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Thermal behaviour and spectral analysis of the organometallic complex Cu(II)2,2'-dihydroxy azobenzene

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Abstract

Copper complex Cu(II) 2,2'-dihydroxy azobenzene - $Cu(DAB)_2$ was studied by thermal analysis and by Fourier transform infrared spectroscopy in order to establish its physical and chemical behaviour. Thermal analysis was performed in RT-600 ^{0}C range in air and argon at heating rate of 2 K·min^{-1}. FTIR spectroscopy in the range 4000-650 cm^{-1} identified chemical bonds and functional groups of the compound that confirm the attributed chemical formula.

Keywords: $Cu(DAB)_2$, FTIR, Thermal analysis

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1 Introduction

Organometallic complex Cu(II) 2,2'-dihydroxy azobenzene or $Cu(DAB)_2$ is a novel material with important scientific, industrial and economic potential for non-linear optical coatings and applications in optical storage and sensors [1]-[2].

Laser deposition of organometalic complex compounds represent a solution in obtaining chemically intact thin films [3]-[6]. This paper examines thermal behaviour and infrared absorption of the organometallic complex Cu(II) 2,2'-dihydroxy azobenzene. Thermal analysis was performed on $Cu(DAB)_2$ in order to establish its thermal behaviour and physical and chemical transformations as a function of temperature.

2 Experimental

2.1 *Cu(II) 2,2'-dihydroxy azobenzene preparation*

Cu(II) 2,2'-dihydroxy azobenzene complex was synthesized starting from hot solution of ligand (2,2'-dihydroxy azobenzene, 0.6 mM) in ethanol, mixed with a solution of hydrated copper(II) chloride (1.2mM) in ethanol. The mixture was furtherly stirred and refluxed for 1.5 hours in water bath until the complex precipitated. The pH of the solution was adjusted with ammonia solution up to 7-7.5 during the reaction. The crystalline product was separated when cooling the solution. This was filtered, recrystallized and washed

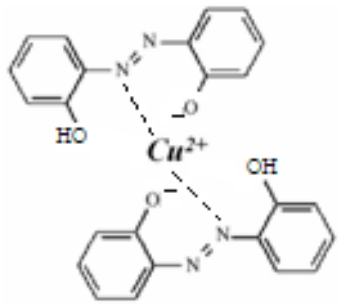


Figure 1: Structural formula of the $Cu(DAB)_2$

with ethanol [2], [7]-[11]. The structural formula of $Cu(DAB)_2$ is presented in Figure 1 [6].

2.2 *Methods and techniques*

Thermal analysis measurements (TG, DTG, DTA and DSC) of $Cu(DAB)_2$ were carried out in dynamic air or argon atmosphere (150 $cm^3 \cdot min^{-1}$), under non-isothermal liniar regimes, using a horizontal Diamond TG/DTA Differential/Thermogravimetric Analyser from PerkinElmer Instruments. Samples at 0.631 mg in air and at 2.030 mg in argon, contained in aluminium crucibles were heated in the temperature range of RT-600 ^{0}C. Heating rate was 2 K·min^{-1} in both air and argon.

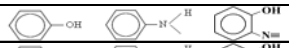
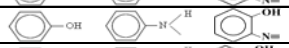
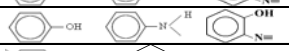
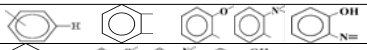
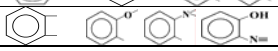
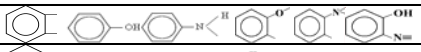
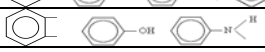
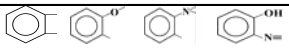
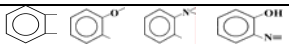
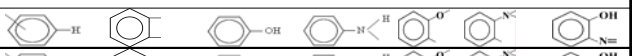
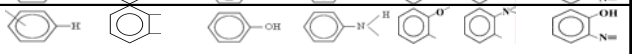
Spectral analysis was investigated by FTIR spectroscopy, with a PerkinElmer Spectrum 100 spectrometer in the range of 650-4000 cm^{-1} wavenumber. All spectra were obtained using universal attenuated total reflection infrared (UATR) accessory, at a resolution of 4 cm^{-1}, with 4 scans and CO_2/H_2O correction, in transmittance mode.

3 Results and discussion

3.1 *Fourier transform infrared spectroscopy (FTIR)*

FTIR is frequentely used to determine chemical bonds and functional groups of organic substances. FTIR spectrum of the free ligand (2,2'–dihydroxy azobenzene = DAB) presents intense characteristical bands at 3320, 1590, 1470, 1170, 1140 and 745 cm^{-1}, that are assigned to –N=N-, -C=C- aromatic ring, C-N=, kelatic –OH and phenolic –OH. The FTIR spectrum for $Cu(DAB)_2$ (in transmitance) is represented in Figure 2. The typical bands are related to –N=N-, which give a split signal that become a maximum around 1588 cm^{-1}, and phenolic –OH, that is shifted to 1259 cm^{-1} after complexation.

Table 1 Vibration wavenumber of the $Cu(DAB)_2$ exhibited in the FTIR transmission spectrum

(cm^{-1})	Intensity	Assignments
3314	m	
3247	m	
3167	m	
3056	w	
2621	w	
2550	w	
2171	w	
1696	w	
1588	s	
1568	m	
1538	m	
1466	vs	
1452	m	
1401	m	
1341	w	
1326	m	
1290	m	
1259	m	
1216	m	
1203	m	
1177	m	
1143	vs	
1122	m	
1104	m	
1034	w	
947	m	
876	w	
843	s	
757	vs	
744	vs	

The kelatic band at 3056 cm^{-1} is unaffected in the complex, and the bands corresponding to coordinated water molecules are absent. These data show that the ligand binds the metal by the azo group and by one –OH group that is shifted to 1259 cm^{-1} after complexation, while the other gives the unaffected band at 3056 cm^{-1}. The most intense absorption bands of $Cu(DAB)_2$ that have been identified in the IR spectrum, were attributed to the following functional groups (Table 1).

- transmission lines at 3056, 1588, 1568, 1466, 1452, 1259, 1216, 1203, 1177, 757 and 744 cm^{-1} are related to ortho-substituted aromatic compounds;

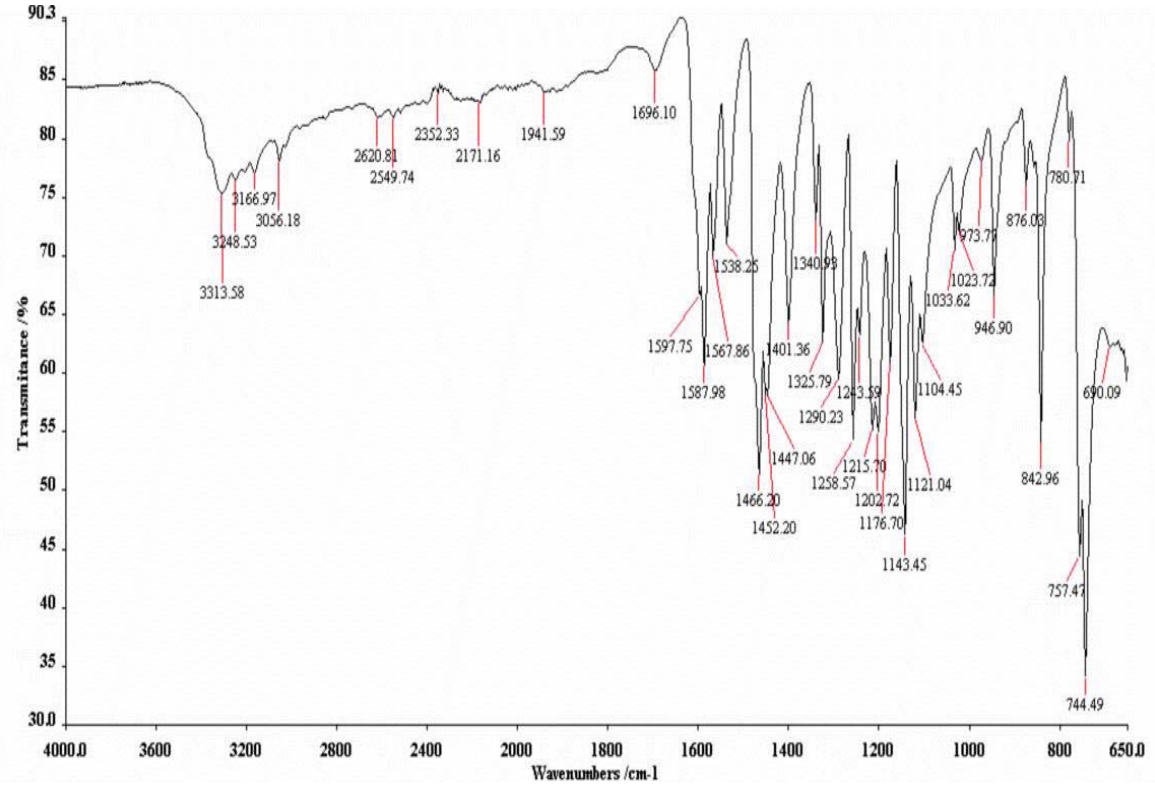


Figure 2: FTIR spectrum of $Cu(DAB)_2$ organometallic complex

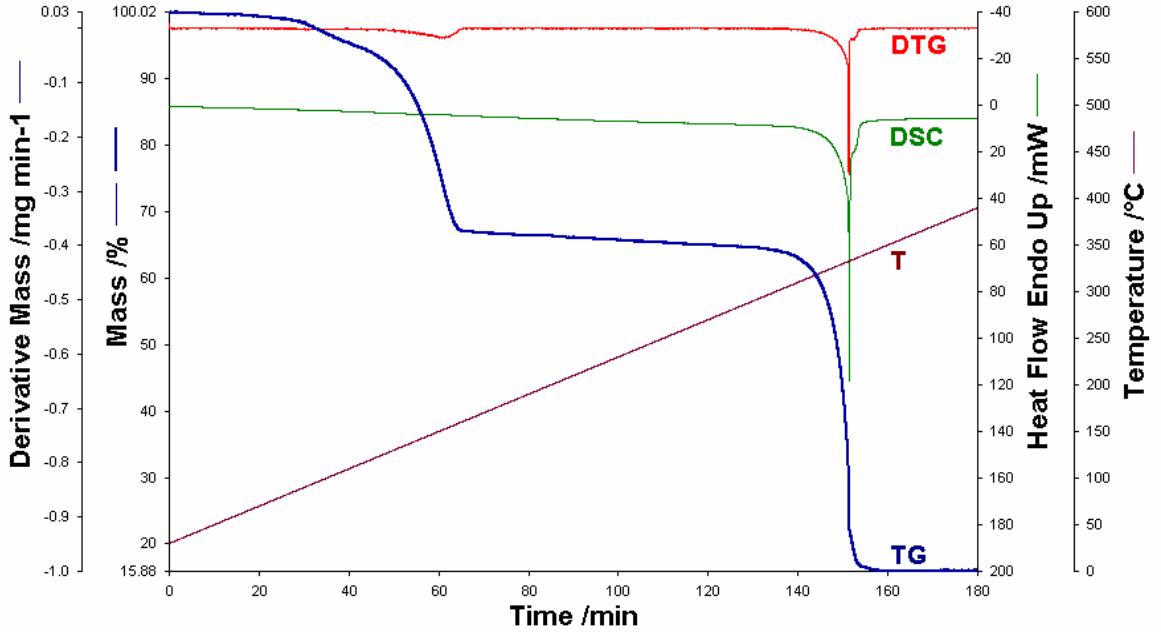


Figure 3: $Cu(DAB)_2$ complex decomposition in air with 2K/min at 600^0C

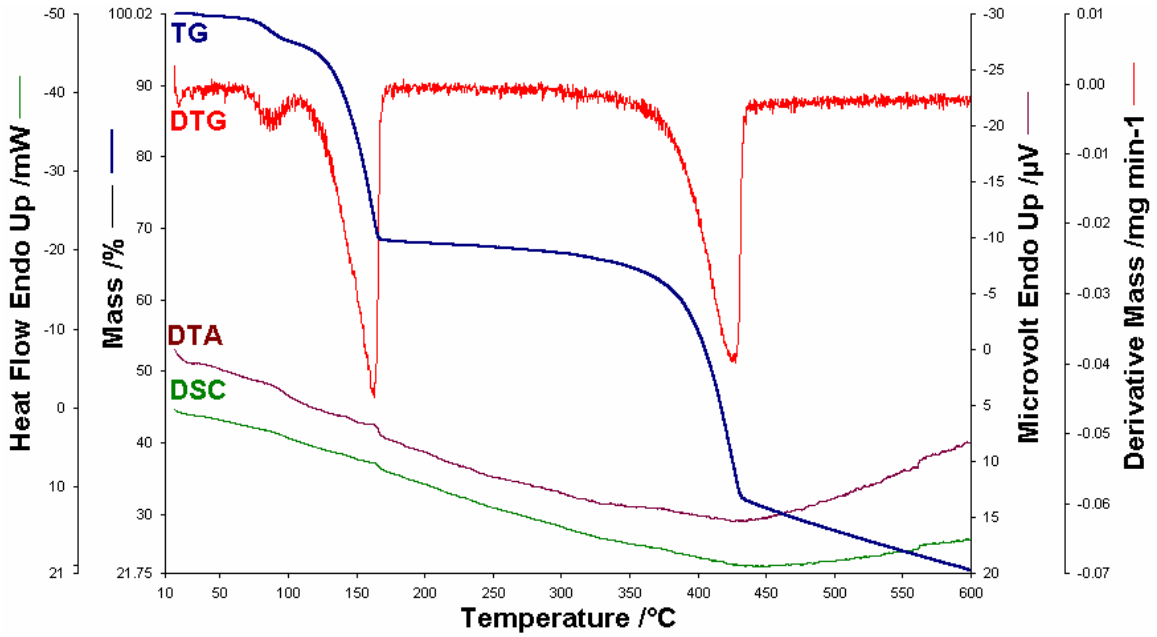


Figure 4: $Cu(DAB)_2$ complex decomposition in argon with 2K/min at 600^0C

- transmission lines at 3314, 3247, 3167, 1588, 1568, 1466, 1452, 1259, 1034, 757 and 744 cm^{-1} are related to hydroxyl or amino-substituted aromatic compounds;

- transmission lines at 3314, 3247, 3167, 1588, 1568, 1466, 1341, 1259, 1216, 1203, 1177, 1143, 876, 843, 757 and 744 cm^{-1} are related to ortho-substituted aromatic compounds by hydroxyl and azo groups [6].

3.2 *Thermal analysis (TA)*

Thermal behavior of the $Cu(DAB)_2$ complex have been determined by TA at different temperatures. The thermal effects can be observed in the diagrams of the decomposition processes in air (Figure 3) and argon (Figure 4).

Decomposition in air of the complex is done in two step. The first step is lightly endothermic, while the second step is very strong exothermal. The enthalpy variation of the complex, during the oxidative decomposition in air at 344 ^{0}C is around $\Delta H = -16kJ \cdot g^{-1}$.

Decomposition in argon of the complex is done in three steps. The first two steps are weakly endothermic, while the third one is weakly exothermal. The mass loss at 2 K/min heating rate are presented in Table 2.

Table 2: Gravimetric effect of the decomposition at heating rate of 2K/min

Gas	Mass loss (%)	Residue (%)
air	84.12	15.88
argon	78.25	21.75

4 Conclusions

Thermal analysis and FTIR spectroscopy of a organometallic compound Cu(II) 2,2'-dihydroxy azobenzene was performed in order to establish its physical and chemical properties. The thermal decomposition takes place different in air and in argon flow.

The decomposition in air is oxidative and perform in two stages. The decomposition in argon perform in three stages, but up to 600^0C there preserve copper compounds with carbon. The FTIR spectroscopy confirm the expected functional groups and namely the aromatic ortho-substituted, the hydroxyl-substituted aromatic compounds, the azo and the hydroxyl groups.

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