

THERMAL STABILITY OF SOME NEW COMPLEX COMPOUNDS WITH ALLYLACETOACETATE AS LIGAND

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This paper reports the investigation of the thermal stability of two new complexes with allylacetate anion, $\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$ (**1**) and $\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{OH}_2)_2$ (**2**), respectively. The bonding and stereochemistry of the complexes have been characterised by IR, electronic and EPR spectra. The main decomposition steps were evidenced. The two complexes exhibit a different thermal behaviour. Thus, the copper complex suffers an oxidative degradation of allylacetate ligand leading to copper carbonate, which is decomposed to copper oxide. The Ni(II) complex loses the water molecules first and then the organic ligand decomposition occurs. An intermediary malonaldehyde complex seems to be obtained. Complex (**1**) presents *in vitro* antimicrobial activity.

Keywords: allylacetate anion, Cu(II) complex, Ni(II) complex, thermal stability

Introduction

Allylacetate (AAA) is a very interesting organic derivative that acts as bidentate ligand in complexes with many transition metal ions [1]. The complexes with similar ligands could adopt extended supramolecular structures induced by the presence of hydrogen bonds. The interest in using this ligand increased recently because the obtained complexes have interesting magnetic and catalytic properties. Moreover, they can be used as monomers in order to include some metallic ions in polymeric matrix [2, 3].

Complexes could be copolymerised with proper organic monomers in order to obtain new materials with predefined properties. Also, this process improves the properties of monomers and leads to the development of new ones. In the solid-state, when compounds contain an unsaturated polymerisable ligand (as allylacetate), reactions such as polymerisation induced by thermal and/or radiation sources may lead to the formation of valuable compounds. On the other hand, the obtained metal-containing copolymers could be used to synthesize metal-polymer composites having unusual physico-chemical and mechanical properties [4]. These are widely used as optical and magnetic materials [5], catalyst for various reactions, drugs and coatings [2]. There are less data reported concerning the thermal behaviour of polymers [6].

We report here the thermal behaviour of two new complexes of Cu(II) and Ni(II) with allylacetate

($\text{C}_7\text{H}_9\text{O}_3$) anion, that represent the products of a first step in the synthesis of polymeric materials. The compounds were formulated as $\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$ (**1**) and $\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{OH}_2)_2$ (**2**) respectively on the basis of chemical analysis, IR and electronic spectra as well as EPR study.

Considering their intended use as metal containing monomers their thermal stability and behaviour are supposed to be clearly known. The thermal analysis (TG, DTG, DTA) of these complexes was performed in order to elucidate the composition and also the number and nature of water molecules. In both cases, the final residue was the metal oxide, indicated by powder X-ray diffraction.

Experimental

All reagents were of commercial analytical quality and have been used without further purification. Chemical analysis of carbon, nitrogen and hydrogen has been performed using an EA 1110 analyzer. Copper and nickel were determined gravimetrically in the laboratories of Inorganic Chemistry Department.

IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the range 400–4000 cm^{-1} . Electronic spectra by diffuse reflectance technique, with MgO as standard, were recorded in the range 380–1100 nm, on a VSU 2P-Zeiss Jena spectrometer. The EPR spectra were recorded on

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a JES-ME-3 spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl ($g=2.0036$). The heating curves (TG, DTA and DTG) were recorded in a static air atmosphere using a Shimadzu DTG-TA-51H thermogravimetric analyzer with a sample mass of 4 and 8 mg over the temperature range 20–1000°C, using a heating rate of 10 K min⁻¹.

Synthesis of the complexes

Complex Cu(C₇H₉O₃)₂, (**1**): to 25 mL of aqueous solution of 10 mmoles of Cu(CH₃COO)₂·H₂O ammonia solution was added dropwise, under continuous stirring until the colour of the solution turned dark blue as a result of copper tetraammine formation. Under continuous stirring, ethanolic solution of 20 mmoles allyl-acetoacetate was added. The dark green solution was left at room temperature for several days until needle blue-green crystals were formed. The compound was filtered off, washed with water and air-dried. Analysis, found: Cu, 18.34; C, 47.79; H, 5.18%; calculated: Cu, 18.38; C, 48.64; H, 5.20%; IR (KBr pellet), cm⁻¹: $\nu(\text{C}=\text{O})$, 1602vs; $\delta(\text{CH}=\text{CH})$, 1537s; $\nu(\text{C}-\text{O})$, 1283s, 1175m; $\gamma(\text{CH})$, 928w, $\rho(\text{CH}_3)$, 776m.

Complex Ni(C₇H₉O₃)₂(H₂O)₂, (**2**): to 25 mL of aqueous solution of 10 mmoles of Ni(CH₃COO)₂·4H₂O an ethanolic solution of 20 mmoles allyl-acetoacetate was added dropwise under continuous stirring. The light green solution was stirred for 30 min and then the pH was adjusted to 8 with ammonia solution. After several days, at room temperature needle light green crystals were obtained. The compound was filtered off, washed with water and air-dried. Analysis, found: Ni, 15.53; C, 44.58; H, 5.76%; calculated: Ni, 15.58; C, 44.62; H, 5.84%; IR (KBr pellet), cm⁻¹: $\nu(\text{OH})$, 3400s, $\nu(\text{C}=\text{O})$, 1600vs; $\delta(\text{CH}=\text{CH})$, 1535s; $\nu(\text{C}-\text{O})$, 1280s, 1175m; $\gamma(\text{CH})$, 930w, $\rho(\text{CH}_3)$, 770m.

Results and discussion

Physico-chemical and biological characterisation of complexes

The major goal of this paper was to determine the thermal behaviour of these complexes that could be used as intermediates for obtaining some polymer metal containing species. The complexes have been formulated on the basis of chemical analysis, IR and electronic spectra as well as EPR study at room temperature.

The new complexes were synthesized by direct reaction between metal acetates and allyl-acetoacetate in alkaline medium. The complexes have different chemical formulae and IR spectra; (**1**) does not contain water or solvent molecules in spite of the fact that it was obtained under similar condition as complex (**2**). Com-

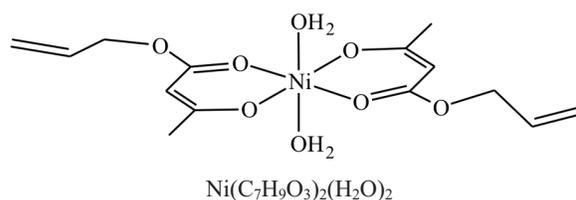
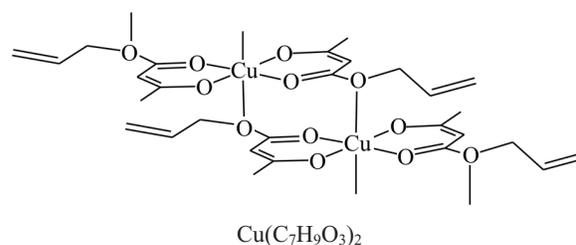
plex (**1**) is very soluble in ethanol and in other common organic solvents while (**2**) is sparingly soluble even in organic solvents having coordinative properties.

In the IR spectra of the complexes the characteristic patterns of the estheric groups are present as is presented in the experimental part. These groups lead to strong bands around 1600 cm⁻¹, assigned to $\nu(\text{C}=\text{O})$ vibrations. The presence of these bands at lower wavenumbers sustains their implication in interactions with the metal ions. The allylic fragment could be identified due to the band located at 1535 cm⁻¹. The band at 1175 cm⁻¹ assigned to $\nu(\text{C}-\text{O})$ vibration indicates the presence of the ligand in the enolic form [7]. In the spectrum of complex (**2**) the broad band at 3400 cm⁻¹ could be associated with the presence of water molecules [8].

The electronic spectra of complexes are shown in Fig. 1. The diffuse-reflectance spectrum of Cu(II) complex in the Vis-near-IR range shows a single broad band at 18 020 cm⁻¹, as is usually observed for this ion due to the different nature of the ligands and also of the Jahn–Teller effect [9, 10]. In the spectrum of complex (**2**) the bands at 10 300, 16 666 and 24 390 cm⁻¹ could be assigned to the spin allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ [9]. The positions of the absorption maxima are in agreement with an octahedral stereochemistry for a [NiO₆] chromophore.

The EPR spectrum presented in Fig. 2 contains an isotropic signal.

On the basis of the above data the coordination proposed for the complexes are as it follows:



Biological activity

Antimicrobial activity of the complexes has been carried out against strains of bacteria (*Bacillus subtilis* and *Escherichia coli*), fungus (*Aspergillus niger* and *Aspergillus oryzae*) and yeasts (*Saccharomyces cerevisiae* and *Hansenula anomala*) using liquid me-

dium dilution method. The values of minimum inhibitory concentration (MIC) indicate that only the complex (1) is active against the *Escherichia coli* with a MIC of 75 ppm.

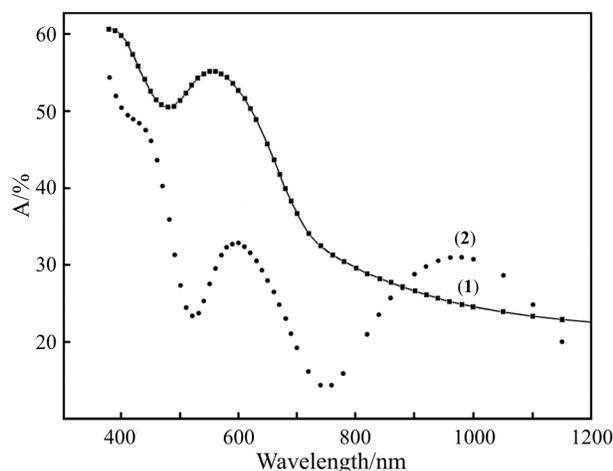


Fig. 1 Diffuse reflectance spectra of complexes (1) and (2)

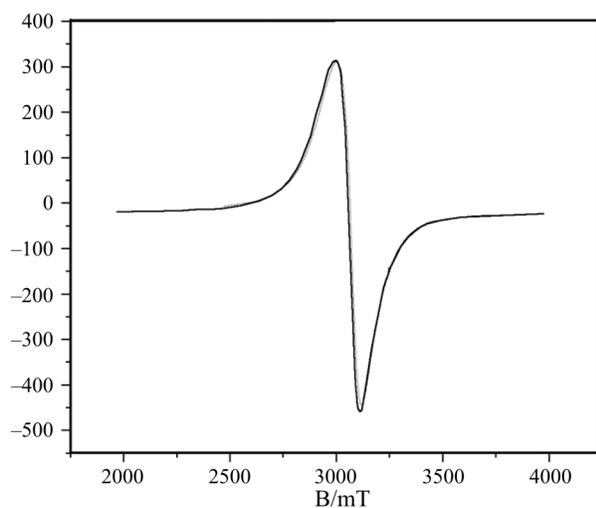


Fig. 2 EPR spectrum of complex (1)

Thermal behavior of complexes

Thermal decomposition of $\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$

The TG, DTG and DTA curves corresponding to the complex (1) are presented in Fig. 3.

The thermal analysis has confirmed the compound formulation, the complex being stable until 112°C .

The thermal decomposition occurs in two basic, exothermic steps. One step corresponds to the complex transformation to CuCO_3 , while the second one corresponds to decomposition of CuCO_3 to CuO . Unlike the first step that is a single one, the decomposition of CuCO_3 seems to occur in three steps (according to DTA curve). Considering the tendency of copper to form basic salts, it could be supposed that the intermediates are oxocarbonates with different mol $\text{CuCO}_3:\text{CuO}$ ratio.

The copper oxide obtained at 412°C as final product of decomposition is stable until 650°C .

Thermal decomposition of $\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{H}_2\text{O})_2$

The TG and DTG curves (Fig. 4) indicate that the thermal decomposition occurs in a different way.

As the IR spectrum indicates, the complex (2) contains water, which is eliminated in two successive well-separated steps [11]. The first decomposition step corresponds to the elimination of 0.5 water molecules while the second one could be associated with the elimination of 1.5 water molecules per nickel atom. On the basis of the thermal interval that corresponds to the decomposition one can conclude that the water molecules are involved in interactions having different strength. Another essential difference in the thermal behaviour of this compound arises from the ligand decomposition mode. Unlike complex (1), complex (2) gives as intermediate a complex with an organic ligand resulted after the partial oxidative degradation of allylacetate. According to the mass loss and IR spectrum, the remaining compound seems to be $[\text{Ni}(\text{C}_3\text{H}_5\text{O}_2)_2]$. In the next step, the oxidative degradation of this compound leads to NiO , stable until 750°C .

Table 1 Thermal behaviour data (in static air atmosphere) for the allylacetate complexes

Complex	Step	Thermal effect	Temperature interval/ $^\circ\text{C}$	$\Delta m_{\text{exp}}/\%$	$\Delta m_{\text{calc}}/\%$	Residue used for calculation
$\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$	1	exothermic	112–225	64.34	64.26	CuCO_3
	2	exothermic	225–295	4.14	4.24	$1/3(2\text{CuCO}_3 \cdot \text{CuO})$
	3	exothermic	295–346	4.28	4.24	$1/3(\text{CuCO}_3 \cdot 2\text{CuO})$
	4	exothermic	346–412	4.18	4.24	CuO
		residue (CuO)		23.06	23.02	
$\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{H}_2\text{O})_2$	1	endothermic	27–83	2.24	2.38	$\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{H}_2\text{O})_{1.5}$
	2	endothermic	83–137	7.32	7.16	$\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2$
	3	exothermic	137–280	37.21	37.17	$\text{Ni}(\text{C}_3\text{H}_5\text{O}_2)_2$
	4	exothermic	280–436	33.28	33.45	NiO
		residue (NiO)		19.95	19.84	

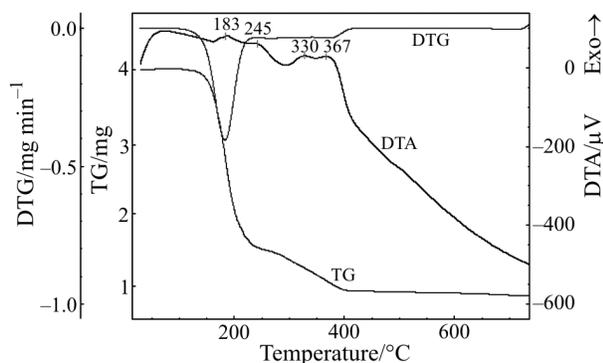


Fig. 3 TG, DTG and DTA curves of $\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$

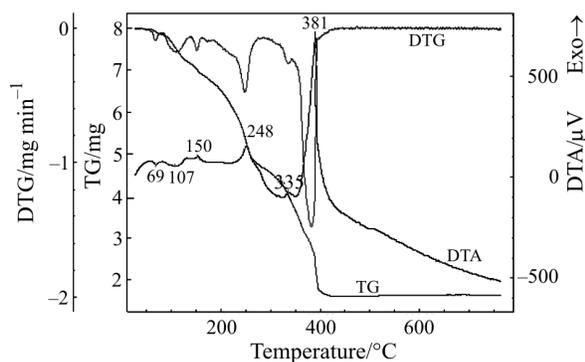


Fig. 4 TG, DTG and DTA curves of $\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{H}_2\text{O})_2$

Conclusions

Two new complexes, $\text{Cu}(\text{C}_7\text{H}_9\text{O}_3)_2$ and $\text{Ni}(\text{C}_7\text{H}_9\text{O}_3)_2(\text{OH}_2)_2$ were characterized by the chemical analysis, IR, electronic and EPR spectra.

The main decomposition steps of these compounds have been determined in order to establish the interval of thermal stability having in view the possibility to include these compounds into polymeric matrix.

The thermal analysis (TG, DTG and DTA) of the complexes elucidated the composition, the number and nature of water molecules. The presence of the water molecules for Ni(II) complex generated two decomposition steps which indicate a different bonding character of water molecules as ligands. The following decomposition step in the case of this compound could be associated with formation of a stable intermediate with malonaldehyde, coordinated to metal ion.

In both cases, the final residue is metal oxide, indicated by powder X-ray diffraction.

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