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Synthesis, structural and spectral studies of 5-methyl 2-furaldehyde thiosemicarbazone and its Co, Ni, Cu and Cd complexes

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Abstract

The reaction of cobalt, nickel, copper and cadmium chlorides and bromides with 5-methylfurfural thiosemicarbazone (M5FTSC) leads to the formation of two series of new complexes: $[M(M5FTSC)_2X_2]$, $[M(M5FTSC)X_2]$. They have been characterized by spectroscopic studies (infrared, ¹H NMR, and electronic spectra). The crystal structures of the free ligand M5FTSC and of the compound $[CuCl_2(M5FTSC)]$ have been determined by X-ray diffraction methods. For the Co(II), Ni(II) and Cu(II) complexes, the central atom is coordinated through the sulphur atom and the azomethine nitrogen atom whilst for the Cd(II) complexes, the coordination atoms are the sulphur and furanic oxygen atoms instead of the azomethine nitrogen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Furan thiosemicarbazone; 3d Metals complexes; Crystallographic structures

1. Introduction

Thiosemicarbazones and their complexes have been extensively studied during recent years owing to their pharmaceutical properties. These compounds present a wide variety of biological activity such as antitumoral [1–5], fungicidal [6,7], bactericidal [8] antiviral [3], etc. They have been used for the analysis of metals [9], for device applications relative to telecommunications, optical computing, optical storage and optical information processing [10].

We have previously described the complexes formed between various furan oximes [11] and semicarbazones

with 3d metal dihalides [12]. A study of the cytotoxic activity of some copper complexes characterized in our laboratory has also been recently reported [13] as well as similar compounds [14,15]. In this work we describe a new series of transition metal complexes formed from the ligand 5-methylfurfural thiosemicarbazone M5FTSC (Fig. 1) and the chlorides and bromides of Co(II), Ni(II), Cu(II) and Cd(II). The crystal structures of the ligand M5FTSC and of its copper complex $[CuCl_2(M5FTSC)]$ are also discussed.

2. Experimental

2.1. Synthesis of the ligand M5FTSC

The ligand was obtained as previously reported [16] from 5-methylfurfural and thiosemicarbazide (1:1 molar ratio) in absolute ethanol in the presence of pure acetic acid. The mixture was refluxed for 1 h and then cooled, filtered and recrystallized from a mixture of ethanol (75%) and water. Yellow microcrystalline products are obtained. All analytical and spectroscopic data are in good agreement with the expected values.

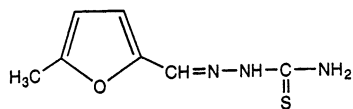


Fig. 1. Chemical structure of 5-methyl 2-furaldehyde thiosemicarbazone.

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2.2. Synthesis of the complexes

All the complexes were prepared starting from 5 mmol (0.92 g) of M5FTSC dissolved in EtOH, unless otherwise specified (used vol. in brackets). This solution was heated until the solvent refluxed and then the ethanolic solution of the metal halide was added slowly while stirring. The complexes were removed by filtration, washed with MeOH and finally dried in vacuum over silica gel.

2.3. Dichloro (5-methylfurfural thiosemicarbazone) cobalt(II) [CoCl₂(M5FTSC)]

CoCl₂·6H₂O (1.2 g; 5 mmol; 10 cm³) was added to the M5FTSC ethanolic solution (10 cm³) under refluxing conditions. The reflux was maintained for 24 h.

2.4. Dichloro bis (5-methylfurfural thiosemicarbazone) nickel(II) [NiCl₂(M5FTSC)₂]

This complex was prepared from a mixture of nBuOH solution of M5FTSC (10 cm³) and NiCl₂·6H₂O (0.6 g, 2.5 mmol, 10 cm³) after a 24 h reflux.

2.5. Dibromo bis (5-methylfurfural thiosemicarbazone) nickel(II) [NiBr₂(M5FTSC)₂]

The bromo complex was obtained from an EtOH solution of M5FTSC (70 cm³) and NiBr₂·2H₂O (2.5 mmol; 0.64 g; 10 cm³), refluxing for 5 h.

2.6. Dichloro (5-methylfurfural thiosemicarbazone) copper(II) [CuCl₂(M5FTSC)]

CuCl₂·2H₂O (0.85 g; 5 mmol; 10 cm³) was added to M5FTSC in EtOH (10 cm³). Although the complex appeared instantaneously, the reflux was maintained for 1 h. After recrystallisation in EtOH, a dark green microcrystalline product is obtained

2.7. Dibromo (5-methylfurfural thiosemicarbazone) copper(II) [CuBr₂(M5FTSC)]

A solution of CuBr₂ (1.3 g; 5 mmol; 20 cm³) was added to the solution of M5FTSC (20 cm³) using an excess of 10% of the metal salt. The complex precipitated instantaneously but the reflux was maintained for 2 h.

2.8. Dichloro bis (5-methylfurfural thiosemicarbazone) cadmium(II) [CdCl₂(M5FTSC)₂]

A slight excess of M5FTSC (1 g; 5 mmol; 15 cm³) was mixed with CdCl₂ (0.92 g; 5 mmol; 15 cm³). The complex precipitated during the addition of the metal salt, but, the solution was refluxed for 1 h.

2.9. Dichloro (5-methylfurfural thiosemicarbazone) cadmium(II) [CdBr₂(M5FTSC)]

This complex was prepared from M5FTSC (10 cm³) and CdBr₂·4H₂O (0.86 g; 2.5 mmol). The complex precipitated instantaneously, but the reflux was maintained for 1 h.

2.10. Physical 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 capillary technique. Magnetic measurements were made at 298 K, with a Squid magnetometer (MPMS-5) from Quantum Design Corporation. The molar susceptibility was corrected for the effect of the sample holder and diamagnetic contributions of all atoms (Institut des Matériaux de Nantes, C.N.R.S. France).

Conductance values were obtained with a Tacussel CD6NG conductimeter at 298 K from 10⁻³ mol dm⁻³ solutions of the complexes in absolute EtOH. The solvent had a conductance of 10⁻⁸ S cm² mol⁻², the conductance of NaI (10⁻³ mol dm⁻³) was 33 S cm² 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 de Nantes, France). Electronic spectra were recorded with a Perkin–Elmer Lambda 19 spectrometer from ethanolic solutions (10⁻³ mol dm⁻³). The ¹H NMR spectra were recorded on a Bruker Advance DRX500 in DMSO-D₆ operating at 500 MHz. The chemical shifts, δ , are given in parts per million (relative to TMS) and the coupling constants are in hertz.

2.11. X-ray crystallography

For both crystals, X-ray diffraction data were collected at 293 K on an Enraf Nonius MACH3 four-circle diffractometer ($\lambda_{\text{Mo K}\alpha} = 0.71069 \text{ \AA}$) equipped with a graphite monochromator (IMMO, UMR 6501 C.N.R.S). The structures were solved by direct methods (SIR) using MolEN package programs [17] and F was refined by a full-matrix least-squares techniques.

Non-hydrogen atoms were refined anisotropically for M5FTSC and [CuCl₂(MFTSC)]. The positions of the hydrogen atoms were calculated from the HYDRO program [17] and Fourier difference synthesis in the ligand. The small size of the crystal of the complex did not allow us to obtain enough data to specify the hydrogen atoms coordinates. Crystallographic data for M5FTSC and [CuCl₂(M5FTSC)] are given in Table 1.

Table 1
Crystallographic data for the free ligand and copper complex

| Compound | M5FTSC | CuCl ₂ (M5FTSC) |
|---|---|---|
| Formula | C ₇ H ₉ N ₃ OS | C ₇ H ₉ Cl ₂ CuN ₃ OS |
| Molecular weight | 183.23 | 317.68 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> (Å) | 7.3403(9) | 9.748(3) |
| <i>b</i> (Å) | 8.542(4) | 7.8375(7) |
| <i>c</i> (Å) | 15.2587(9) | 15.856(2) |
| α (°) | 90 | 90 |
| β (°) | 98.099(7) | 104.47(2) |
| γ (°) | 90 | 90 |
| <i>V</i> (Å ³) | 947.2(6) | 1173.0(7) |
| <i>Z</i> | 4 | 4 |
| Color | Yellow | Dark green |
| <i>D</i> _{calc} (g cm ⁻³) | 1.28 | 1.80 |
| <i>F</i> (000) | 384 | 636 |
| μ (mm ⁻¹) | 0.299 | 2.468 |
| <i>hkl</i> limits | –10,10/0,12/ –16,21 | 0,10/–8,0/ –17,16 |
| θ_{\min} , θ_{\max} | 2.5, 29.96 | 2.5, 22.97 |
| Number of data with <i>I</i> > 3 σ (<i>I</i>) | 1898 | 937 |
| Weighting scheme | 4 <i>F</i> _o ² /(σ 2(<i>F</i> _o ²) + 0.0064 <i>F</i> _o ⁴) | 4 <i>F</i> _o ² /(σ 2(<i>F</i> _o ²) + 0.0064 <i>F</i> _o ⁴) |
| Number of variables | 133 | 101 |
| <i>R</i> | 0.041 | 0.081 |
| <i>R</i> _w | 0.059 | 0.130 |

3. Results and discussion

The analytical and physical data for the ligand and the metal complexes are listed in Table 2. The analytical data are in close agreement with the above empirical formulae. The isolated solid complexes are stable in air and their molar conductivities are in a range that indicates a non-electrolytic nature. On heating all the complexes decomposed and did not present a clear melting point.

Table 2
Analytical data

| Elemental analysis found (Calc.)% | | | | | | | | |
|--|---------|-----------|--------------|------------|--------------|--------------|--------------|--|
| Compound | Color | M.p. (°C) | C | H | X | M | μ (B.M.) | λ (S cm ² mol ⁻¹) |
| [M5FTSC] | Yellow | 165 | 45.71(45.89) | 4.95(4.95) | | | | 0.82 |
| [CoCl ₂ (M5FTSC)] | Blue | 240 d | 26.98(26.86) | 2.98(2.90) | 23.03(22.65) | 18.17(18.82) | 2.80 | 24.5 |
| [NiCl ₂ (M5FTSC) ₂] | Green | 222 d | 33.61(33.90) | 3.58(3.66) | 14.83(14.29) | 11.06(11.83) | 2.21 | 31 |
| [NiBr ₂ (M5FTSC) ₂] | Green | 236 d | 28.89(28.75) | 3.17(3.10) | 27.32(27.32) | 10.24(10.03) | 1.25 | 39 |
| [CuCl ₂ (M5FTSC)] | Green | 235 d | 26.50(26.47) | 2.99(2.86) | 21.82(22.32) | 19.31(20) | 0.44 | 23.5 |
| [CuBr ₂ (M5FTSC)] | Dark | 221 d | 20.73(20.68) | 2.21(2.23) | 39.02(39.31) | 16.18(15.63) | 0.54 | 39 |
| [CdCl ₂ (M5FTSC) ₂] | Whitish | 243 d | 21.68(22.94) | 2.43(2.47) | 18.55(19.34) | 29.55(30.64) | diam | 7.3 |
| [CdBr ₂ (M5FTSC)] | Whitish | 223 d | 26.28(26.33) | 2.84(2.84) | 25.11(25.02) | 17.70(17.60) | diam | 4.6 |

3.1. Crystal structure of M5FTSC

For comparison, the main bond distances and bond angles of the free ligand and the copper complex are shown in Table 3. Fig. 2 shows a perspective view of the M5FTSC molecule with the numbering scheme.

The thiosemicarbazone moiety shows an E configuration about both C(2)–N(3) and C(1)–N(2), as found in most thiosemicarbazones [7,18,19]. The molecule is planar except for the hydrogen atoms H01 and H02 and the sulphur atom. This latter atom presents a slight deviation from planarity, of the order of 0.156(1) Å. In any case C–S distance is intermediate between a single C–S bond distance of 1.82 Å and a double-bond distance of 1.56 Å, as quoted by Sutton [20]. Therefore, the C–S bond of thiosemicarbazones possesses only partial double bond character. This hypothesis is supported by the bond distances around C(1) of 1.322(2) and 1.341(2) Å for N(1) and N(2) atoms, respectively, which are indicative of some double-bond character. A comparison of the N(2)–N(3) distance of 1.377(2) Å with the corresponding N–N distance of 1.412(2) Å for the unsubstituted [21], 1.395(2) Å for 1-phenyl [22] and 1.431(6) Å for the 4-phenyl [13] thiosemicarbazides, suggests that the N–N bond also has some double-bond character. A similar shortening of the bond was reported with a weight average distance of 1.37 Å for some thiosemicarbazones which have an extensively delocalized group attached to the azomethine nitrogen N(3). This can be attributed to inclusion of resonance forms involving the furan ring [7].

Two types of intramolecular interactions are observed. The first is the formation of a hydrogen bond, between H05 and the azomethine nitrogen N(3) (H05⋯N3 2.38(2) Å). The second is a Van der Waals interaction between the heterocyclic oxygen and the azomethine nitrogen N(3) atoms (O⋯N(3) 2.078(2) Å). The intermolecular hydrogen bonds which link the molecules are indicated in the molecular packing shown

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

| | M5FTSC | [Cu(M5FTSC)Cl ₂] |
|---------------------|----------|------------------------------|
| <i>Bond lengths</i> | | |
| S–C1 | 1.684(1) | 1.68(2) |
| O–C3 | 1.369(2) | 1.37(3) |
| O–C6 | 1.376(2) | 1.39(2) |
| N1–C1 | 1.322(2) | 1.31(3) |
| N2–N3 | 1.377(2) | 1.37(3) |
| N2–C1 | 1.341(2) | 1.39(3) |
| N3–C2 | 1.282(2) | 1.30(3) |
| C2–C3 | 1.428(2) | 1.40(3) |
| C3–C4 | 1.345(2) | 1.38(3) |
| C4–C5 | 1.407(3) | 1.54(4) |
| C5–C6 | 1.330(3) | 1.34(4) |
| C6–C7 | 1.476(3) | 1.55(4) |
| Cu–Cl1 | | 2.240(5) |
| Cu–Cl2 | | 2.256(7) |
| Cu–S | | 2.249(7) |
| Cu–N3 | | 2.03(2) |
| <i>Bond angles</i> | | |
| C3–O–C6 | 106.2(1) | 110(1) |
| C3–C4–C5 | 106.7(2) | 101(1) |
| N3–N2–C1 | 120.7(1) | 114(1) |
| N2–N3–C2 | 114.5(1) | 118(1) |
| C4–C5–C6 | 107.5(2) | 109(1) |
| S–C1–N1 | 122.6(1) | 121(1) |
| S–C1–N2 | 119.7(1) | 122(1) |
| N1–C1–N2 | 117.6(1) | 115(1) |
| N3–C2–C3 | 122.7(1) | 129(2) |
| O–C6–C5 | 109.8(2) | 107(1) |
| O–C3–C2 | 118.8(1) | 121(1) |
| O–C6–C7 | 116.0(2) | 118(1) |
| O–C3–C4 | 109.7(1) | 110(1) |
| C5–C6–C7 | 134.2(2) | 133(2) |
| C2–C3–C4 | 131.4(2) | 127(2) |
| Cl1–Cu–Cl2 | | 93.4(2) |
| Cl1–Cu–S | | 91.9(2) |
| Cl1–Cu–N3 | | 166.5(5) |
| Cl2–Cu–S | | 153.6(2) |
| Cl2–Cu–N3 | | 95.6(5) |
| S–Cu–N3 | | 84.5(5) |
| Cu–S–C1 | | 98.3(8) |
| Cu–N3–N2 | | 118(1) |
| Cu–N3–C2 | | 122(1) |

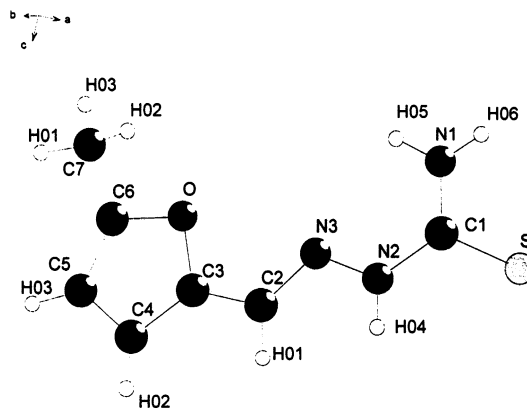


Fig. 2. Molecular structure and atom numbering of the free ligand M5FTSC.

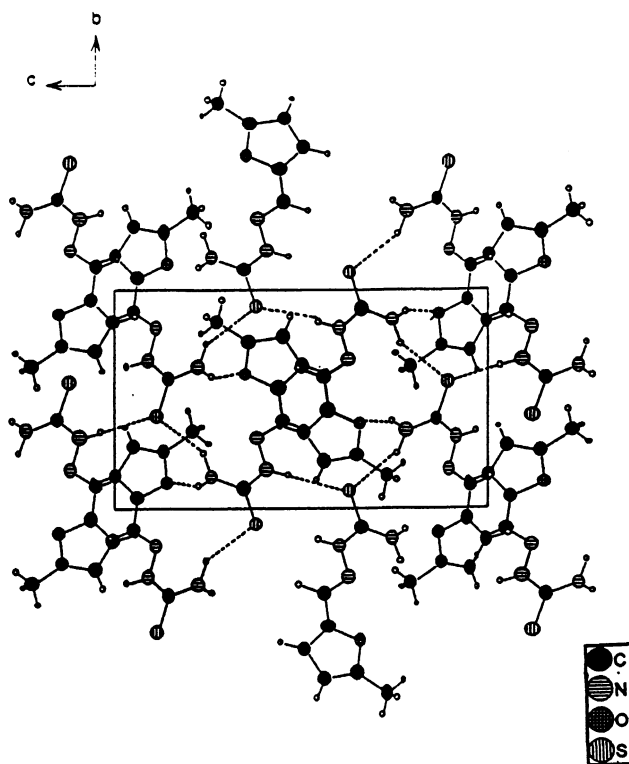


Fig. 3. Packing arrangement for M5FTSC.

in Fig. 3. The length of the bonds and the positions of their atoms are indexed in Table 4.

3.2. Crystal structure of [CuCl₂(M5FTSC)]

The molecular structure of the complex [CuCl₂(M5FTSC)] is shown in Fig. 4. In this compound, the M5FTSC is a neutral bidentate ligand, coordinated to the central metal atom via the azomethine nitrogen N(3) and the thiolate sulphur atom, with the third and fourth coordination sites being occupied by the two chlorine atoms Cl(1) and Cl(2).

In the literature, most thiosemicarbazone ligands coordinate via the enolic form. For example, in the case of bis(thiophene-2-carboxaldehyde thiosemicarbazonato-N,S) dichlorotin (IV): [Sn(tctsc)₂Cl₂] [6], the C(1)–N(1) distance is reduced from 1.34 to 1.29 Å. In our case this bond distance is increased from 1.34 to 1.39 Å which is the length of a simple bond, and this indicates the absence of the enolic form in this complex. Furthermore, in the presence of the enolic form the length C(1)–S increases from 1.69 to 1.76 Å. Again in our case we do not remark any such increase and this

Table 4
Bond lengths (Å), angles (°) and position of atoms of hydrogen bonds

| Hydrogen bonds | Distance (Å) | Angles (°) | Position of hydrogen atoms | Position of no hydrogen atoms |
|----------------|--------------|------------|----------------------------|-------------------------------|
| N1–S···H04 | 2.52(2) | 145(9) | (1–x, 0.5+y, 1.5–z) | (x, –0.5–y, –0.5+z) |
| N2–S···H05 | 2.46(2) | 163.6(3) | (x, –0.5–y, –0.5+z) | (x, 0.5–y, –0.5+z) |
| N1–O···H06 | 2.36(2) | 147.7(6) | (x, 0.5–y, –0.5+z) | (1–x, 1–y, 1–z) |

confirms that this complex is not of the enolic form. During the formation of this complex, the ligand remains in the planar form. The copper atoms also form part of the plane, while the chlorine atoms Cl(1) and Cl(2) stick out on both sides of the plane by 0.547(5) and 1.001(5) Å respectively. The configuration of the ligand is unchanged and this has been reported in several works [10,23]. It shows that this configuration favours the coordination through the azomethine nitrogen and the thione or the thiolato sulfur atoms in the thiosemicarbazones ligands. The van der Waals interaction, noted in the uncomplexed ligand, between the azomethine nitrogen N(3) and the oxygen atoms, is not present here, but the formation of a new one is observed between the nitrogen N(2) and the oxygen atoms.

The coordination geometry of the copper atoms is shown in Fig. 3. The ideal dihedral angle in tetrahedral geometry for S; Cu; N(3) and Cl(1); Cl(2); Cu is 90°. In our case this angle is about 27° which indicates that this is certainly not a tetrahedral structure. This observation is further supported by the fact that ideal bond angles for S–Cu–Cl(2) and N(3)–Cu–Cl(1) are 109.47° for a tetrahedral structure whereas we have calculated these angles to be approximately 160°. As these angles in a square planar configuration have an ideal value of 180°, we propose that the structure of our complex lies somewhere between that of tetrahedral and square planar configuration.

The Cu–S bond length of 2.249(7) Å remains within the range of bond lengths for the two atoms in other heterocyclic ⁴N-substituted copper thiosemicarbazone complexes, as quoted in the work of Ali et al.; 2.236 Å for the bromo complex of copper (II) and 2.282 Å for the chloro complex of copper (II) [23]. The same authors have reported that the N–Cu, this distance increases by 0.03 Å, in the range of 1.949–2.00 Å. This small difference is probably due to the fact that the ligand used in [23] coordinates by three atoms including the nitrogen atoms.

As regards the bond distances Cu–Cl(1) 2.24 Å and Cu–Cl(2) 2.25 Å, they are comparable with the bond lengths Cu–Cl 2.234(2) Å in the complex [Cu(HBZTP)Cl₂] where Cu presents a four coordination, and Cu–Cl(1) 2.236 Å and Cu–Cl(2) 2.660 Å in the complex [Cu(HBZTP)Cl₂] where Cu presents a five coordination.

The molecules of the complex [CuCl₂(M5FTCS)] form a zigzag chain parallel to the *b*-axes in the most common setting. The packing is governed by van der Waals interactions between the nitrogen atoms N(1) (x, 0.5–y, 0.5+z) and the chlorine atoms Cl(1) (1–x, 0.5+y, 0.5–z) and Cl(2) (1–x, 1–y, 1–z) where the distances are 3.29(2) Å for Cl(1)···N(1) and 3.28(2) Å for Cl(2)···N(1) respectively.

3.3. Infrared spectra

Selected vibration bands of M5FTSC and of its metal complexes are given in Table 5.

In principle, the ligand can exhibit thione-thiol tautomerism, since it contains a thioamide –NH–C=S functional group [10]. The $\nu(\text{S–H})$ band at 2570 cm^{–1} is absent from the IR spectra of the Schiff base but the $\nu(\text{N–H})$ band at ca. 3150 cm^{–1} is present, indicating that in the solid state the ligand remains as the thione tautomer.

The bands appearing around 1345 and 785 cm^{–1} in the spectrum of the ligand are either weakened or shifted to higher wavenumbers in all the complexes [24,25], and this shift can be assigned to the $\nu(\text{C=S})$ vibration. On the other hand, the bands in the region 3440–3270 cm^{–1} attributed to symmetrical and asymmetrical stretching modes $\nu(\text{NH}_2)$ in the spectra of the ligand, undergo appreciable change in the spectra of the complexes. This is a consequence of the coordination of the sulphur from the C=S(NH₂) group as reported earlier [26]. This coordination is confirmed by the pres-

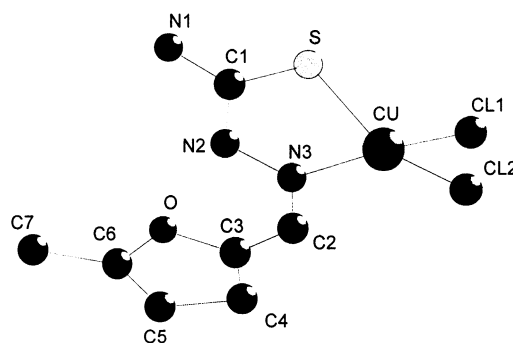


Fig. 4. Molecular structure and atom numbering of [CuCl₂(M5FTSC)].

Table 5
Main IR spectral vibrations (cm^{-1})

| | NH ₂ | NH | C=S | C=N | C–O–C | C–N | N–N | Ring | M–X | M–N | M–S | M–O |
|------------------------------|-----------------|------|----------|------|-------|-----------|-----|-------|---------|-----|-----|-----|
| M5FTSC | 3447a 3274s | 3150 | 1344 84 | 1600 | 1285 | 1092 | 930 | 1023 | | | | |
| [CuCl ₂ (M5FTSC)] | 3442 3282 | 3077 | 1388 95 | 1609 | 1289 | 1123 | 947 | 1023 | 250 267 | 445 | 390 | |
| [CuBr ₂ (M5FTSC)] | 3380 3253 | 3096 | 1365 808 | 1619 | 1290 | 1126 | 939 | 10242 | 257 274 | 448 | 395 | |
| [NiCl ₂ (M5FTSC)] | 3297 | 3076 | 1386 805 | 1628 | 1289 | 1130 | 949 | 1026 | 245 260 | 455 | 385 | |
| [NiBr ₂ (M5FTSC)] | 3432 3297 | 3085 | 1385 804 | 1622 | 1288 | 1128 | 946 | 1028 | 265 | 450 | 385 | |
| [CoCl ₂ (M5FTSC)] | 3297 | 3085 | 1379 802 | 1618 | 1288 | 1127 | 945 | 1027 | 262 | 449 | 390 | |
| [CdBr ₂ (M5FTSC)] | 3443 3277 | 3180 | 1381 802 | 1557 | 1299 | 1118 | 932 | 1034 | 236 | | 160 | 467 |
| [CdCl ₂ (MFTSC)] | 3365 3298 | 3187 | 1352 781 | 1558 | 1128 | 1200 1113 | 931 | 1030 | 226 | | 158 | 463 |

ence of a new band at $380\text{--}395\text{ cm}^{-1}$ [5,27] that can be assigned to $\nu(\text{M}=\text{S})$ for all complexes.

In the ligand spectrum, the strong band observed at 1600 cm^{-1} can be assigned to $\nu(\text{C}=\text{N})$ frequencies [26]. This latter frequency shift to higher region frequencies [24,26] in the spectra of all metal complexes, except those of cadmium, indicates the coordination of nitrogen of the azomethine group to the central metal atoms in these complexes. The presence of a new band in the region $440\text{--}450\text{ cm}^{-1}$ due to $\nu(\text{M}=\text{N})$ is another indication of the involvement of nitrogen in the azomethine group coordination [5,27]. However, we did not observe any shifts of frequency of the $\nu(\text{Cd}=\text{N})$ for the complexes of Cd(II). On the contrary we noted a significant displacement of the frequency of the ring breathing and $\nu(\text{C}=\text{O}=\text{C})$ vibrations, and this shows that the coordination may be through the furanic oxygen atom instead of the azomethine nitrogen [12]. This coordination is supported by the appearance of $\nu(\text{Cd}=\text{O})$ vibration for [CdCl₂(M5FTSC)] and [CdBr₂(M5FTSC)] at 467 and 463 cm^{-1} , respectively.

G. Ibrahim [12] and E. Bernejo [7] have reported that the bands observed in the region $220\text{--}280\text{ cm}^{-1}$ are due to metal–chlorine and metal–bromine stretching vibrations.

3.4. Electronic spectra

The spectra of the nickel complexes show three bands at 8165 , 13985 and 29678 cm^{-1} (Cl^-) and 7875 , 13160 and 23950 cm^{-1} (Br^-). The use of König's relation [28] lead to relative values of 10 Dq : 8165 cm^{-1} (Cl^-) and 7875 cm^{-1} (Br^-) while the Racah's B parameters are equal to 1145 and 874 cm^{-1} respectively and the β ratio ($\beta = B$ free gaseous ion/ B complex) is 1.105 and 0.672 . There is no significant difference between experimental and calculated values of ν_1 , ν_2 and ν_3 . These values are in good agreement with those of trans dihalogeno octahedral structures [29a].

The four coordination and the blue colour of the cobalt complex indicate a tetrahedral geometry [29b]. In order to compare the experimental and theoretical frequencies and the calculation of 10 Dq , B and β for d^7 configuration in tetrahedral species, we used König's

relation. The following values for the Ni(II) derivatives were obtained: $10\text{Dq} = 6945\text{ cm}^{-1}$, $B = 540\text{ cm}^{-1}$ and $\beta = 0.51$ moreover, it may be underlined that the values of theoretical and experimental bands are in good agreement.

We may remark that the copper complex has two broad $d\text{--}d$ absorption bands located at 10952 and 11148 cm^{-1} for the chlorine and bromine complexes respectively. These positions are typical of a pseudo-tetrahedral structure [29(c)].

3.5. NMR spectra

The ^1H NMR spectrum of (M5FTSC), (Fig. 6) shows a singlet at 11.3 ppm due to the NH group next to C=S, while the signal of the proton on C=N double bond appears at 7.50 ppm . It is interesting to note the presence of two broad singlets for the two NH₂ protons, respectively at 7.78 and 8.15 ppm : it means that the free rotation around the C–N bond is blocked because of its partial double bond character [10].

The spectra of the complexes [CdCl₂(M5FTSC)]₂ and [CdBr₂(M5FTSC)] show no differences as compared to that of the free ligand. This enhances the hypothesis

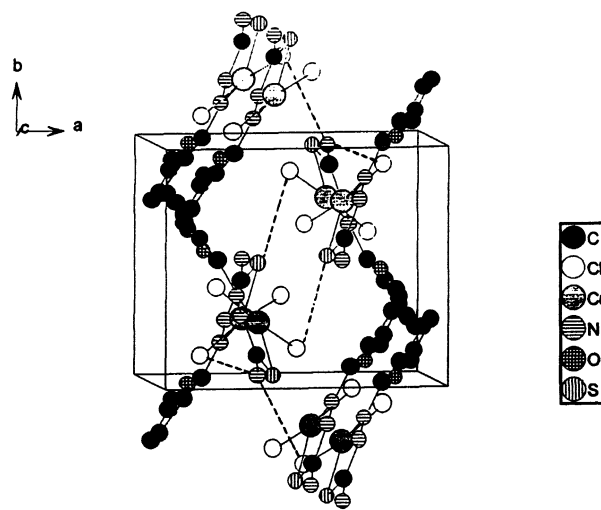


Fig. 5. Packing arrangement for [CuCl₂(M5FTSC)].

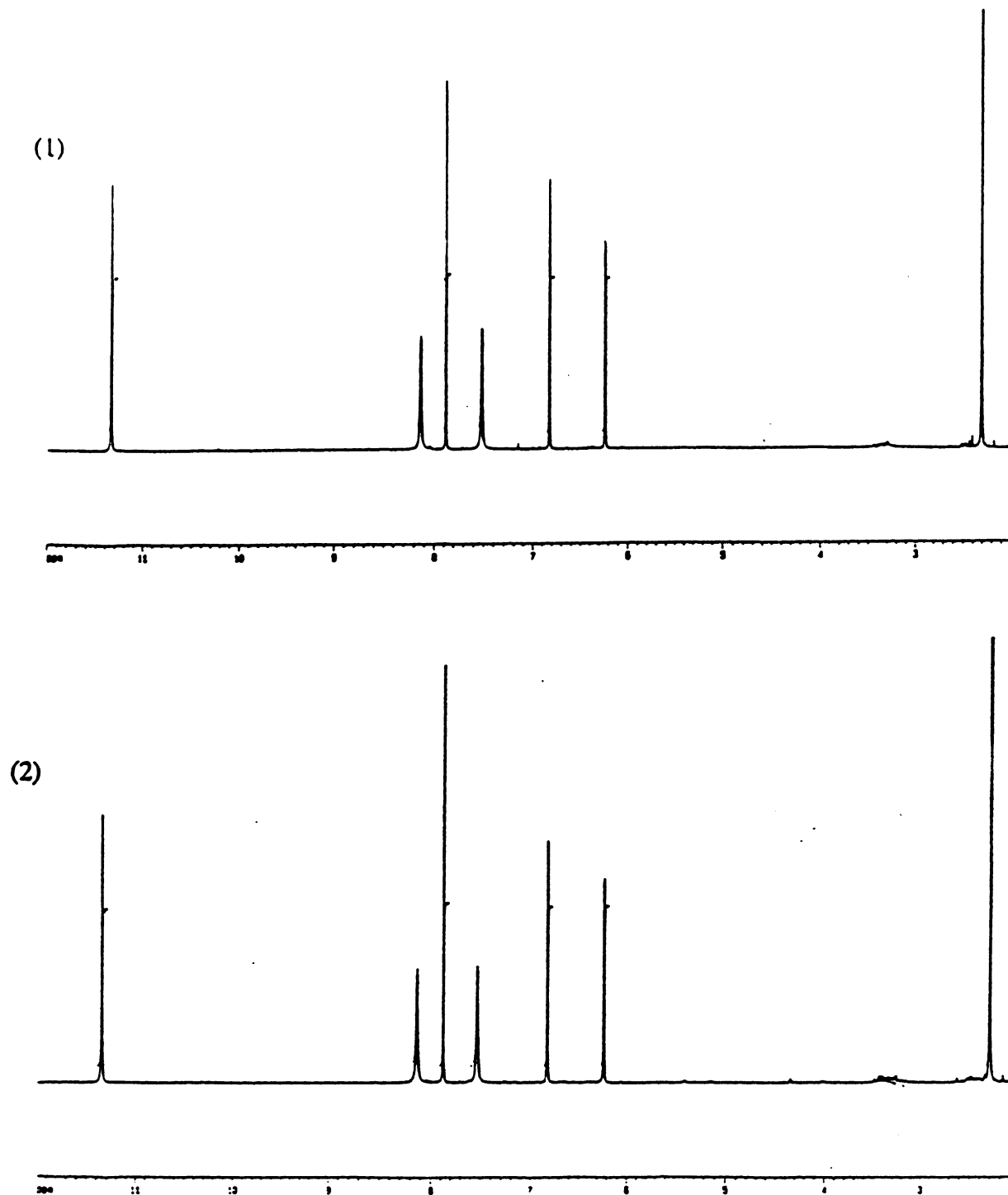


Fig. 6. ¹H NMR spectra of M5FTSC (1) and [CuCl₂(M5FTSC)] (2).

that N(11) and N(12) are not the coordinating atoms. The fact that there is no disappearance of the peak at 11.3 ppm due to the NH protons in the spectrum of the complexes indicates that the ligand remains its thionic form even after complexation, as shown in Fig. 5.

In theory, the complexation by azomethine nitrogen affects the chemical shift of the C=N protons [5]. In our case no shift of this signal was observed, confirming our earlier hypothesis, formulated from infrared data, that the second coordinating atom is the oxygen of the furanic ring in the Cd complexes.

4. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 147 005 for compound M5FTSC and CCDC 147 006 for compound [CuCl₂(M5FTSC)]. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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