

COMPLEXES WITH AMIDES. Part 3. SYNTHESIS, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF A Cu(II) COMPLEX WITH 2-iodoanilide-3- CHLOROBENZO[b]THIOPHENE-2-CARBOXYLIC ACID

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abstract: A new complex of Cu(II) with 2-iodoanilide-3-chlorobenzo[b]thiophene-2-carboxylic acid (L) $[\text{CuL}(\text{CH}_3\text{COO})_2]$ (**2**) has been synthesised and characterised. The bonding and stereochemistry of the complex have been characterised by IR and electronic spectroscopy. The results concerning the thermal behaviour of the complex are reported. The amide ligand behaves as unidentate and coordinates through the amidic oxygen atom while the acetate acts as chelate. The copper (II) ions adopt a square-pyramidal stereochemistry.

Introduction

Copper as a component of numerous enzymes is involved in energy production, is necessary for neurotransmission in the brain and is active in cell protection from the damage generated by the free radicals. The copper deficiency is associated with the anaemia and bone demineralisation [2]. For understanding the biological role of this biometal, many current studies are concerned on the complexes with amides. We have prepared and characterised complexes of this type with polyfunctional amides [1,3].

Moreover many copper complexes, including amide complexes, are reported to be anti-inflammatory [4-6], analgesic [7] or antitumor agents [8]. Also the copper species exhibit numerous biological activities as antiviral [9], antifungal [10,11] and antibacterial [12-14] etc. Having in view that the benzothiophene derivatives are the components of some dyes and drugs used for the osteoporosis and inflammatory diseases [15] we report herein the synthesis and characterisation of new complex of copper (II) with 2-iodoanilide-3-chlorobenzo[b]thiophene-2-carboxylic acid (**1**). The complex was formulated as mononuclear specie according to analytical and spectral data as well as thermal behavior.

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Experimental part

IR spectra were recorded in KBr pellets with an UR 20 Zeiss Jena instrument, *electronic spectra* were obtained by diffuse reflectance technique, using MgO as standard, with a VSU-2P Zeiss Jena instrument. *Thermal decomposition* was studied with a MOM (Budapest) derivatograph, type Paulik-Paulik-Erdey, in a static air atmosphere with a sample weight of 38.6 mg over the temperature range 20-800°C at a heating rate of 10°C min⁻¹.

The ligand (**1**) was prepared as reported in literature and were recrystallised from EtOH prior to use. The melting point (165.5-166) and ¹H NMR (CDCl₃) data (δ: 8.38 (1H), 7.35-7.85 (m, 7H), 6.90(1H)) agree with literature data [16]. Copper (II) acetate monohydrate (Merck) was of analytical grade. The chemical analyses were performed by usual micromethods.

The complexes were prepared by adding the ligand (2 mmoles) dissolved in minimal quantities of ethanol into the copper (II) acetate (4 mmoles) solution in 50 mL ethanol. Reaction mixture was heated and stirred for 4 hours. After concentration until the solution volume was reduced to about 15 mL, the resulting precipitate was filtered off, washed several times with a small volume of ethanol and air dried.

2-iodoanilide-3-chlorobenzo[b]thiophene-2-carboxylic acid (L, **1**): IR data (cm⁻¹, KBr): 3200-3600 m (ν_{NH}), 1670 s (ν_{C=O}, AI), 1530 s (δ_{NH} + δ_{C-N}, AII), 1500, 1450, 1320 s (δ_{C-N} + δ_{NH}, AIII), 780 m (γ_{CH}).

Compound [CuL(CH₃COO)₂] (**2**): Analysis found: Cu, 10.62; N, 2.60; S, 5.45 %; requires for CuC₁₉H₁₅NCIIIO₅S: Cu, 10.67; N, 2.35; S, 5.38 %; IR data (cm⁻¹, KBr): 3336m, 3298m (ν_{NH}), 1655 m (ν_{C=O}, A I), 1636 m (ν_{COO as}), 1526 vs (δ_{NH} + δ_{C-N}, AII), 1433 s (ν_{COO s}), 1294m (δ_{C-N} + δ_{NH}, AIII), 750 m (ν_{CH}), 422 w (ν_{Cu-O}).

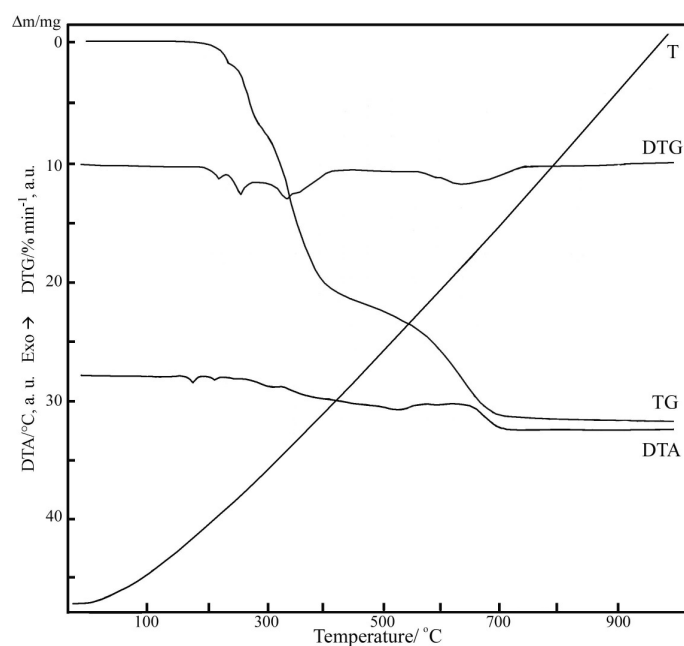
Results and discussion

In this paper we report the preparation and physico-chemical characterization of a new complex (**2**) of Cu(II) with N-(2-chloro-pyrid-3-yl)-4-chlorobenzamide (L, **1**). The molar ratio M:ligand was 1:1 and the isolated complex has the formula [CuL(CH₃COO)₂] as indicate the chemical analyses and the thermogramm (figure 1).

Thermal behaviour of complexes was investigated by thermal gravimetric analysis and the final residues were examined by X-ray diffraction on powder. The majority of intermediate products formed during thermolysis were not possible to identify because the steps were not distinct. By thermogravimetric analysis it was proved that (**2**) it is anhydrous specie and the oxidative degradation of this compound was made in four steps in range 180 - 770 °C with CuO as final residue. The first endothermic step corresponds to the ligand decarbonilation. The second one consists in transformation of acetate in carbonate according to the mass loss (table 1). In the next two steps occur the oxidative degradation of the residual ligand and the carbonate decomposition.

Table 1. Thermal behaviour data (in static air atmosphere) for the complex

Step	Thermal effect	Temperature interval / °C	$\Delta m_{\text{exp}} / \%$	$\Delta m_{\text{calc}} / \%$
1.	Endothermic	180-220	4.66	4.70
2.	Exothermic	220-280	9.82	9.74
3.	Exothermic	280-440	42.66	42.69
4.	Exothermic	440-770	29.53	29.66
Residue (CuO)			13.33	13.21

**Fig. 1.** The TG, T, DTG and DTA curves of complex (2)

The most important IR absorption bands for the ligand and complex are given in the experimental part. The presence of sharp strong bands in the 1670-1690, 1560-1580 and respectively 1290-1310 cm^{-1} range is suggestive for amide group [17-20]. All the three combined amide bands are shifted by 15-25 cm^{-1} to lower wavenumbers in the spectrum of complex (2). These modifications indicate that the ligand (1) is coordinated as unidentate through oxygen of amidic moiety [17-20]. Two bands at 1636 and 1433 cm^{-1} may be assigned to the coordinate acetate in chelate mode ($\Delta\nu = 103\text{cm}^{-1}$) [21]. The band that appears at 422 cm^{-1} could be assigned to $\nu(\text{Cu-O})$ stretching vibrations [22].

Electronic spectrum of the complex (Fig.2) shows a broad band centred at 13160 cm^{-1} . The band position and the presence of the greater intensity absorption to higher energy agree with a square-pyramidal coordination [23].

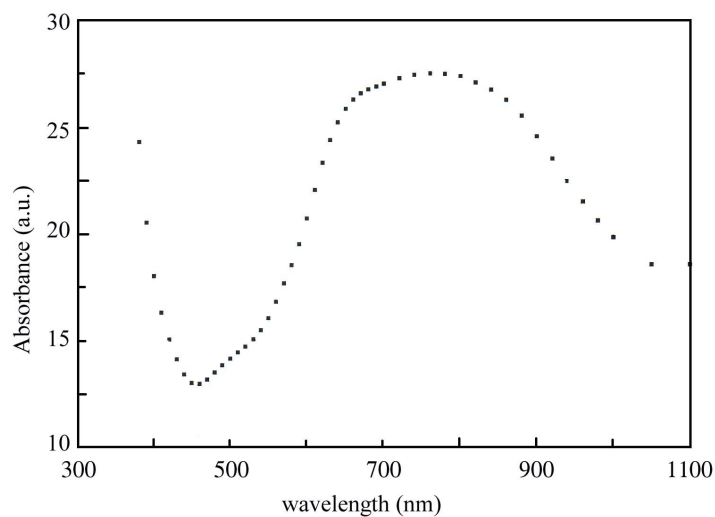


Fig. 2. Diffuse reflectance spectra of $[\text{CuL}(\text{CH}_3\text{COO})_2]$ (**2**)

By the present, the DMF solutions of the ligands and new complexes were tested for the activity against pathological microorganisms *Proteus*, *Escherichia Coli* and *Staphilococcus* but they show no important modifications in culture area. The works are in progress in our laboratory to perform the testes of compounds against other microorganisms cultures.

Taking into account the complex stoichiometry and the spectral features, it seems most probably a mononuclear structure for complex (**2**) with amide acting as unidentate (fig.3).

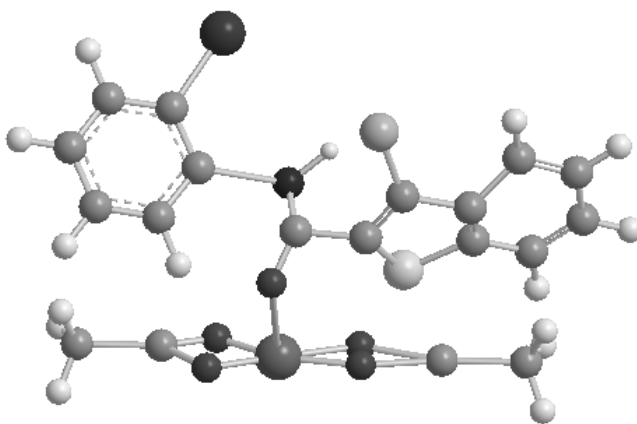


Fig. 3. The proposed coordination for copper complex

Conclusion

The copper (II) complex with 2-iodoanilide-3-chlorobenzo[b]thiophene-2-carboxylic acid has been synthesised.

Thermal decomposition of complex gave the possibility to establish the composition of complex and also the intervals of thermal stability.

The bond and stereochemistry were characterised by means of IR and electronic spectroscopy. The modifications evidenced in the IR spectrum were correlated with the presence of 2-iodoanilide-3-chlorobenzo[b]thiophene-2-carboxylic as unidentate coordinated through amidic oxygen while the acetate acts as bidentate. The diffuse-reflectance spectrum in the VIS-near-IR region shows a single band in agreement with a square- pyramidal surrounding.

REFERENCES

1. Marinescu, D., Olar, R., Simonescu, C.M., Ivan, L., Grandclaudon, P., Meghea, A. and Stanica N. (2002) *Rev. Roum. Chim.* **47**, 437-41.
2. R. Olar (2001) **Chimie bioanorganica. Biometale**, Ed. Universitatii din Bucuresti, Bucuresti, 37-39.
3. Cristurean, E., Olar, R., Simonescu, C.M., Ivan, L., Couture, A. and Stanica, N. (2000) *Sci. Bull. „Politehnica” University of Bucharest, Series B* **62**, 55-62.
4. Z. Korolkiewicz, Z., Hac, E., Gagalo, I., Gorczyca, P. and Lodzinska, A. (1989) *Agents Actions* **26**, 355-9.
5. Kovala-Demertzi, D. (2000) *J. Inorg. Biochem.* **79(1-4)**, 153-7.
6. Bonomo, R.P., Bruno, V., Conte, E., De Guidi, G., La Mendola, D., Maccarrone, G., Nicoletti, F., Rizzarelli, E., Sortino, S. And Vecchio, G. (2003) *J. Chem. Soc. Dalton Trans.* 4406-15.
7. Jacka, T., Bernard, C.C.A. and Singer G. (1983) *Life Sci.* **32**, 1023-8.
8. Singh, N.K., Singh, S.B., Singh, N and Shrivastav A. (2003) *Biometals.* **16(3)**, 471-7.
9. Ranford, J.D., Sadler, P.J. and Tocher, D.A., (1993) *J. Chem. Soc. Dalton Trans.* 3393-9.
10. Carcelli, M., Mazza, P., Pelizzi, C., Pelizzi, G. And Zani, F. (1995) *J. Inorg. Biochem.* **57(1)**, 43-62.
11. Ramadan, A.M. (1997) *J. Inorg. Biochem.* **65(3)**, 183-9.
12. Blasco, F., Ortíz, R., Perello, L., Borrás, J., Amigo, J. and Debaerdemaeker, T. (1994) *J. Inorg. Biochem.* **53(2)**, 117-26.
13. Blasco, F., Perello, L., Latore, J., Borrás, J. and Garcia-Granda, T. (1996) *J. Inorg. Biochem.* **61(2)**, 143-54.
14. Zoroddu, M.A., Zanetti, S., Pogni, R. and Basosi, R. (1996) *J. Inorg. Biochem.*, **63(4)** 291-300.
15. Bradly, D.A., Godfrey, A.G. and Schmid, C.R. (1999) *Tetrahedron Lett.* **40**, 5155-9.
16. Baciú, I. and Paraschivescu, C. (2002) **Colloque Franco-Roumain de chimie appliqué**, Ed Alma Mater, Bacău and Tehnica-Info, Chisinau, 49-50.
17. R.C. Paul, A.K. Moudgil, S. L. Chadha and S.K. Vasisht, *Ind. J. Chem.*, **1978**, 8, 1017-1019.
18. H.O. Desseyen and M.A. Herman, *Spectrochim. Acta*, **1967**, 23A, 2457-2463.
19. D.G. Brewer, P.T.T. Wong and M.C. Sears, *Can. J. Chem.*, **1969**, 46, 3137-3141.
20. M.C. Sears, W.V.F. Brooks and D.G. Brewer, *Can. J. Chem.*, **1970**, 48, 3786-3789.

21. Deacon, G.B. and Philips, J.R. (1970) *Coord. Chem. Rev.* **5**, 217-262.
22. Nakamoto, K. (1986) **Infrared and Raman Spectra of Inorganic and Coordination Compounds**, Wiley, New York, 227-230.
23. A.B.P. Lever, (1984) **Inorganic Electronic Spectroscopy**, Elsevier, Amsterdam, London, New York, 554-572.