

## Synthesis and Spectral Studies of Zn(II), Cd(II) and Hg(II) Complexes with 1*H*-Pyrrole-2-carbothioic Acid Dibenzofuran-3-ylamide

LIANA-SIMONA SBIRNA, AURORA REISS\*, ANISOARA PREDA† and FLORINA CIOLAN  
University of Craiova, Faculty of Chemistry, 107 I Calea Bucuresti, Craiova, Romania  
E-mail: reissaurora@yahoo.com

The aim of this paper is to identify 1*H*-pyrrole-2-carbothioic acid dibenzofuran-3-ylamide (PCADY) is coordinated to Zn(II), Cd(II) and Hg(II), by finding a quantum-mechanical explanation for the spectral data. The study proves that the heteroatoms from the thioamide group are the ones involved in coordination. The result has been verified and confirmed by IR and NMR spectral analyses.

**Key Words:** Complex compounds, Bidentate ligand, Quantum-mechanical explanation.

### INTRODUCTION

Recently, various complexes with bidentate ligands were synthesized and characterized<sup>1-5</sup>. Some new complex compounds with heterocyclic ligands of the dibenzofuran series have been synthesized and investigated in some of our previous work<sup>6</sup>. This paper reports about the way in which the ligand 1*H*-pyrrole-2-carbothioic acid dibenzofuran-3-ylamide (PCADY) (Fig. 1) is coordinated to Zn(II), Cd(II) and Hg(II).

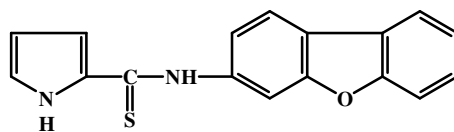


Fig. 1. 1*H*-pyrrole-2-carbothioic acid dibenzofuran-3-ylamide (PCADY)

### EXPERIMENTAL

All the chemicals used were of analytical grade. Elemental analysis was performed on a Perkin-Elmer 2380 (USA) analyzer. Metal contents were measured by standard methods<sup>7</sup>. The molar conductivities were determined by using an OK-102 (Hungary) conductivity-meter at 25 °C. The magnetic susceptibility measurements were performed on a Gouy balance (UK), at 25 °C as well. The electronic spectra

†National R&D Institute for Cryogenics and Isotopic Technologies-ICIT Rm. Valcea, Romania.

were performed in  $10^{-3}$  M DMSO solutions, with an Ocean Optics (UK) spectrophotometer. The IR spectra were recorded on a Perkin-Elmer FT-IR 1600 Hewlett Packard (USA) instrument, using anhydrous KBr pellets. NMR data were obtained on a Varian Gemini 300 BB (USA)-300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ , using DMSO as a solvent.

**Synthesis of the complexes<sup>8</sup>:** A 0.01 M thioamide (PCADY) in ethanol solution was added to an aqueous solution of the respective metal dichloride (0.01 M), in a 1:1 molar ratio, under continuous stirring for 2 h and then left at room temperature (25 °C) for 6 h. The resulting metal complexes have been filtered on a G<sub>4</sub> porosity glass filter, washed with 96 % ethanol and diethyl ether and then dried under vacuum.

## RESULTS AND DISCUSSION

The complex compounds were obtained as microcrystalline yellow powders, whose melting points are higher than the one of pure thioamide, stable at room temperature. The elemental analysis proved that these complexes exhibit the general formula  $[\text{MLCl}_2]$ , where M = Zn(II), Cd(II) or Hg(II), L = PCADY, which is therefore proved to act as a bidentate ligand. All the Zn(II), Cd(II) or Hg(II) complexes are diamagnetic ( $\mu_{\text{eff}} = 0$  BM). The molar electric conductivities showed that the complexes are non-electrolytes in  $10^{-3}$  M DMSO solutions at room temperature (Table-1). The complex compounds have been characterized by UV-Vis, IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral analyses.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF LIGAND AND ITS COMPLEXES

Compound	Colour (Yield, %)	Elemental analysis (%): Calcd. (Found)				$\lambda_{\text{M}}^*$ ( $\Omega^{-1}$ $\text{cm}^3 \text{mol}^{-1}$ )
		C	H	N	M	
[ZnLCl <sub>2</sub> ]	Greenish yellow (80)	47.29 (47.67)	3.07 (2.80)	6.85 (6.53)	14.97 (15.21)	1.42
[CdLCl <sub>2</sub> ]	Pale yellow (85)	43.12 (42.98)	3.07 (2.52)	6.12 (5.89)	23.02 (23.31)	1.23
[Hg LCl <sub>2</sub> ]	Deep yellow (75)	35.97 (36.25)	3.07 (2.13)	5.07 (4.97)	35.32 (35.62)	1.31

\*In  $10^{-3}$  M DMSO solutions at room temperature.

The electronic spectra of these complexes contain only one absorption band, appearing at 405, 420 and 440 nm, for the Zn(II), Cd(II) and Hg(II) complexes, respectively. These are expected to be due to charge-transfer (CT) transitions, taking into account the fact that the electronic configuration of each central metal ion is  $d^{10}$ , so there are no predicted  $d-d$  bands.

In order to explain this situation in quantum mechanics terms, the geometry has been optimized for the ligand by using the computational program HYPERCHEM 8.0, in the MM<sup>+</sup> approach (the cartesian coordinates of all the atoms were used into the ICONC program (an improved version of ICON<sup>9</sup>), the parameters being replaced by the ones proposed by Underwood *et al.*<sup>10</sup>.

The ligand PCADY molecule contains four 'heteroatoms' (two nitrogen atoms, an oxygen atom and a sulfur one), so that the coordination manner is not obvious. The structure of the  $[M(II)LCl_2]$  complex compounds was also represented on the computer, for each of the possible coordination manners and EHT calculation has been performed each time, in order to decide which of these is real (the paper only presents the quantum-mechanical study corresponding to the coordination through S and N from the thioamide group, which has proved to be correct).

Thus, the energies for the most important molecular orbitals were calculated and their occupation with electrons were given. Moreover, each molecular orbital was located on the complex compound, by means of the mixing coefficients, that represent the extent in which the different atoms participate to the molecular orbital creation. In order to perform the quantum-molecular interpretation of the absorption maxima occurring in the electronic spectrum, one must only consider the molecular wavefunctions that might be involved in the coordination - *i.e.* HOMO, LUMO and a few others, either occupied molecular orbitals with high energies or unoccupied molecular orbitals with low energies and study the possible transitions between them.

Keeping the most important coefficients only,  $\psi_{51}$  (HOMO) and  $\psi_{50}$  (LUMO) may be written for the first complex (analogous expressions for the other two complexes):

$\psi_{51} \approx 0.8202 \text{ Zn } (d_{xy})$  – it is essentially a metal orbital;

$\psi_{50} \approx 0.4054 \text{ S } (p_y) + 0.4123 \text{ S } (p_z)$  – it is actually localized on the sulfur atom.

The charge transfer band is therefore assigned to the transition  $\psi_{51} \rightarrow \psi_{50}$ , which satisfies both the the zonal criteria and energetic criteria, the separation between these two molecular levels being 3.05 eV ( $24601 \text{ cm}^{-1}$ ) for  $[ZnLCl_2]$  - compared to  $24691 \text{ cm}^{-1}$  (experimental), 2.93 eV ( $23633 \text{ cm}^{-1}$ ) for  $[CdLCl_2]$  - compared to  $23810 \text{ cm}^{-1}$  (experimental) and 2.82 eV ( $22746 \text{ cm}^{-1}$ ) for  $[HgLCl_2]$  - compared to  $22727 \text{ cm}^{-1}$  (experimental).

One may observe that the sulfur atom from the thioamide group of PCADY is obviously involved in the coordination. Unfortunately, there is no possibility to decide, on this basis, which is the nitrogen atom also involved in chemical bonding.

It is stated in the literature that thioamide forms a complex vibrational group<sup>11</sup>. A comparative interpretation of the IR spectral data (shown below) suggests that PCADY acts as a bidentate ligand in the investigated complex compounds, using both sulfur and nitrogen as donor atoms (Table-2).

The bands that occur at  $3060$  and  $1600 \text{ cm}^{-1}$  in the IR spectrum of the ligand appear in complexes at lower frequencies and more flattened. These changes indicate the coordination of the nitrogen from the thioamide group with the metal ions. The position of the thioamide bands I and III in the spectrum of the ligand are not appreciably shifted in the spectra of the complexes, while the position of thioamide bands II and IV suffer a considerable shift towards higher and respectively lower wavenumbers in the complexes. These changes confirmed the previous conclusion that the sulphur participates in bonding to the metal ion. Each metal complex is also characterized by the occurrence of a new band of medium intensity, due to the M-N stretch.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF LIGAND AND ITS COMPLEXES

Compound	Colour (Yield, %)	Elemental analysis (%): Calcd. (Found)				$\lambda_M^*$ ( $\Omega^{-1}$ $\text{cm}^2 \text{mol}^{-1}$ )
		C	H	N	M	
[ZnLCl <sub>2</sub> ]	Greenish yellow (80)	47.29 (47.67)	3.07 (2.80)	6.85 (6.53)	14.97 (15.21)	1.42
[CdLCl <sub>2</sub> ]	Pale yellow (85)	43.12 (42.98)	3.07 (2.52)	6.12 (5.89)	23.02 (23.31)	1.23
[Hg LCl <sub>2</sub> ]	Deep yellow (75)	35.97 (36.25)	3.07 (2.13)	5.07 (4.97)	35.32 (35.62)	1.31

\*In  $10^{-3}$  M DMSO solutions at room temperature.

<sup>13</sup>C NMR spectrum of the free organic ligand shows a signal at  $\delta = 197.5$  ppm due to the carbon atom from the C=S group. In the spectra of its complex compounds with Zn(II), Cd(II) and Hg(II) the signal appears at lower values (192.1, 193.8 and 194.5 ppm, respectively), proving-once again-the involvement of the sulfur atom in the coordination.

The <sup>1</sup>H NMR spectrum shows two signals at  $\delta = 2.9$  ppm and  $\delta = 6.8$  ppm, corresponding to the two protons in the -NH groups. In the spectra of the complex compounds, the signal produced by the hydrogen attached to the nitrogen in the thioamide group which appears at 0.6 ppm shifted towards lower values at  $\delta = 2.3$  ppm, while the other one (from the pyrrole heterocycle) remains unshifted. Therefore, this is the nitrogen atom involved in covalent-coordinative bond.

In conclusion, PCADY acts as a bidentate ligand, coordinating to Zn(II), Cd(II) or Hg(II) by means of the sulfur and nitrogen atoms in the thioamide group.

## REFERENCES

1. Y. Matsunaga, K. Fujisawa, Y. Miyashita and K. Okamoto, *Transition Met. Chem.*, **31**, 210 (2006).
2. V.V. Glodjovic, F.W. Heinemann and S. Trifunovic, *J. Chem. Crystallogr.*, **38**, 309 (2008).
3. Z. Yan, Y. Tang, W.S. Liu, H.X. Cui and M.Y. Tan, *J. Fluorescence*, **18**, 123 (2008).
4. D. Visinescu, G.I. Pascu, M. Andruh, J. Magull and H.W. Roesky, *Inorg. Chim. Acta*, **340**, 201 (2002).
5. G. Marinescu, M. Andruh, R. Lescouëzec and M.C. Muñoz, *New J. Chem.*, **24**, 527 (2000).
6. L.S. Sbirna, S. Sbirna, C.I. Lepadatu, V. Muresan and N. Muresan, *J. Indian Chem. Soc.*, **82**, 1 (2005); L.S. Sbirna, S. Sbirna, C.I. Lepadatu and V. Muresan, *J. Indian Chem. Soc.*, **81**, 150 (2004); L.S. Sbirna, S. Sbirna and C.I. Lepadatu, *Rev. Roum. Chim.*, **49**, 1015 (2004); V. Muresan, L.S. Sbirna, S. Sbirna, C.I. Lepadatu and N. Muresan, *Acta Chim. Slov.*, **48**, 439 (2001); A. Kriza, A. Reiss, V. Muresan and S. Florea, *J. Indian Chem. Soc.*, **72**, 406 (1999); V. Muresan, A. Reiss, L.S. Sbirna, N. Muresan and S. Florea, *Polish J. Chem.*, **72**, 2034 (1998).
7. C. Gh. Macarovici, *Analiza Chimica Cantitativa Anorganica*, Ed. Academiei R.S.R. Bucuresti, p. 22 (1979).
8. S. Florea, *Rev. Roum. Chim.*, **39**, 1138 (1994).
9. G. Calzaferri and M. Brände, *QCPE Bull.*, **12**, 73 (1992).
10. D.J. Underwood, R. Hoffmann, K. Tatsumi and Y. Yamamoto, *J. Am. Chem. Soc.*, **107**, 5980 (1985).
11. B. Hutchinson, D. Eversdyk and S. Olbrich, *Spectrochim. Acta*, **30A**, 1605 (1974).