

# Synthesis, characterization and crystal structure of Ni(II) and Cu(II) complexes with *N*-furoyl-*N',N'*-diethylthiourea.

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## Introduction

*N*-acyl-*N',N'*-disubstituted thioureas are well known as bidentate chelating ligands with S and O as donor atoms. This kind of ligand form stable metal complexes with heavy, transition and noble metal ions, given rise to highly colored compounds<sup>1</sup>. During complex formation, the ligand is deprotonated, which results in a neutral complex. With these metal ions, *N*-acylthioureas form very stable complexes (*cis* conformation preferred) with a six-membered ring chelate structure, the complex stoichiometry generally being 1:2 (M:L, with M = metal ion and L = ligand). The complexes were prepared by a procedure previously reported<sup>2</sup>, and characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. Its structures were determined by single-crystal X-ray diffraction.

## Results and Discussion

Regarding IR spectra, both metal complexes display strong bands in the region of 1500-1100 cm<sup>-1</sup>. No absorption was detected in the range between 1700 and 1600 cm<sup>-1</sup>, where the uncoordinated ligands are supposed to exhibit C=O stretching vibrations. This absorption shifts to lower frequencies is a clear proof of complex formation with a large degree of electron delocalization within the chelate rings<sup>3</sup>.

In the <sup>1</sup>H NMR spectra, the absence of the singlet corresponding to the NH proton of the acylthioureido group in the range between 8.80-8.32 ppm, corroborates the coordination of the ligand to the metal through these groups. As far as <sup>13</sup>C NMR spectra is concerned, the signals around 180.0 (C=S) and 150.0 ppm (C=O), typical of the free ligand<sup>2</sup>, disappeared. Two new peaks, assigned to quaternaries carbon atoms, were found about 170.0 (CS) and 160.0 ppm (CO) instead, what is in accordance with the proposed structures.

In the molecular structure of complexes, two furoyllthiourea molecules adopt a *cis* conformation, bounded to the central ion by two S and two O atoms. The coordination geometry of both complexes is a distorted square-plane as reflected

by O-M-S (M=Ni, Cu) angles<sup>3</sup>. The angles are significantly shorter for [CuL<sub>2</sub>] complex. This indicates a more accented distortion for the copper complex from square planar towards tetrahedral geometry. The bond distances of the C-S and C-O in the chelate ring are longer than average C=S and C=O double bond distances of thiourea derivatives<sup>4</sup>. These results can be explained by the existence of delocalization in the chelate rings, which is also supported by IR and NMR data. In the [NiL<sub>2</sub>] complex, all the atoms of one ethylamine group are disordered over two sites, which is a common feature of Ni(II) complexes with *N*-acyl-*N',N'*-dialkylthioureas<sup>5</sup>.

\* Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 689279 for the Ni(II) complex and CCDC No. 689280 for the Cu(II) complex.

## Conclusions

Ni(II) and Cu(II) complexes with *N*-furoyl-*N',N'*-diethylthiourea were synthesized. The coordination geometry of both complexes is a distorted square-plane, but a more accented distortion for the copper complex from square planar towards tetrahedral geometry, and their molecular structures show delocalization in the chelate rings, which is also supported by IR and NMR spectra.

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