

## TRANSITION METAL COMPLEXES WITH A NEW THIOAMIDE OF THE DIBENZOFURAN SERIES

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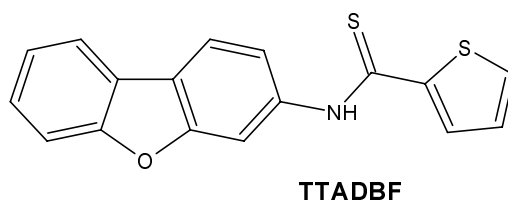
### Abstract

The paper reports the conclusions about the structure of some new complexes of Fe(II), Co(II), Ni(II) and Cu(II), with a new thioamide, 3-(2'-thiothenoylamino)dibenzofuran (TTADBF). These were obtained by elemental analysis, UV-VIS, IR and EPR spectral analysis, conductivity and magnetic susceptibility measurements.

### Introduction

The coordination chemistry of sulphur donor ligands is an active area of research. A great deal of attention in this area has been focused on the complexes formed by transition metals with thioamides, that act as bidentate ligands using both sulphur and nitrogen as donor atoms.<sup>1-5</sup>

We here report the preparation and characterization of the complex compounds of Fe(II), Co(II), Ni(II) and Cu(II) with a new thioamide, 3-(2'-thiothenoylamino)dibenzofuran (TTADBF).<sup>6</sup>



### Experimental

All the chemicals we used were of analytical grade: FeCl<sub>2</sub>·2H<sub>2</sub>O (Fluka A.G. p.a.), CoCl<sub>2</sub>·6H<sub>2</sub>O (Merck p.a.), NiCl<sub>2</sub>·6H<sub>2</sub>O (Merck p.a.), CuCl<sub>2</sub>·2H<sub>2</sub>O (Merck. p.a.), TTADBF (double recrystallized).

The IR spectra were recorded on a Perkin Elmer F.T.-1600 Hewlett Packard instrument in anhydrous KBr pellets. The electronic spectra were obtained in 10<sup>-3</sup> M acetone solutions, with an Unicam UV 2-300 spectrophotometer, while the EPR spectra were registered in powder form at room temperature by means of an Art-5-Ifin Bucharest

spectrometer, that operates in X band, the modulation of magnetic field being 100 kHz, using  $\text{Mn}^{2+}$  as an internal standard. The molar conductivities were determined by using an OK-102(Hungary) conductivity meter at 22 °C. The magnetic susceptibility measurements were performed on a Gouy balance at room temperature.

All the complexes were prepared using the reported method.<sup>1</sup>

General procedure: A 0.02 M thioamide (TTADBF) in ethanol solution was added (dropwise with continuous stirring) to an ethanolic or aqueous solution of the metal dichloride (0.02 M), in a 1:1 molar ratio. It was gently stirred for one hour, and then left at room temperature for three hours. The resulting metal complexes were washed with ethanol and diethyl ether and then dried under reduced pressure.

### Results and discussion

The complexes obtained were microcrystalline colored powders, whose melting points are higher than of the pure thioamide. They are stable at room temperature and their solubilities in common inorganic and organic solvents are medium.

The elemental analysis of these complexes led to the formula:  $[\text{FeLCl}_2(\text{H}_2\text{O})_2]$ ,  $[\text{CoLCl}_2]$ ,  $[\text{NiLCl}_2]$ ,  $[\text{CuLCl}_2]$ , where  $\text{L}=\text{TTADBF}$ .

Molar electric conductivities showed that all the complexes are non-electrolytes with  $\lambda = 0.98 - 1.45 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in DMF ( $10^{-3} \text{M}$ ) solutions at room temperature.

We have recorded IR spectra both for pure thioamide and for the corresponding complexes in the  $600\text{-}1650 \text{cm}^{-1}$  and  $3000\text{-}3500 \text{cm}^{-1}$  ranges, where characteristic bands of ligand appear and the changes due to the complex formation can be seen. In literature<sup>7</sup> it is stated that thioamide forms a complex vibrational group. A comparative interpretation of the infrared spectral data suggests that 3-(2'-thiothenoylamino)dibenzofuran (TTADBF) act as a bidentate ligand in the investigated complex compounds, using both sulphur and nitrogen as donor atoms.

The bands in the  $3030\text{-}3150 \text{cm}^{-1}$  interval, characteristic for  $\nu_{\text{NH}_2}$ , appear in complexes at lower frequencies than in the respective thioamide. The changes suggest that the  $\text{NH}_2$  group participates to the coordination. The characteristic band of the thioamide at  $1450 \text{cm}^{-1}$  ( $\nu_{\text{C-N}}$ ,  $\nu_{\text{C-S}}$  coupling) is displaced towards higher frequencies with

a lower intensity. These changes may be explained by electronic migrations corresponding to the thioamidic group. Very important for the discussion of the bond character is the band at  $1220\text{ cm}^{-1}$ , in which the frequency of the C=S bond has an important contribution. In complexes, this band almost disappears. This is a proof that the sulphur atom participates as a donor atom in the complex formation. The band in the  $630\text{--}680\text{ cm}^{-1}$  interval is also significant. Generally assigned to the C=S vibration, it appears with a much lower intensity in the complexes, thus confirming that the sulphur atom participates as a donor atom to the coordination of the thioamide to the transition metal ion. A band due to coordinated water appears in the spectrum of the Fe(II) complex around  $890\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$ .

The magnetic moment value of  $[\text{Fe}(\text{TTADBF})\text{Cl}_2(\text{H}_2\text{O})_2]$  is 4.88 B.M., which indicates that the complex is spin-free and it has octahedral geometry. The electronic spectrum shows a broad absorption band at  $16700\text{ cm}^{-1}$ , which may be assigned to the  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition.

For  $[\text{Co}(\text{TTADBF})\text{Cl}_2]$ , the magnetic moment value is 2.18 B.M. and its electronic spectrum displays two bands, at  $16850\text{ cm}^{-1}$  and  $21600\text{ cm}^{-1}$ , which may be assigned to the  ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{2g}$  transition and to the  ${}^2\text{A}_{1g} \rightarrow {}^2\text{E}_g$  transition, respectively, in a square-planar configuration around the transition metal ion.<sup>8</sup>

As far as  $[\text{Ni}(\text{TTADBF})\text{Cl}_2]$  is concerned, it appears to be diamagnetic. Its electronic spectrum exhibits four bands, at  $21200\text{ cm}^{-1}$ ,  $30300\text{ cm}^{-1}$ ,  $33500\text{ cm}^{-1}$  and  $38300\text{ cm}^{-1}$ . The first band and the second one are of low intensity, being purely d-d transitions, assigned to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  transition and to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$  transition, respectively. The third band is developed by a strong charge transfer transition, while the fourth one is due to interligand interactions ( $\pi \rightarrow \pi^*$ ). These results also suggest a square-planar configuration around the transition metal ion.<sup>9</sup>

The room temperature magnetic moment value is 1.90 B.M. for  $[\text{Cu}(\text{TTADBF})\text{Cl}_2]$ , indicating the presence of one free electron. The electronic spectrum displays three spectral bands, at  $14500\text{ cm}^{-1}$ ,  $20600\text{ cm}^{-1}$  and  $26500\text{ cm}^{-1}$ . The first band corresponds to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transition and the second one to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  transition, the third band being assigned to a charge transfer transition. All these observations lead to

the conclusion that the geometry is also square planar. The compound  $[\text{Cu}(\text{TTADBF})\text{Cl}_2]$  present a very intense EPR spectrum, with anisotropic parameters  $g_{\parallel} = 2.2404$  and  $g_{\perp} = 2.0704$ , in agreement with the  $d^9$  electronic configuration for Cu(II) in this square-planar complex compound (Figure 1).

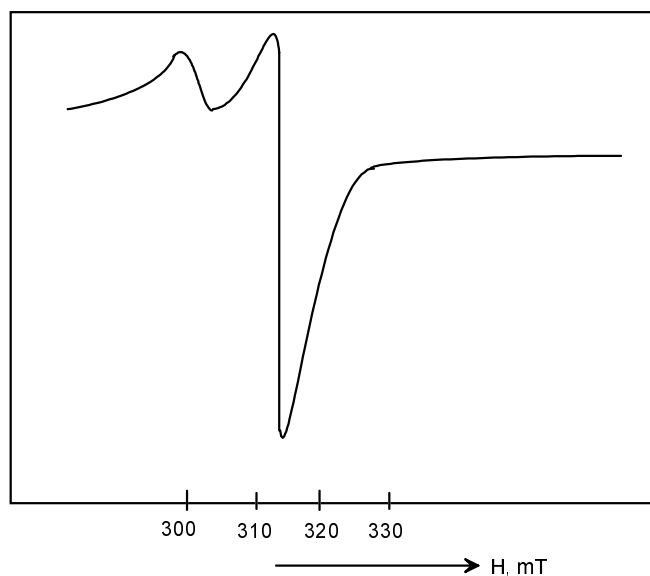
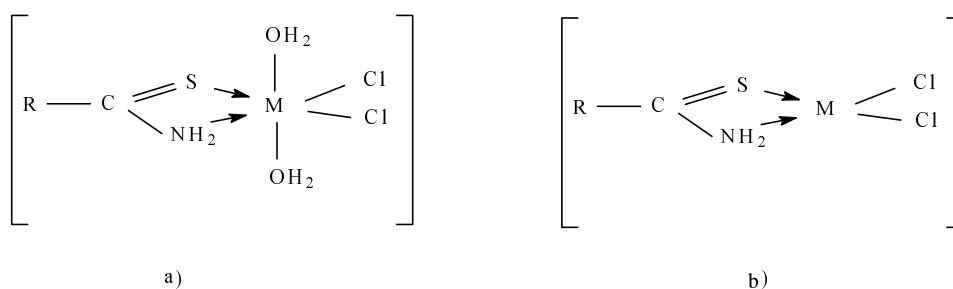


Figure 1. EPR spectrum of  $[\text{CuLCl}_2]$

### Conclusions

On the basis of all these results, obtained by elemental analysis, UV-VIS, IR, EPR spectral analysis, conductivity and magnetic susceptibility measurements, the following structure are proposed for the complex compounds:



a)  $[\text{MLCl}_2(\text{H}_2\text{O})_2]$ , where  $\text{M}=\text{Fe}(\text{II})$  and  $\text{L}=\text{TTADBF}$

b)  $[\text{MLCl}_2]$ , where  $\text{M}=\text{Co}(\text{II})$   $\text{Ni}(\text{II})$   $\text{Cu}(\text{II})$  and  $\text{L}=\text{TTADBF}$

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### Povzetek

Določili smo strukture kompleksov Fe(II), Co(II), Ni(II) in Cu(II) z novim tioamidom 3-(2'-tietenoilamino)dibenzofuranom (TTADBF). Strukture smo potrdili z elementno analizo, UV/Vis, IR in EPR spektroskopijo ter z merjenjem prevodnosti in magnetne susceptibilnosti.