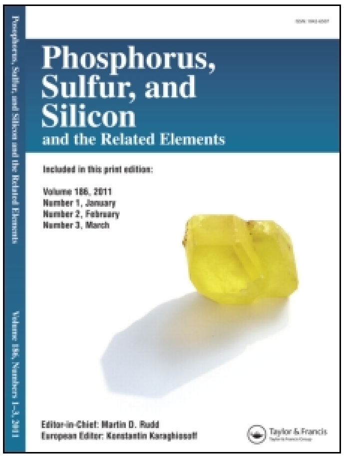

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Furannic Thiosemicarbazone Complexes of Co(II), Ni(II), and Cu(II) in Ethanol Solutions and of Co(II) in the Solid State

El Mostapha Jouad[a]; Gilles M. Bouet[a]; Mustayeen Ahmed Khan[a]; Diana Dogaru[b]; Constantin Mateescu[b]
[a] Laboratoire de Chimie de Coordination, Angers Cedex 01, France [b] Faculty of Food Processing Technology, Banat University of Agricultural Sciences and Veterinary Medicine, Timisoara, Romania

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Furannic Thiosemicarbazone Complexes of Co(II), Ni(II), and Cu(II) in Ethanol Solutions and of Co(II) in the Solid State

El Mostapha Jouad
Gilles M. Bouet
Mustayeen Ahmed Khan
Laboratoire de Chimie de Coordination, Angers Cedex 01, France

Diana Dogaru
Constantin Mateescu
Faculty of Food Processing Technology, Banat University of Agricultural Sciences and Veterinary Medicine, Timisoara, Romania

Thiosemicarbazone complexes with cobalt(II), nickel(II), and copper(II) metal ions are studied in ethanol solutions. The stability constants of all the identified complexes are calculated, and we found that stability increases from cobalt to copper. The stability of the complex is increased by the presence of a donor group like methyl, whereas it is not affected by the length of the thiosemicarbazone side chain. A further study of the cobalt(II) complexes in the solid state permits the identification of the coordinating atoms. With the help of additional results from electronic spectra structures of the cobalt(II) complexes are proposed.

Keywords 3D transition metals; IR spectroscopy; stability constants; thiosemicarbazone complexes; UV-visible spectroscopy

INTRODUCTION

Metal complexes of oximes, semicarbazones, and thiosemicarbazones have known biological activities. Their antiviral and cytotoxic activities have been widely reported in the scientific literature.[1–10] Many furan derivatives have been studied in this regard,[11–15] and a detailed study in solution of different semicarbazones as ligands coordinated to copper(II) was reported by our laboratory.[16] This study showed that the identified complexes were fairly stable, their stability constants being of the order of 3 ± 1 log units. However, with other metals the same

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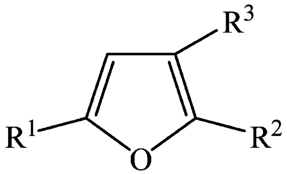
Address correspondence to Mustayeen Ahmed Khan, Laboratoire de Chimie de Coordination, SONAS EA 921, UFR Pharmacie, 16 bd Daviers, 49045 Angers cedex 01, France. E-mail: mustayeen.khan@univ-angers.fr



R^1	R^2	R^3	Abbreviation
H	CH=N-NH-CS-NH_2	H	FTSC
CH_3	CH=N-NH-CS-NH_2	H	M5FTSC
H	H	CH=N-NH-CS-NH_2	3FTSC
H	CH=CH-CH=N-NH-CS-NH_2	H	FATSC

FIGURE 1 General structure and substitution pattern of the thiosemicarbazone ligands.

ligands form very weak complexes. This is expected, however, as it was shown earlier that the Irving-Williams Order of Stabilities is equally valid in such systems;[17] hence, the stability of the complexes is highest with copper as compared to other metals.

In the present study, four furan-substituted thiosemicarbazones were synthesized. Their general structure is presented in Figure 1.

The complexes of these thiosemicarbazones with cobalt(II), nickel(II), and copper(II) were prepared, their relative stability in solution was determined and compared with that of the corresponding semicarbazone complexes. As these complexes have shown potential therapeutic properties, attempts were made to study their structures in the solid state.

EXPERIMENTAL

For the synthesis of the ligands, the experimental procedure given by West et al. was followed.[18] All ligands were synthesized by refluxing the corresponding furaldehyde with thiosemicarbazide (1:1 molar ratio) in 50 mL absolute ethanol in the presence of pure acetic acid (5 mL) for 1 h. The mixture was then cooled to ambient temperature, filtered, and the solid recrystallized from ethanol/water (3:1). The ligands were obtained as yellow microcrystalline solids. All analytical and spectroscopic data are in good agreement with the expected data.

For spectrophotometric experiments the final analytical concentration of the metal was 2.10^{-4} mol dm^{-3} in case of copper(II), and 2.10^{-3} mol dm^{-3} for solutions of cobalt(II) and nickel(II). Ligand solutions were kept away from light in order to avoid degradation and were prepared in the concentration range of 10^{-5} to 10^{-4} mol dm^{-3}. No analysis could be done for higher molar ratios due to precipitation. Under such experimental conditions, only mononuclear and dinuclear complexes were envisaged.

The UV-visible spectra between 200 and 500 nm were recorded using a Perkin Elmer (UV/VIS/NIR) Lambda 19 spectrophotometer equipped with a thermostat and matched 10 mm quartz cell. The temperature at which the experiments were performed was maintained at $25.0 \pm 0.2^\circ$C. The final solutions of metal and ligand were prepared just before the measurements and ethanol was used as spectrophotometric reference solution. The electronic spectra were recorded in the whole range of UV-VIS-NIR.

The IR spectra were obtained with a Perkin Elmer (Spectrum One FTIR) instrument between 4 000 and 400 cm^{-1} using KBr discs. For measurements in the far IR between 400 and 50 cm^{-1}, a Nicolet FTIR 20F spectrometer with polyethylene disc was used at the Institut des Matériaux, University of Nantes.

Dichlorobis(furfural Thiosemicarbazone) Cobalt (II) [$CoCl_2(FTSC)_2$] and Dibromobis(furfural Thiosemicarbazone) Cobalt (II) [$CoBr_2(FTSC)_2$]

These complexes were prepared by mixing 20 mL of a FTSC solution (0.85 g, 5 mmol) in methanol with 20 mL of a methanol solution of cobalt(II) chloride, $CoCl_2{\cdot}6H_2O$ (0.59 g, 2.5 mmol), or cobalt(II) bromide, $CoBr_2$ (0.85 g, 2.5 mmol). The mixture was refluxed for 24 h, and then cooled to ambient temperature when the complex precipitated.

Dichloro(5-methylfurfural Thiosemicarbazone) Cobalt (II) [$CoCl_2$(M5FTSC)]

The complex [$CoCl_2$(M5FTSC)] was prepared from 1.19 g (5 mmol) of cobalt(II) chloride, $CoCl_2.6H_2O$, dissolved in 10 mL of absolute ethanol. To this solution M5FTSC (0.92 g, 5 mmol) in 10 mL of absolute ethanol were added and the mixture was maintained for 24 h at the reflux temperature of ethanol. The complex precipitated on cooling to ambient temperature.

Dichlorobis(3-(2-furryl)prop-2-enal Thiosemicarbazone) Cobalt(II) [$CoCl_2(FATSC)_2$]

This complex was obtained by the addition of a solution of $CoCl_2{\cdot}6H_2O$ (0.6 g, 2.5 mmol) in 10 mL of ethanol to a solution of FATSC (0.98 g, 5 mmol) in 20 mL of ethanol with constant stirring under reflux conditions. The complex precipitated after 3 h of reaction time.

RESULTS AND DISCUSSION

Complexes of Co(II), Ni(II), and Cu(II) with the ligands FTSC, M5FTSC, 3FTSC, and FATSC were prepared. Since the most stable complexes are formed with copper, detailed results with this metal ion are presented here. For the other complexes the results of calculations are given.

Experimental UV-VIS Spectra

In ethanolic solution copper(II) shows a characteristic maximum at 263 nm with a shoulder peak around 245 nm. The principal bands of the ligands in this solvent in the UV-VIS region are for FTSC at 323 nm, for M5FTSC at 330 nm, for 3FTSC at 295 nm, and for FATSC at 350 nm. The experimental spectra of the copper(II) chloride solutions with FTSC, M5FTSC, 3FTSC and FATSC are presented in Figures 2-5, respectively.

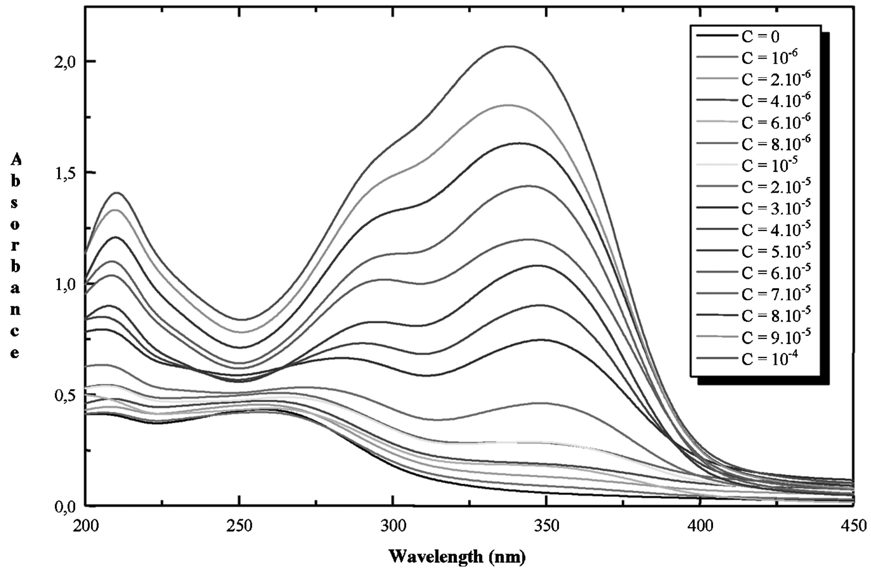


FIGURE 2 Absorption spectra of copper(II)-FTSC solutions. $[Cu^{2+}] = 10^{-4}$ mol L^{-1}; $l = 1$ cm; C = ligand concentration.

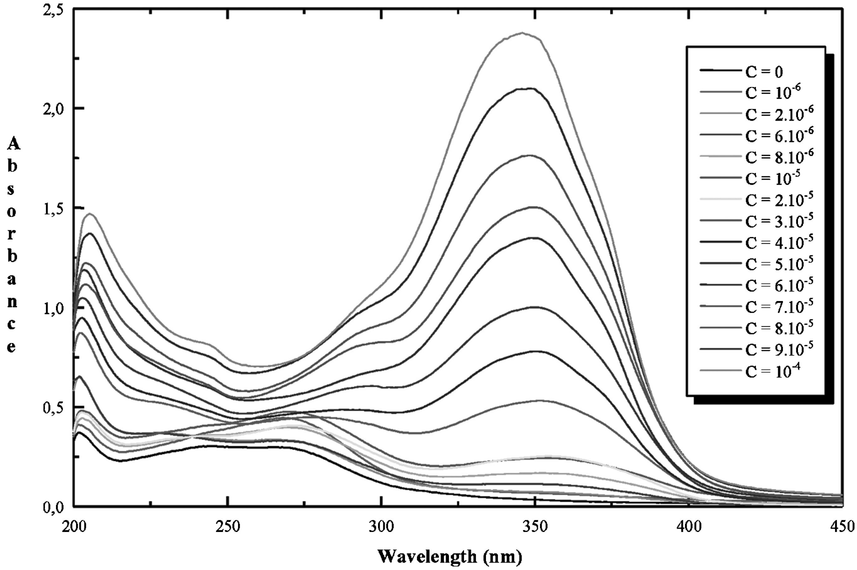


FIGURE 3 Absorption spectra of copper(II)-M5FTSC solutions. $[Cu^{2+}] = 10^{-4}$ mol L^{-1}; $l = 1$ cm; C = ligand concentration.

Figure 2 shows that with increasing concentration of FTSC two new bands are observed: a clear maximum at 350 nm and a shoulder peak around 295 nm. In the case of M5FTSC, both the metal and the ligand maxima undergo a bathochromic shift with the appearance of two bands at 267 and 350 nm at concentration as low as 8.10^{-6} mol dm^{-3} (Figure 3). For 3FTSC also, the appearance of two new bands around 275 and 328 nm is observed. They tend to coalesce into one maximum—that of the ligand, indicating the presence of free ligand in the solution (Figure 4). Finally, in Figure 5 it can be seen, that FATSC solutions with copper(II) equally exhibit the presence of two new bands at 250 and 375 nm.

Determination of the Stability Constants

The equilibrium under study is:

$$M^{2+} + L \rightleftharpoons [ML]^{2+}, \quad (1)$$

where L is the ligand and M = Co, Ni or Cu. The equilibrium is defined by the stability constant β:

$$\beta = [ML^{2+}]/[M^{2+}][L]. \quad (2)$$

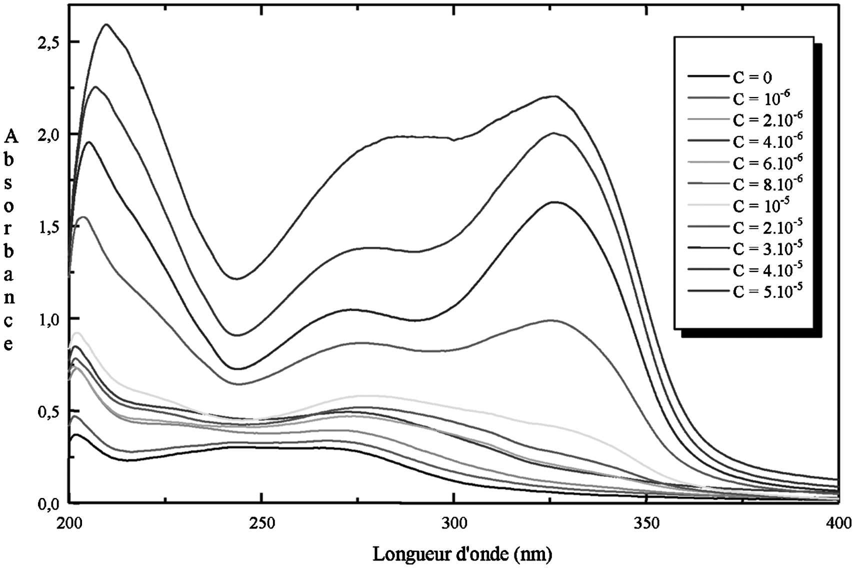


FIGURE 4 Absorption spectra of copper(II)-3FTSC solutions. $[Cu^{2+}] = 10^{-4}$ mol L^{-1}; $l = 1$ cm; C = ligand concentration.

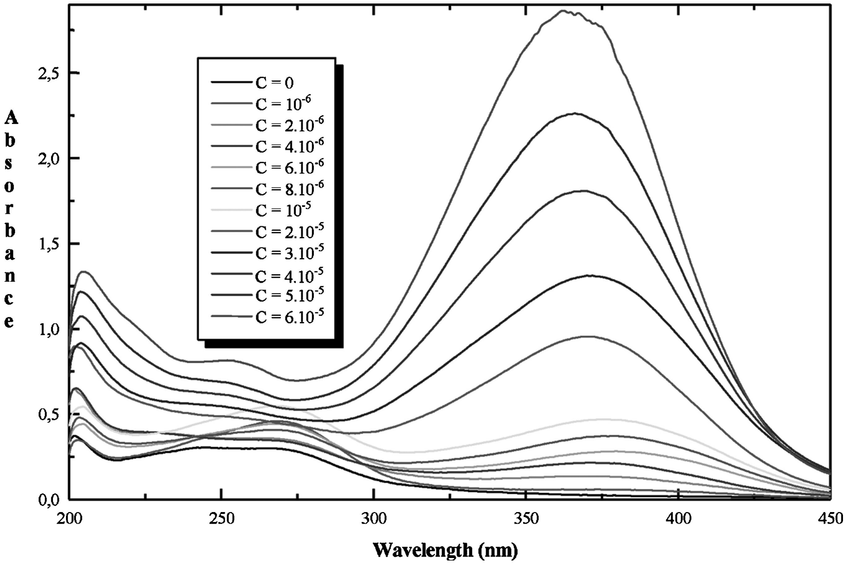


FIGURE 5 Absorption spectra of copper(II)-FATSC solutions. $[Cu^{2+}] = 10^{-4}$ mol L^{-1}; $l = 1$ cm; C = ligand concentration.

TABLE I Detailed Results for the System Cu(II)-FTSC Using the SIRKO Program

Model		
$CuCl_2$	FTSC	
1	0	log $\beta = 0$
0	1	log $\beta = 0$
1	2	log $\beta = 1.951$ Refined
Parameters	λ(nm)	
$\varepsilon(3,1) = 16548 \pm 4740$	290	
$\varepsilon(3,2) = 15986 \pm 5113$	310	
$\varepsilon(3,3) = 18945 \pm 6051$	330	
$\varepsilon(3,4) = 20592 \pm 6032$	340	
$\varepsilon(3,5) = 19640 \pm 5955$	350	
$\varepsilon(3,6) = 17953 \pm 5707$	360	
$\varepsilon(3,7) = 14389 \pm 5905$	370	
log $\beta = 1.951 \pm 0.073$		
5 iterations	R factor $= 3.53 \pm 0.05\%$	

The calculation of the stability constants is based on the computer program SIRKO, which was conceived for the determination of these and related parameters from spectrophotometric, potentiometric and calorimetric experimental data.[19] The essential details of the program are given in our earlier publication.[16]

Table I gives the detailed results obtained from the program for the system $CuCl_2$-FTSC. In this presentation, the theoretical model proposed is given in the top left-hand corner, $CuCl_2$:1 and FTSC:2, i.e., M:L = 1:2 complex. The best value obtained for the stability constant of this model is log $\beta = 1.951$ with a dispersion of ± 0.073. The molar absorption coefficients ε given at the left are those of the complex calculated for the different wavelengths λ. The numbers in parentheses are programme codes. The first number indicates the nature of the absorbing species, i.e., 1 for the metal, 2 for the ligand, and 3 for the complex; the second number indicates the code for the successive wavelengths, e.g. 1 for 290 nm, 2 for 310 nm, etc. These values are obtained after five iterations with an R factor of 3.53 %. The R factor defines the compatibility of the theoretical model with the experimental data and should be as small as possible, 5% or less.

Table II summarizes the final results obtained for the stability constants of the four thiosemicarbazone ligands with cobalt(II), nickel(II) and copper(II).

TABLE II Logarithm of Stability Constants of the Four Thiosemicarbazone Ligands with Cobalt(II), Nickel(II) and Copper(II)

	Cobalt (II)	Nickel (II)	Copper (II)
FTSC	1.00	1.07	1.95
M5FTSC	1.87	2.03	3.82
3FTSC	2.18	2.39	4.51
FATSC	0.83	0.90	1.64

Stability of the Complexes

For each ligand, the complexes formed with different metals increase in stability from cobalt to nickel and strongly from nickel to copper. This result is in accord with the Irving–William Order of Stabilities and we reported earlier such behaviour in similar systems.[17]

The complexes formed with the ligand 3FTSC have the highest stability when compared with the other three ligands. This can be explained by the position of the thiosemicarbazone part on the furanic cycle. Indeed, the position 3 of the ring is more favorable for complexation than the position 2 of the ring because of much less steric hindrance and consequently gives more stable complexes. Amongst the other three ligands with the thiosemicarbazone part at position 2 of the ring: FTSC, M5FTSC and FATSC, the stability of the complexes is higher in the case of M5FTSC than in the case of the other two ligands. This is certainly due to the donor effect of the methyl group, which increases the electron density at the coordinating atoms. Finally the only difference in the structures of the ligands FTSC and FATSC is the length of the side chain. Since stability constants with these ligands are of the same order, it is postulated that the length of the thiosemicarbazone side chain has no appreciable effect on the stability of the complexes.

Comparison with Semicarbazone Complexes

The reported results of the semicarbazone complexes with copper(II) [16] can be compared with those obtained for the corresponding thiosemicarbazone complexes in this study. The log β values in case of FTSC (1.95), FSC (2.02), and M5FTSC (3.82), M5FSC (3.84) are essentially the same. This is explained by the simple fact, that oxygen and sulfur are members of the same group of elements in the periodic table and have, therefore, similar physicochemical properties. However, there is significant difference in the values with FATSC (1.64) and FASC (4.52). This exception is most probably due to different coordination sites.

Cobalt(II) Complexes in the Solid State

The thiosemicarbazone complexes have shown important biological activities and consequently, for a better understanding of the chemistry of these complexes, studies in the solid state were carried out, as well. Some of the results have already been reported.[20–22] In this study the results of the cobalt(II) complexes are presented and a comparison is made with the results obtained in solution. It must be mentioned that in contrast to the corresponding Ni(II) and Cu(II) complexes, no structure determination by X-ray diffraction on single crystals of the cobalt(II) complexes could be performed. The four cobalt complexes synthesized were studied in the solid state by spectroscopic methods.

IR Spectra

Analysis and a comparative study of the IR spectra of the ligands and those of their complexes with cobalt(II) show that the ligands undergo deprotonation at the nitrogen atom of the hydrazine moiety N(2), as shown below:

$$\mathrm{C = N(3) - N(2)H - C(1)(= S) - N(1)H_2 \rightarrow C = N(3) - N(2) = C(1)(-S) - N(1)H_2.} \tag{3}$$

Following X-ray diffraction results with metals other than cobalt, a numbering scheme was devised to identify readily the different atoms. These numbers are placed within brackets and the detailed schemas were given in our earlier publications.20–22

It is further revealed that the coordination of the metal occurs through the nitrogen atom of the imine moiety and the sulfur atom. In case of sulfur, this is possible due to the delocalisation of the double bond and the resulting increase of electron density on the sulfur atom.

Indeed, the bands which appear at 1609, 1600, and 1597 $\mathrm{cm^{-1}}$ in the IR spectra of FTSC, M5FTSC, and FATSC, respectively, corresponding to the vibration ν(C=N), are shifted to lower wave numbers in the case of the complexes. This shift is on the average about 43 $\mathrm{cm^{-1}}$ for complexes with FTSC and with M5FTSC, and about 15 $\mathrm{cm^{-1}}$ for complexes with FATSC. These shifts indicate the participation of the nitrogen atom of the imine moiety, N(3) in the numbering scheme, in the coordination to the metal.23–26

The intense band that appears around 3150 cm^{-1} in the spectra of the ligands, which is attributed to the NH vibration of the hydrazine moiety N(2)H, disappears in the spectra of all complexes. This shows the loss of this hydrogen atom on complexation. The presence of a well-resolved band around 1625 cm^{-1} in the spectra of these compounds confirms the deprotonation. The band corresponds to the formation of the double bond after the loss of hydrogen in the thiosemicarbazone moiety between the carbon atom numbered 1, C(1) and the nitrogen atom numbered 2, N(2), as shown in the scheme above.

Regarding the two characteristic ν(C=S) vibration bands in the spectra of the ligands, it is observed that the band appearing at 1280 cm^{-1} disappears in the spectra of all complexes, whereas the band at around 840 cm^{-1} undergoes a shift to lower wave numbers. These two phenomena are indicative of the participation of the sulfur atom in the coordination to the metal in these complexes.[23–26]

In the literature, the bands appearing between 160 and 300 cm^{-1} are assigned to the vibration of the Co–X bond, where X = Cl or Br.[23,26–31] In this study, the frequencies ν(Co-X) are in accordance with the reported data and appear between 220 and 300 cm^{-1}.

Electronic Spectra

The calculation of the parameters 10 Dq, B and of the theoretical positions of the bands in the electronic spectra, were made with the program Quick Basic, which is based on König's relations.[32] The cobalt(II) complexes have three bands, *viz.*, ν_1, ν_2, ν_3, which are presented in Table III. Table IV gives the mean values of the calculated 10 Dq and B.

The values of 10 Dq are quite similar in all the hexacoordinated complexes as well as in the two cobalt salts. These values are in accord with those found for the corresponding complexes of semicarbazones of $[CoX_2(L)_2]$ type, which have an octahedral geometry.[31,33]

TABLE III Electronic Spectra Data of Cobalt(II) Complexes in Ethanol Solution

Complex	ν_1 (cm^{-1})	ν2 (cm^{-1})	ν3 (cm^{-1})
$[CoCl_2(FTSC)_2]$	7350	15,112	17,822
$[CoBr_2(FTSC)_2]$	7360	15,604	17,620
$[CoCl_2(M5FTSC)]$	4108	6820	14,213
$[CoCl_2(FATSC)_2]$	7548	15,625	17,953

TABLE IV Mean Values of 10 Dq and of B for the Cobalt(II) Complexes and Their Salts

Salt/Complex	10 Dq (cm^{-1})	B (cm^{-1})
$CoCl_2 \cdot 6H_2O$	8030	710
$CoBr_2 \cdot 6H_2O$	8200	680
$[CoCl_2(FTSC)_2]$	7990	760
$[CoBr_2(FTSC)_2]$	8290	750
$[CoCl_2(M5FTSC)]$	4110	590
$[CoCl_2(FATSC)_2]$	8265	755

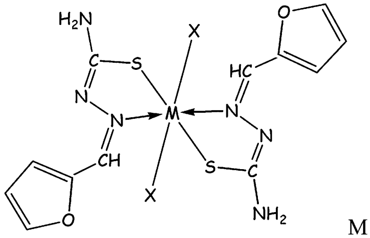
Ferguson et al.[34] showed that the existence of an asymmetric band in the UV-VIS spectrum centred at around 17 000 cm^{-1} is typical of octahedral complexes of cobalt(II), and that a shoulder band situated towards the side of higher energies corresponds to forbidden spin transitions. The complexes $[CoCl_2(FTSC)_2]$, $[CoBr_2(FTSC)_2]$ and $[CoCl_2(FATSC)_2]$ present this type of bands between 17,600 and 18,000 cm^{-1}. With regards to Racah's B parameter for the same three complexes, the calculated values are close to those of the corresponding semicarbazones as reported by Ibrahim et al., [31,33] and they are also comparable to the values of other cobalt(II) complexes derived from thiosemicarbazones.[29,35]

On the other hand, the tetracoordinated structure of the $[CoCl_2(M5FTSC)]$ complex and its blue color, indicate tetrahedral geometry for this compound.[36] The values of 10 Dq and of the B parameter confirm this environment. This explains the unique value of this complex, different from the others in Table IV. The results of these calculations (Table IV), are comparable to those of other complexes of tetrahedral geometry.[15,29] Consequently, it can be assumed, that$[CoCl_2(M5FTSC)]$ also adopts this geometry.

Regarding the ionic character of the complexes, one of the criteria proposed by Lever [36] is the value of the ratio of ν_1 and ν_2, which is generally around 2. For non-ionic complexes this ratio is about 2.1 and according to Lever it reaches 2.2 for compounds having a high ionic character. In the present study, this ratio varies between 2.06 and 2.12. The cobalt(II) thiosemicarbazone complexes are therefore non-ionic or feebly ionic in character and this is confirmed by measurements of their molar conductivity.

Structures

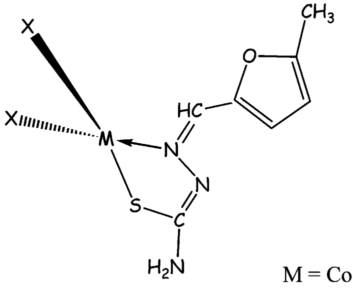
The coordinating atoms in the complexes are identified by infrared studies. The results of structural studies based on X-ray diffraction of Ni(II)



M = Co(II), X = Cl, Br

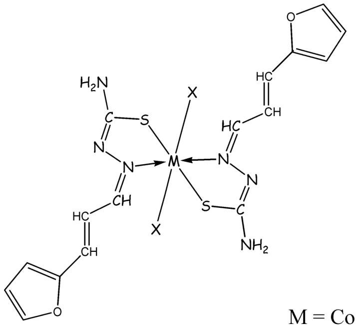
FIGURE 6 Proposed structure for [$CoCl_2(FTSC)_2$] and [$CoBr_2(FTSC)_2$].

and Cu(II) complexes with the same ligands[20,22] show, that the coordinating atoms are in trans configuration, with respect to the C(1)=N(2) bond. By analogy, it would be the same in the case of these cobalt(II) complexes. In the process of complex formation, all ligands lose the hydrogen atom of the NH group of the hydrazine moiety. The study of the electronic spectra in ethanol helps in elucidating the geometry of each complex. Taking into consideration all these structural aspects, the structures of the complexes proposed are given in Figures 6–8. It may be emphasized here that these structures are proposed after considering the spectroscopic data only, which in itself is not sufficient and should be complemented with crystallographic investigations. However, as pointed out earlier, single crystals of the cobalt(II) complexes could not be obtained and therefore, a profound crystallographic study could not be undertaken to confirm these propositions. Nevertheless, these structural propositions are supported by analogy to the X-ray diffraction results of Ni(II) and Cu(II) complexes with identical ligands. It is hoped that knowledge of the structures of these complexes will help in a better understanding of their biological activities.



M = Co(II), X = Cl

FIGURE 7 Proposed structure for [$CoCl_2(M5FTSC)$].



M = Co(II), X = Cl

FIGURE 8 Proposed structure for [$CoCl_2(FATSC)_2$].

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