Novel Cu(II) Complex with Non-steroidal Anti-inflammatory Drugs

Synthesis, characterization and thermal investigation of the complex with ibuprofen

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Copper (II) complex with the non-steroidal anti-inflammatory drug (NSAID) ibuprofen has been synthesised and characterized. The complex was characterized by elemental analysis, FT-IR spectroscopy, X-ray powder diffraction and thermal analysis. By the mentioned methods, but especially elemental and thermal analysis was determined the following empirical formula: $[Cu(IB)_2]_2$. The FT-IR spectroscopy and X-ray powder diffraction show that the crystal structure of $[Cu(IB)_2]_2$ consist of a binuclear quadruply-bridged neutral molecule. The four carboxylate groups from four ligands are in the familiar bidentate bridging mode. The thermal investigation was performed by simultaneous TG/DTG/DTA methods, under non-isothermal conditions and in a dynamic air atmosphere. According to the thermal curves, especially TG curves, the complex is not containing water of co-ordination or crystallization. The process of thermal decomposition is a complex one and the final product, formed at 1034 C, was metallic copper.

Keywords: anti-inflammatory drug, ibuprofen, elemental analysis, FT-IR spectroscopy, X-ray analysis, thermal analysis

Non-steroidal anti-inflammatory drugs (NSAIDs) are a class of pharmacological agents, whose therapeutic activity is related to the prevention of the development of inflammation or a decrease in its intensity.

The anti-inflammatory activity of NSAIDs and most of its other pharmacological effects are related to the inhibition of the conversion of arachidonic acid to prostaglandins, which are mediators of the inflammatory process [1,2].

Ibuprofen (IB) [2-methyl-4(2-methylpropyl)benzene-acetic acid], which structural formula is shown in figure 1, is a potent inhibitor of cyclo-oxygenase in vitro and in vivo, thereby decreasing the synthesis of prostaglandins, prostacyclin and tromboxane products.

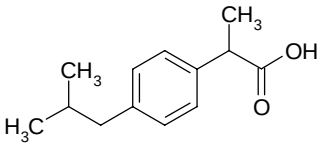

Fig. 1. The chemical structure of Ibuprofen

Recently, two different cyclo-oxygenase isoforms have been characterised: Cox-1 and Cox-2. Inhibition of Cox-1 or Cox-2 leads to very different pharmacological effects. The Cox-1 inhibition is predominantly responsible for anti-thrombotic effects, while anti-inflammatory effects are mediated mainly through Cox-2. The cyclo-oxygenase Cox-1 is expressed constitutively in all tissues, and is thus always present and active. As far as it is known, this is the case for Cox-2 only in kidney, brain and ovaries. During inflammatory processes Cox-2 is increasing expressed in affected tissues, and consequently production of the pain-mediating prostaglandins is also increased. New studies from the last years revealed that in addition to arthritis and pain, cancer and neurodegenerative diseases like Alzheimer's disease could potentially be treated with Cox-2 inhibitors [3,4].

Gastrointestinal side effects constitute the most frequent of all the adverse reactions of NSAIDs. Even though ibuprofen is very potent and widely used among other clinically used NSAIDs, literature is abundant with its gastric and other side effects because of presence of free carboxylic group. If the carboxylic acid functionality is masked, the gastrointestinal toxicity decreases. In this sense, interactions of carboxylic anti-inflammatory drugs with metal ions attracted increasing attention over recent years [5,6].

It is well established that metal ions play a wide range of important roles in biological systems. The presence of drugs that can compete with other biological molecules for the metal ions, changes the distribution of these ions in blood plasma and other fluids. On the other hand, presence of these metal ions can affect the bio-availability of these drugs [7-10].

Synthesis and study of metal complexes with active drugs as ligands is a research area of increasing interest for inorganic, pharmaceutical and medicinal chemistry and has concentrated much attention as an approach to new drug development. The goal is to prepare new compounds with better or different pharmaceutical profile than that of the free ligand. Knowledge of the species formed by combining a metal ion with a drug provides useful information to approach the mechanisms of action of the drug for a disease under treatment and ultimately this can also diminish collateral effects and enhance the efficacy of the parent drug.

Copper, an essential element, has received considerable attention with regard to its presence in normal blood plasma and serum components. Cu(II)-NSAID complexes are reported to have enhanced anti-inflammatory activity and reduced gastrointestinal toxicity compared to the bare drugs. A variety of recent observations indicate that copper when co-administered with anti-inflammatory drugs exhibit synergistic activity. Other pharmacological

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activities of copper complexes, and their potential as antiarthritic, antiulcer, anticancer, antidiabetic and antiepileptic drugs, have been reported [11-14].

For the characterization of the new compounds with possible pharmacological properties, beside the classical methods such as UV-Vis and FT-IR spectroscopy, respectively X-ray diffraction, the thermal methods are used in an increased proportion.

Thermal analysis is one of the most widely used methods for studying the solid state of pharmaceutical substances. The thermoanalytical curves provide important information regarding the physicochemical properties of the pharmaceutical compounds (stability, polymorphism, phase transition, kinetic analysis, compatibility etc.[15-19].

In our previous works [20-25] we provided the importance of the thermal analysis in estimation of the thermal stability for different pharmaceuticals, by thermal behaviour and kinetic analysis, respectively their compatibility.

The preparation of the Zn(II) complex with ibuprofen has been reported earlier [26].

In the present paper we report the synthesis of a mixed ligand complex of Cu(II) and ibuprofen which was investigated by elemental analysis, infrared spectroscopy, X-ray powder diffraction and thermal analysis techniques.

Experimental part

Materials and methods

All chemicals used were analytical reagent products.

The IB drug was supplied by Basf Aktiengesellshaft, Germany. $Cu(CH_3COO)_2 \times H_2O$ and KOH were obtained from Merk, Germany.

Synthesis of complex

2.0 mmoles (0.412 g) of ibuprofen react with 2.0 mmoles (0.112 g) of KOH dissolved in 20 mL of distilled water, to give the potassium salt of the ligand.

1.0 mmoles (0.1996 g) $Cu(CH_3COO)_2 \cdot H_2O$ (aqueous solution) was added by stirring. The turquoise precipitate formed was collected by filtration, washed several times with distilled water and acetone, and dried in vacuum.

Elemental analyse of C and H was carried out on a Vario El elemental analyzer. The Cu(II) content was determined by complexonometric titration with EDTA, in buffer solution (NH_3-NH_4Cl) and *p*H = 8, using Murexid as indicator.

Infrared spectra (400-4000 cm^{-1}) for ibuprofen and its complex with Cu(II) were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. The samples for the FT-IR spectra measurements were prepared as KBr discs.

X-ray diffraction patterns (XRPD) were obtained with a Brucker D8 Advance X-ray diffractometer using MoKα radiation (Zr filter on the diffracted beam, 50 kW and 40 mA) in a Bragg-Brentano θ:2θ configuration, with soller and fixed slits and a NaI (Tl) scintillation detector. The measurements of 2θ ranged between 0 and 30°. Data analysis and acquisition were performed using DIFRACT plus software from Bruker AXS.

Thermal stability and decomposition of the complex was determined by Netzch-STA 449 TG/DTA instrument, recording TG, DTG and DTA curves. The determination was made at heating rate (β) of 10 °C'"min^{-1} with full scale. The sample (≈20 mg) was heated in platinum crucible, under a dynamic atmosphere of air (20 mL . min^{-1}) up to 1200°C.

Results and discussions

Synthesis

The complex Cu(II) metal ion has been prepared by a simple reaction which involves depronation of the ligand by KOH in aqueous solution, followed by complexation with a metal salt.

$$\text{I} \quad 4HIB + 4KOH \xrightarrow{H_2O} 4KIB + 4H_2O$$

$$\text{II} \quad 4KIB + 2Cu(CH_3COO)_2 \xrightarrow{H_2O} [Cu(IB)_2]_2 + 4CH_3COOK$$

where: HIB is actually IB (one acid);
KIB is the potassium salt of IB

To establish the combination ratio we have studied the systems Cu(II)-KIB in the ratios 1:1 ; 1:2 and respectively 1:3. From these systems, we were able to isolate and characterize the following type of binonuclear complex: $[Cu(IB)_2]_2$. Figure 2 presents the chemical structure of the complex obtained.

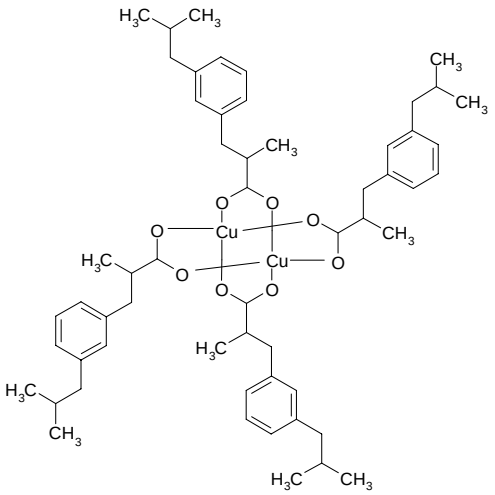

Fig. 2. The proposed chemical structure of Cu-Ibuprofen complex

The formula proposed for this compound was established on the basis of elemental chemical analysis, correlated with physico-chemical investigations (FT-IR spectroscopy and X-ray diffraction) and thermal analysis, especially for the determination of the co-ordination and crystallization water, as well as the molecular formulae.

The results of the elemental analysis for the complex with the formulae: $C_{52}H_{68}O_8Cu_2$ (M = 948.3) are the followings: Anal. Calcd. C 65.80 ; H 7.17 ; Cu 13.40. Found: C (66.18±0.62) ; H (6.98±0.06) ; Zn (13.25±0.12). These results confirm the combination ratio Cu:IB = 1:2.

Infrared spectroscopy

The FT-IR spectroscopy is the most suitable technique of the non-destructive spectroscopic methods and has become an attractive method in the analysis of pharmaceutical solids, since the materials are not subject to thermal or mechanical energy during sample preparation, therefore preventing solid-state transformation. The appearance, respectively disappearance of new absorption bands, broadening of bands, and alteration in intensity are the main characteristics to evidence the difference between substances (samples) [1,4,15,27-29].

The ibuprofen and Cu(II) complex with ibuprofen were characterized by FT-IR spectra (table 1, fig.3).

In the FT-IR spectrum of complex the absence of some bands of absorbtion in the region 3500 – 3000 cm^{-1}, characteristic for ν_{O-H} vibrations, confirms the fact that the obtained complex does not contain water molecules.

The IR spectrum of complex exhibits absorption bands of ibuprofen ligand. The major characteristic of the FT-IR

IB	$[Cu(IB)_2]_2$	Assignement
3350 – 3000 w	–	ν_{OH} (COOH) ; ν_{OH} (H_2O)
2956 – 2869 m-w	2954 – 2869 m-w	ν_{asym} CH_3;CH_2 ν_{sym} CH_3;CH_2
1720 vs	–	$\nu_{C=O}$ (COOH)
–	1588 vs	ν_{asym} (COO)
1508 m-w	1514 w	C–$C_{ring\ str.}$
1461 m-w	1457 w	C–$C_{ring\ str.}$
1420 m	1410 m	ν_{sym} (COO)
1380 – 1184 m-w	1368 – 1293 w	δ_{asym} CH_3;CH_2;CH δ_{sym} CH_3;CH_2;CH
1068 w	1064 w	i.p. CH(ring)
1007 w	997 vw	i.p. CH(ring)
936 m	–	o.p. CH(ring)
866 w	852 vw	o.p. CH(ring)
780 m	799 vw	o.p. CH(ring)
668 w	–	i.p. CH(ring)
–	553 w	ν_{Cu-O}

Table 1
PRINCIPAL FT-IR ABSORPTION BANDS (cm^{-1}) FOR IB AND ITS COMPLEX WITH Cu(II)

where: vs-very strong, s-strong, m-medium, w-weak, vw-very weak, str-streching, asym-asymetric, sym-symetric, i.p.-in plane, o.p.-out of plane

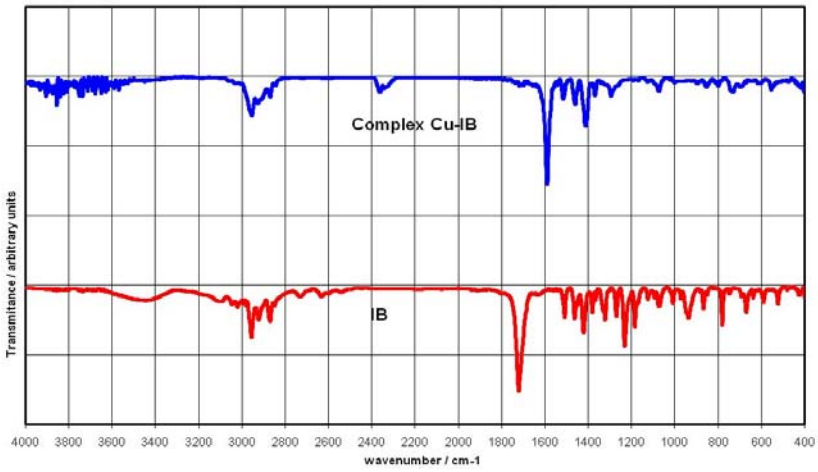

Fig. 3. FT-IR spectra of IB and Cu(II) complex

spectrum of complex is the frequency of the $\nu_{asym.}$(COO) and $\nu_{sym.}$(COO) stretching vibrations. The frequency of these bands depends upon the co-ordination mode of the carboxylate ligand. For the – COO – group, unidentate or bidentate modes of coordination have been observed. The unidentate mode of binding shows two very strong broad $\nu_{asym.}$ and $\nu_{sym.}$ Stretching bands in the region 1560-1620 and 1370-1425 cm^{-1} respectively with an average $\Delta\nu$ value 190 cm^{-1}. For the bidentate chelate co-ordination mode the $\nu_{asym.}$(COO) band occurs at a lower frequency, at 1520-1570 cm^{-1}, while the $\nu_{sym.}$(COO) stretching frequency increases to 1410-1450 cm^{-1} giving an average $\Delta\nu$ value of 115 cm^{-1}.

No distinguished differences between bidentate double bound and bidentate triple bound co-ordination mode could be extracted from $\nu_{asym.}$(COO) and $\nu_{sym.}$(COO) stretching frequencies or to $\Delta\nu$ values.

For the complex with ibuprofen the $\nu_{asym.}$(COO) occurs at 1588 cm^{-1} and the $\nu_{sym.}$(COO) at 1410 cm^{-1} with an average $\Delta\nu$ value of 178 cm^{-1} suggest bidentate chelate co-ordination mode, with one oxygen atom to one metallic ion.

X-ray diffraction

To investigate the configuration of the complex obtained, besides the FT-IR spectroscopy which is a qualitative analysis technique, the X-ray powder diffraction (XRPD) has been used for qualitative and quantitative identification of crystallinity. The number of the speciality papers which use XRPD is growing [7,22,23,30,31].

The appearance of new lines and disappearance of some of the lines present in the ligand, respectively the shifting of some of the diffraction lines of higher moderate and lower intensities in the complex, which are originally present in the X-ray diffraction patterns of the ligand indicates the presence of a new compound.

The X-ray diffraction patterns of ibuprofen and of its complex with Cu(II) are shown in figure 4.

To complete the general image, in table 2 are presented the main X-ray diffraction data for ligand and complex.

From figure 4 and table 2 can be remarked a great difference between the diffractograms of the ligand, respectively complex, by the disappearance, respectively the appearance of some meaningful lines.

The number of missing lines, respectively appeared is higher, but these lines are not significant because the values of I% are less than or around 10%.

Thermal analysis

The thermal stability of Cu(II) complex was studied in air and its TG, DTG and DTA curves were registered (fig.5)

The thermal decomposition of the complex $[Cu(IB)_2]_2$ unfolds practically in four stages, without being able to afford to delimit the first three stages.

It is very difficult to specify the nature of the intermediate compounds because of the complexity of decomposition process with simultaneous and/or competitive reactions.

The first stage of thermolysis of $[Cu(IB)_2]_2$ occurs in the range of 200 – 311°C and is characterised by large mass loss (65.5%) which corresponds to partially decomposition of the organic ligand.

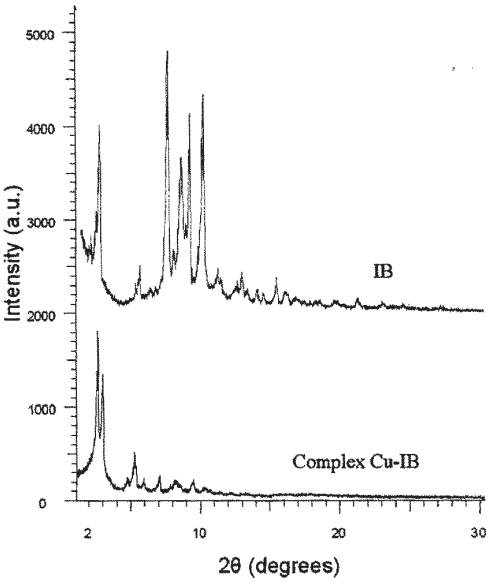

Fig. 4. X-ray diffractogram of ibuprofen, respectively of its complex with Cu(II)

Table 2
X-RAY DIFFRACTION DATA FOR IBUPROFEN AND ITS COMPLEX WITH Cu(II)

Ibuprofen		Complex	
2θ	I%	2θ	I%
2.156	27.7		
2.553	37.3	2.607	100
2.812	71.6	2.967	76.6
		4.736	12.5
		5.222	28.2
		5.32	20.8
5.648	17.3		
		5.927	13.1
6.437	10.6		
		6.538	6.3
6.802	11.1		
		7.043	14.9
7.685	100	7.803	8.7
8.119	24.7	8.255	11.6
8.628	60.5	8.52	8.6
8.975	34.5		
9.295	68.8	9.33	10
		9.443	11.3
		10.134	7.3
10.255	80.2	10.358	6.9

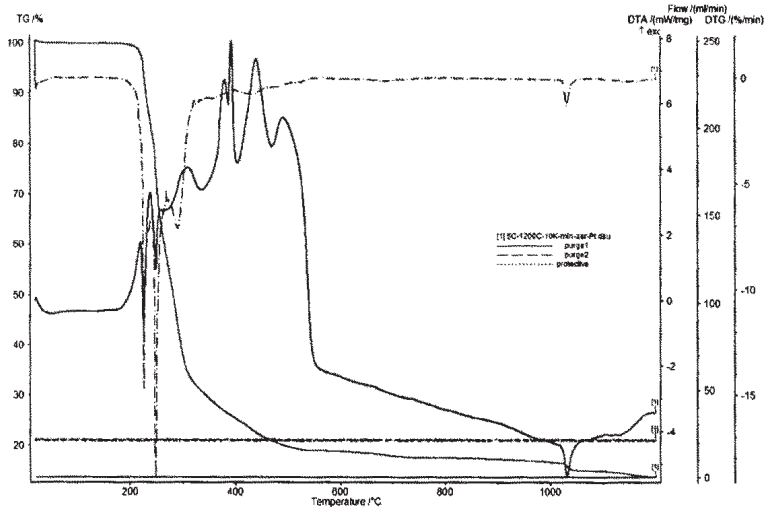

Fig.5. TG, DTG and DTA curves of $[Cu(IB)_2]_2$

The next step of pyrolysis (between 311 – 547°C) is characterised by a mass loss of 17.95%.

The TG curve, but especially DTG and DTA show the complexity of the thermal decomposition for the first two stages through the related DTG peaks (229.1 ; 250.0 ; 290.9 °C, respectively 436.4 °C), respectively DTA peaks (229.1 – endo; 250.0 – endo; respectively 342.7 – endo; 393.6 – exo; 445.5 – exo; 492.6 – exo).

The third stage, in the range 547 – 1027°C, without considerable effects, corresponds to the formation of CuO.

The last mass losses between 1027 – 1200°C corresponds of the decomposition of CuO to Cu. This process is characterised by an endothermic peak on the DTA curve ($T_{peak} = T_{peak\ DTG} = 1033.6$ °C).

Calculations based on the mass loss up to 1200°C are in agreement with the formation of Cu as final residue (exp. 13.5% ; calc. 13.4%).

Conclusions

Ibuprofen is a very interesting ligand from point of view of their application. It could form several complexes with metal (II). In this work, the synthesis and properties of these types of compounds were investigated. The new complex of empirical formulae $[Cu(IB)_2]_2$ was prepared as a crystalline compound.

The structure of the complex of IB with Cu(II) has been confirmed from the elemental analysis, FT-IR spectroscopy, X-ray diffraction and thermal analysis. Thus, from the FT-IR spectrum and X-ray diffractogram, it is concluded that the complex of Cu(II) with ibuprofen is a binuclear molecule. The four carboxylate groups from four ligand are in a bidentate bridging mode.

The FT-IR spectrum, together with the thermal analysis confirmed the absence of the co-ordination, respectively crystallization water.

The thermal investigation (studied by TG, DTG and DTA techniques) shows that the thermal decomposition process is one complex with simultaneous and/or competitive reactions. The final product of the thermal decomposition is Cu, which through its percentage confirms the empirical formulae of the new complex prepared.

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