the shift of the ring breathing and  $\delta$ (C—O—C) to higher wavenumbers; the appearance of new bands in the range 190–500 cm<sup>-1</sup> assigned to  $\nu$ (M—O keto),  $\nu$ (M—O ring),  $\nu$ (M—Cl) or  $\nu$ (M—Br) respectively<sup>(23)</sup> (see Table 2).

In [CdX<sub>2</sub>(FSC)] (X = Cl, Br), FSC also acts as a bidentate ligand, but coordinating *via* the azomethine nitrogen (C=N) and the heterocyclic oxygen. This mode of complexation is supported by the following observations: the  $\nu$ (C=N) moved to lower wavenumbers and the ring breathing shifted to higher wavenumbers; the appearance of new bands in the regions 425–437, 478–480 and 147–190 cm<sup>-1</sup>, relative to  $\nu$ (M—N),  $\nu$ (M—O ring) and  $\nu$ (M—X) respectively<sup>(23)</sup> (Table 2).

The spectra of [CoCl<sub>2</sub>(MFSC)], [CoBr<sub>2</sub>(MFSC)<sub>2</sub>], [CuCl<sub>2</sub>(MFSC)<sub>2</sub>], [CdCl<sub>2</sub>(MFSC)] and [CdBr<sub>2</sub>(MFSC)] exhibit a band in the 1635–1660 cm<sup>-1</sup> range due to the carbonyl stretching vibration, whereas this band is located at 1670 cm<sup>-1</sup> in the spectrum of the free ligand. The ring breathing band is shifted from 1020 (ligand) to 1030–1042 cm<sup>-1</sup> (complexes). This suggests an involving of the carbonyl oxygen and of the ring oxygen atoms. This conclusion is enhanced by the appearance of the following bands:  $\nu$ (M—O ring) at 474–498 cm<sup>-1</sup>

**Table 2.** Main i.r. spectral vibrations for FSC and its complexes

Compd	$\nu$ (NH <sub>2</sub> )	$\nu$ (NH)	$\nu$ (C=O)	$\nu$ (C=N)	$\delta$ (C—O—C)	$\nu$ (N—N)	Ring breath.	$\nu$ (M—X)	$\nu$ (M—N)	$\nu$ (M—O) ring	$\nu$ (M—O) keto
FSC	3475as 3283s	3154 3080	1692	1624	1279	949	1011	—	—	—	—
(1)	3355as 3279s	3164 3112	1663	1626	1273	943	1020	317	—	529	342
(2)	3355as 3285s	3166 3111	1660	1626	1273	943	1015	196	—	502	342
(3)	3360as 3277s	3158 3107	1666	1632	1275	943	1020	328	—	525	365
(4)	— 3268s	— 3094	1653	1636	1277	945	1026	303	—	537	352
(5)	3451as 3297s	3125 3073	1698	1597	1281	943	1026	190	425	480	—
(6)	3438as 3285s	3132 3071	1696	1597	1279	939	1026	147	437	478	—

(as = antisymmetric : s = symmetric).

**Table 3.** Main i.r. spectral vibrations for MFSC and its complexes

Compd	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\delta$ (C—O—C)	$\nu(\text{N—N})$	Ring breath.	$\nu(\text{M—X})$	$\nu(\text{M—N})$	$\nu(\text{M—O})$ ring	$\nu(\text{M—O})$ keto
MFSC	3459a	3135	1670	1630	1286	963	1020	—	—	—	—
	3324s	3100									
(7)	3353a	3144	1660	1630sh	1281	968	1042	299	—	475	346
	3258s	3106									
(8)	3424a	3166	1638	1625sh	1287	963	1030	193	—	474	339
	3240s	3046									
(9)	3457a	3177	1674	1618	1287	961	1022	325	449	—	—
	3256s	3048									
(10)	3436a	3177	1638	1618	1287	963	1020	218	482	—	340
	3244s	3061									
(11)	3489a	3119	1651	1625	1288	960	1032	321	—	488	347
	3254s	3082									
(12)	3457a	3327	1651	1634	1288	962	1028	183	—	489	358
	3294s	3092									
(13)	3489a	3148	1651	1636	1283	955	1032	158	—	498	379
	3320s	3108									

(as = antisymmetric; s = symmetric; sh = shoulder).

$\nu(\text{M—O keto})$  at 339–379  $\text{cm}^{-1}$ , and in addition to this, the bands of the metal-halogen stretching vibrations are also present<sup>(23)</sup>.

The  $[\text{NiCl}_2(\text{MFSC})_4]$  complex shows another coordination mode. The  $\nu(\text{C}=\text{N})$  band is shifted to lower frequency by 12  $\text{cm}^{-1}$ . The mode of coordination can be supported by the presence of the  $\nu(\text{Ni—N})$  band at 449  $\text{cm}^{-1}$  and the absence of bands relative to the stretching vibrations metal-oxygen (keto or cyclic). So, in this complex, the ligand is monodentate through the nitrogen atom of the azomethine group. In the spectrum of  $[\text{NiBr}_2(\text{MFSC})_2]$  there are two new bands at 340 and 482  $\text{cm}^{-1}$  assigned respectively to  $\nu(\text{Ni—O keto})$  and  $\nu(\text{Ni—N})$ . Furthermore, the bands of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{O})$  shift to 1618 ( $-12 \text{ cm}^{-1}$ ) and 1638  $\text{cm}^{-1}$  ( $-32 \text{ cm}^{-1}$ ). This indicates that the carbonyl oxygen and the azomethine nitrogen atoms are involved in coordination.

### Electronic spectra

Table 4 summarizes the experimental and the calculated data for the electronic spectra for cobalt and nickel

**Table 4.** Electronic spectra ( $\text{cm}^{-1}$ )

Compd	Expt			$\nu_1/\nu_2$	Calcd		
	$\nu_1$	$\nu_2$	$\nu_3$		10 Dq	B	$\beta$
(1)	7780	14950	19130	1.92	7800	810	0.84
(2)	7795	15125	19360	1.94	7910	760	0.79
(7)	7875	15290	18615	1.94	7980	770	0.80
(8)	7780	15100	18935	1.94	7890	800	0.83
(3)	7645	13370	25000	—	7645	1000	0.96
(9)	7550	13075	24540	—	7550	970	0.94
(10)	7585	13490	24470	—	7585	965	0.93

complexes. Calculation, according to König's equations<sup>(24)</sup>, gives the 10 Dq values and the Racah's parameter B.

In the cobalt complexes, a  $\nu_1/\nu_2$  ratio of *ca.* 2.0 is a good criterion for a suitable attribution of these two bands<sup>(25)</sup> and our values are in the 1.92–1.94 range. There is no significant difference between the 10 Dq values. Assuming that the magnetic momenta lie between 4.0 and 4.9 B.M. (Table 1), these complexes present a trans dihalogeno octahedral geometry, with a distortion along the *z* axis and strong ionic character for the metal halogen bonds, leading to higher conductance values in EtOH solutions (Table 1).

The nickel(II) complexes exhibit (Table 4) the 10 Dq values and those of B, which are typical for distorted octahedral structure as suggested by magnetic moments (3.20–3.66 B.M.). We note that, under the same experimental conditions, their B values are higher than those of the nickel chloride or bromide: 900 and 830  $\text{cm}^{-1}$  respectively for the latter against 970 and 1000  $\text{cm}^{-1}$  for chloro derivatives or 965  $\text{cm}^{-1}$  for the bromo complex.

The spectra of the cupric complexes show a single broad band centred at *ca.* 12000–13000  $\text{cm}^{-1}$  (830–770 nm), typical of a square-planar geometry around the cupric ion<sup>(26)</sup>. The measured magnetic moments of the  $[\text{CuCl}_2(\text{MFSC})]$  and  $[\text{CuCl}_2(\text{FSC})_2]$  complexes are consistent with monomeric copper(II) complexes<sup>(25)</sup>.

### <sup>1</sup>H and <sup>13</sup>C NMR spectra studies

The n.m.r. spectra of FSC, MFSC and their cadmium diamagnetic complexes were recorded in  $\text{D}_6\text{-DMSO}$ , and the <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in Table 5.

**Table 5.** N.m.r. data: chemical shift (ppm) of ligands and cadmium complexes

Compd	H <sub>A</sub>	H <sub>A'</sub>	H <sub>B</sub>	H <sub>C</sub>	H <sub>D</sub>	NH	NH <sub>2</sub>	C <sub>A</sub>	C <sub>A'</sub>	C <sub>B</sub>	C <sub>C</sub>	C <sub>C'</sub>	C <sub>D</sub>	C <sub>E</sub>
FSC	7.74s	—	6.57m	6.80d	7.76	10.27s	6.35s	144.1	—	112.0	111.0	149.9	130.0	156.6
(5)	7.74d	—	6.56m	6.80d	7.72s	10.25s	6.35s	144.2	—	112.1	111.2	149.9	130.2	156.7
(6)	7.75d	—	6.58m	6.80d	7.73s	10.23s	6.32s	144.1	—	112.0	110.9	149.9	129.9	156.5
MFSC	—	2.29s	6.18m	6.65d	7.67s	10.17s	6.29s	148.9	113.9	112.7	108.3	153.4	130.2	156.6
(12)	—	2.28s	6.18m	6.66d	7.67s	10.15s	6.28s	148.3	113.5	112.9	108.4	153.4	130.4	156.7
(13)	—	2.35s	6.36m	6.86s	7.67s	9.57s	6.86s	146.0	113.6	117.8	108.9	155.4	127.2	156.8

The  $^1\text{H}$  spectra did not show significant differences between the ligands and their complexes. However, the  $^1\text{H}$  chemical shifts of  $\text{H}_\text{D}$  are slightly lowered when passing from ligand to FSC complexes as observed in 3-(2-furyl) propenal semicarbazone cadmium (II) complexes<sup>(1)</sup>. So, in these two series the coordinating atoms are, as indicated above on the basis of *i.r.* spectra, the O-ring and the N-imine. The  $^{13}\text{C}$  chemical shifts of  $\text{C}_\text{A}$  and  $\text{C}_\text{B}$  are not affected by coordination bonding.

In the MFSC cadmium(II) complexes the  $\text{H}_\text{D}$  chemical shift remains the same as in the ligand. The chemical shifts of the protons of the NH and  $\text{NH}_2$  groups are modified. The  $^{13}\text{C}$  chemical shifts of the complexes do not differ significantly from those of the ligands except for the complex  $[\text{CdBr}_2(\text{MFSC})]$  where we observe that the chemical shifts of  $\text{C}_\text{D}$  and  $\text{C}_\text{A}$  are lowered by 2.8 ppm and 2.3 ppm respectively. These results indicate the participation of the nitrogen of the azometine group and the oxygen of the ring in the complexation of the cadmium as postulated on the basis of *i.r.* spectra.

### Conclusions

We have synthesized and characterized 13 new metallic complexes with FSC or MFSC and cobalt(II), nickel(II), copper(II) and cadmium(II) chlorides and bromides. We have determined in each case the coordinating atoms, using different methods such as *i.r.*, far *i.r.* and electronic spectra and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ). Four different possibilities of bonding are shown: (i) N imine for  $[\text{NiCl}_2(\text{MFSC})_4]$ ; (ii) N imine and O keto for  $[\text{NiBr}_2(\text{FSC})_2]$ ; (iii) N imine and O ring:  $[\text{CdX}_2(\text{FSC})]$  and (iv) O keto and O ring:  $[\text{CoX}_2(\text{FSC})_2]$ ,  $[\text{CoCl}_2(\text{MFSC})]$ ,  $[\text{CoBr}_2(\text{MFSC})_2]$ ,  $[\text{NiCl}_2(\text{FSC})_2]$ ,  $[\text{CuCl}_2(\text{FSC})_2]$ ,  $[\text{CuCl}_2(\text{MFSC})]$  and  $[\text{CdX}_2(\text{MFSC})]$ .

The diversity of coordination mode in the semicarbazones can be explained on the basis of steric hindrance depending on the size of the complexing cation. The  $\text{Cd}^{2+}$  ion has a 0.97 Å ionic radii while those of Co, Ni and Cu are lower<sup>(27)</sup>: 0.69, 0.72 and 0.72 Å respectively. It may also be emphasized that the methyl group at position 5 on the furan ring leads to a higher rigidity of the heterocycle and this explains why  $[\text{CdX}_2(\text{FSC})]$  is linked through N imine and O ring while the keto and ring oxygen atoms are involved in  $[\text{CdX}_2(\text{MFSC})]$  species.

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