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SYNTHESIS AND CHARACTERIZATION OF SOME Cr(III), Fe(III) AND Zr(IV) COMPOUNDS WITH SUBSTITUTED *o*-HYDROXY BENZOPHENONE

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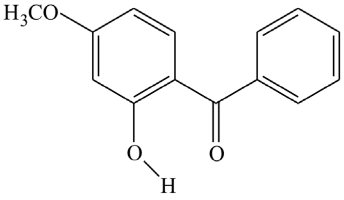
Abstract

This work presents our data concerning the synthesis and characterization of some Cr(III), Fe(III) and Zr(IV) complexes with substituted (2-hydroxy-4-methoxy-phenyl)-phenyl-methanone – $C_{14}H_{12}O_3$, denoted by (L1). The synthesis of these complex compounds was performed using melted urea as reaction medium. The obtained complexes have been studied by chemical analysis, IR spectroscopy, X-ray diffraction and thermogravimetric analysis. Based on the data resulting from the thermal behaviour of the studied complex compounds, the kinetic parameters of the thermal decomposition reactions have been determined.

Keywords: chrome, iron, melted urea, thermal behaviour, zirconium

Introduction

The ligand L1 (sample 4) used for the synthesis of the Cr(III), Fe(III) and Zr(IV) complexes has the following structure:



(2-hydroxy-4-methoxy-phenyl)-phenyl-methanone=L1

The literature presents only a few data concerning the complex compounds of different metallic cations with this ligand, fact due to its reduced reactivity under usual

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conditions. However, under certain reaction conditions concerning the nature of the reaction medium, the pH, the temperature, etc., this ligand is able to form complexes with a series of metallic cations, among which Cr(III), Fe(III) and Zr(IV).

Experimental

The reaction with the Cr(III), Fe(III) and Zr(IV) ions in organic solvents occurs quite difficult under normal conditions. The M-L1 compounds can be formed in solution, but they are difficult to separate in solid-state. The solid-state separation of the mixed compounds of Cr(III), Fe(III) and Zr(IV) with urea and the ligand L1 occurs with very good results if one uses melted urea as reaction medium [1–5].

The urea, which is used as both reaction medium and reagent, was introduced in porcelain crucibles and heated on oil bath. The temperature was kept under control between 160–165°C, below the decomposition temperature of urea, which is of 182.5°C. After the melting of urea, the corresponding chlorides (Merck reagents) of these cations: $CrCl_3\cdot 6H_2O$, $FeCl_3\cdot 6H_2O$ and $ZrCl_4\cdot H_2O$ were added. The heating continues at 165°C for two more hours until no gases or steams are emitted.

After cooling, the samples were washed with DMF in order to remove the urea excess, and subsequently the obtained compounds, $[Cr(urea)_6]Cl_3$, $[Fe(urea)_6]Cl_3$ and $[Zr(urea)_6]Cl_4$, were separated [1–4]. After separation, the $[M(urea)_6]^{n+}$ complexes were dried and used for the synthesis of the mixed complexes M-Urea-L1. For this, the $[M(urea)]^{n+}$ compounds were melted again, and small amounts of ligand L1 were added step by step. The heating goes on for 1.5 h more until the reaction is completed, i.e. no gas (HCl) emission is noticed.

After cooling, the complexes were washed with small amounts of water and ethanol and dried on $CaCl_2$ until the mass remains constant. The dried compounds have been chemically analysed in order to establish their molecular formulas. The Cr^{3+}, Fe^{3+} and Zr^{4+} contents were determined by atomic absorption spectroscopy AAS, redox potentiometry and gravimetric analyses [6–9]. The obtained data are listed in Table 1.

Based on the data obtained by the chemical analysis of the synthesized compounds, the chemical formulas given in Table 2 were suggested. At the same time, the melting points and their solubility in organic and inorganic solvents were determined, all the obtained data being given in the same table.

Results and discussion

Thermal analysis

The thermal stability of L1 and of its complex compounds with the Cr(III) (sample 1), Fe(III) (sample 2) and Zr(IV) (sample 3) has been investigated by thermogravimetric analysis under dynamic conditions of temperature. The experimental measurements were performed with a thermal balance type Paulik–Paulik–Erdey (MOM, Hungary) under the following conditions: m_W=48±2 mg, reference material Al_2O_3, quartz crucible, heating rate 8, 10 and 12°C min^{-1}, in air, at temperatures ranging from 20 to 900°C.

Table 1 The chemical composition of the mixed complex compounds Cr(III), Fe(III) and Zr(IV) with urea and the ligand L1

No.	Compounds	Elemental analysis									
		Theoretical					Experimental				
		Cr	C	H	N	Cl	Cr	C	H	N	Cl
1	$[Cr(urea)_6]Cl_3$	10.2	13.88	4.62	32.40	20.54	9.52	13.20	4.12	31.50	19.95
1’	$[Cr(L)_2(urea)_2]Cl$ (sample 1)	7.83	53.20	4.85	8.43	5.34	6.96	51.42	4.01	7.81	4.85
2	$[Fe(urea)_6]Cl_3$	10.72	13.78	4.59	32.16	20.39	9.95	12.94	3.87	31.50	19.45
2’	$[Fe(L)_2(urea)_2]Cl$ (sample 2)	8.38	53.89	4.82	8.38	5.31	7.58	52.30	3.92	7.67	4.85
3	$[Zr(urea)_6]Cl_4$	15.37	12.14	4.04	28.32	23.6	14.78	11.80	3.42	27.62	22.87
3’	$[Zr_2(L)_2(urea)_4Cl_2]Cl_4$ (sample 3)	16.70	35.20	3.69	10.25	19.5	15.94	34.45	2.86	9.53	18.64

Table 2 The proposed chemical formulas and some physical characteristics of the synthesized complexes

No.	Chemical compound	Melting point/°C	The colour of compounds	The solvent in which they are soluble
1	$[Cr(urea)_6]Cl_3$	72–74	gray-greenish	H_2O, C_2H_5OH
1‘	$[Cr(L)_2(urea)_2]Cl$	80–81	olive-green	DMF, $CO(CH_3)_2$
2	$[Fe(urea)_6]Cl_3$	95–97	scarlet-brown	H_2O, C_2H_5OH
2’	$[Fe(L)_2(urea)_2]Cl$	110–112	dark-brown	DMF, C_2H_5OH
3	$[Zr(urea)_6]Cl_4$	80–82	yellow-gray	H_2O, CH_3OH
3’	$[Zr_2(L)_2(urea)_4Cl_2]Cl_4$	89–91	light-brick	DMF, C_2H_5OH

The experimental results revealed that the degradation occurred in multiple stages, following a complex mechanism. For each stage the kinetic parameters and the thermogravimetric characteristics have been estimated.

The thermal decomposition is a complex process influenced by the nature of the metallic cations, which determine the reaction development in multiple stages, with different mass loss depending on their nature (Table 3).

From the data presented in Table 3 one can observe that the most important mass loss has been registered during the last stage of the thermal decomposition process, at temperatures ranging between 360 and 760°C. This last stage of the thermal degradation has a common characteristic, namely a constant conversion level and a strong thermopositive effect, which increases depending on the nature of the metallic ion, following the sequence:

$$Cr(III)>Fe(III)>Zr(IV)$$

The thermal degradation of the L1 occurs in only one stage, which starts at 160°C and ends at 520°C. According to the data from Table 3, the thermal stability of the analysed complexes, estimated by means of the starting temperature of the decomposition process, decreases as follows:

$$[Fe(L)_2(urea)_4]Cl>L1>[Zr_2(L)_2(urea)_4Cl_2]Cl_4>[Cr(L)_2(urea)_2]Cl$$

On the other hand, if one analyses the temperature domains of the thermal degradation, it is obvious that the compound $Cr(L)_2(urea)_2Cl$ has the lowest thermal degradation rate (140–650°C). In all cases, after degradation remains an amount of solid residue that ranges between 9 and 16%.

Taking into account the importance of the isoconversional methods in the thermal analysis [10, 11], we have performed the kinetic calculations by means of the method proposed by Vyazovkin *et al*. [12–14]. The dependence of the apparent activation energy, E_a, on the reacted fraction, α, is plotted in Figs 1–5. The models of the decomposition processes for every step, $f(\alpha)$ and the pre-exponential factor, $\log A$, are listed in Table 4. The apparent activation energy depends on the reacted fraction, α, revealing the complexity of thermal degradation [15, 16].

Table 3 Thermogravimetric data concerning the thermal decomposition of the ligand L1 and its complexes (10°C min^{-1})

Thermogravimetric data	Sample 1			Sample 2				Sample 3			Sample 4
	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 1
DTA characteristic data	exo	exo	exo	endo	exo	endo	exo	endo	endo	exo	exo
T_i/°C	140.00	250.00	440.00	180.00	270.0	340.00	500.00	140.00	220.00	360	160
T_m/°C	200.00	305.00	550.00	240.00	320.0	440.00	570.00	200.00	260.00	460	345
T_f/°C	250.00	440.00	650.00	270.00	340.0	500.00	655.00	220.00	360.00	540	520
The mass loss/%	26.95	24.57	33.29	24.19	13.6	15.11	37.41	13.84	35.38	40	100
Residue/%		15.19			9.69				10.78		0

Table 4 The models of the decompositions processes and the pre-exponential factors

Kinetic parameters	Sample 1			Sample 2			
	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Stage 4
$f(\alpha)$	$-\ln(1-\propto)$ first order	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order	$-\ln(1-\propto)$ first order	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order
$\log A$	15.6–21.8	19.3–31.5	24.3–40.0	17.5–24.5	21.3–26.9	24.0–38.0	31.0–44.0

Table 4 Continued

Kinetic parameters	Sample 3			Sample 4
	Stage 1	Stage 2	Stage 3	Stage 1
$f(\alpha)$	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order	$(1-\propto)^{-1}-1$ second order
$\log A$	15.7–25.6	21.3–37.8	28.0–44.0	15.8–28.2

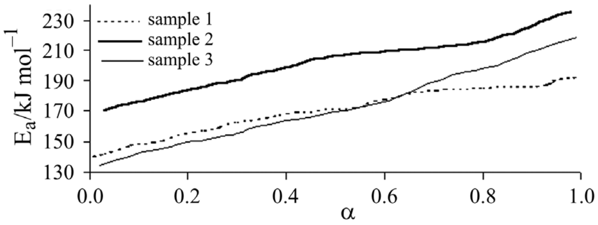


Fig. 1 The apparent activation energy as a function of the reacted fraction for the first stage of the decomposition process

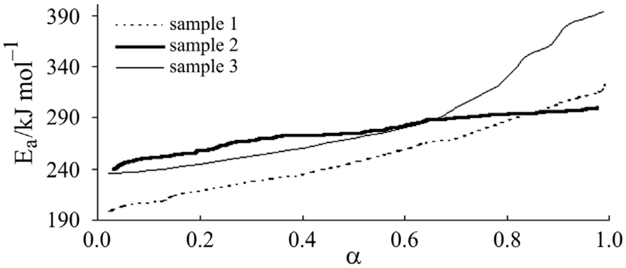


Fig. 2 The apparent activation energy as a function of the reacted fraction for the second stage of the decomposition process

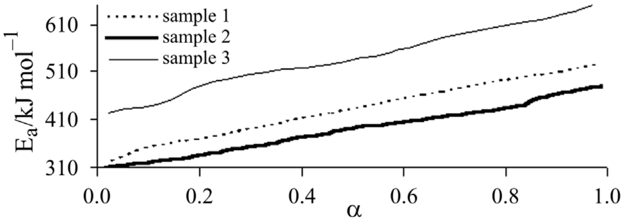


Fig. 3 The apparent activation energy as a function of the reacted fraction for the third stage of the decomposition process

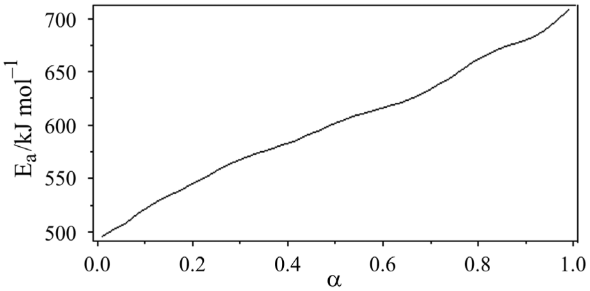


Fig. 4 The apparent activation energy as a function of the reacted fraction for the last stage of the decomposition process (sample 2)

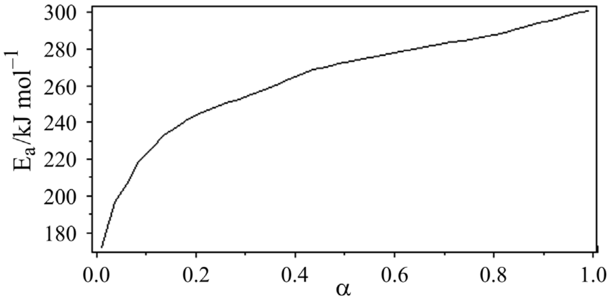


Fig. 5 The apparent activation energy as a function of the reacted fraction for the decomposition process (sample 4)

The IR absorption spectra

The IR absorption spectra were recorded for the separated complexes, urea and the ligand L1 by means of a UNICAM spectrometer within the frequency range 400–4000 cm^{-1}. The spectra were analysed and compared to those of L1 and urea. One can notice important modifications in the vibration spectra of the –NH$_2$ group from urea, as well as in those of the –OH and >c=O groups from the ligand's structure. The IR spectra of the obtained compounds present new absorption bands within the 420–490 cm^{-1} range, which are characteristic to the M–O bonds resulted from the complexing process [17–19].

X-ray diffraction spectra

The structure of the complex combinations of Cr(III), Fe(III) and Zr(IV) with this ligand has been studied by means of the X-ray diffraction (powder method) at the room temperature with a Siemens D. 500 diffractometer and nickel filter [20, 21]. The diffractograms have been recorded using CuK$_\alpha$ radiation, within the range 2–80° (2θ), at a step of 0.1° s^{-1}. Figure 6 presents the diffractograms of the complex compounds with (2-hydroxy-4-methoxy-phenyl)-phenyl-methanone.

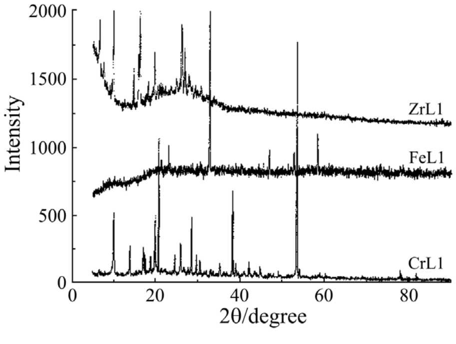


Fig. 6 The X-rays diffractograms of the complex compounds [Cr(L)$_2$(urea)$_2$]Cl, [Fe(L)$_2$(urea)$_2$]Cl and [Zr$_2$(L)$_2$(urea)$_4$Cl$_2$]Cl$_4$

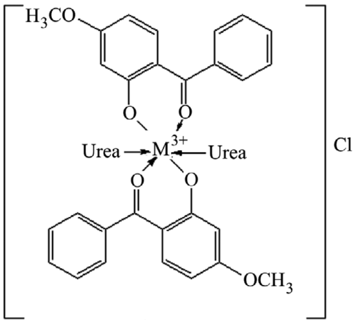
Table 5 Unit cell parameters of the synthesized complexes

Compound	Crystalline parameters			Angles			Volume/Å^3
	a/Å	*b*/Å	*c*/Å	∝	β	γ	
Cr-L1 sample 1	11.666(5)	7.484(4)	9.723(5)	90	105.105	90	819.67
Fe-L1 sample 2	17.957(6)	6.884(2)	5.484(2)	90	90	90	678.08
Zr-L1 sample 3	11.061(8)	9.6583(2)	8.624(4)	90	101.101	90	904.48

The diffractograms were indexed by means of the TREOR software [22], the results being presented in Table 5. The data indicate that the reactions between the above mentioned metallic ions and the ligand L1 occurred with the generation of the complex compounds. One can notice that these complex combinations crystallize in the orthorhombic and monoclinic systems.

Proposed structures for the obtained complexes

As it has already been shown, the newly synthesized compounds were analysed by a series of methods, including the chemical and physico-chemical analyses. At the same time, it was analysed the behaviour of these compounds in the reaction with silver nitrate. Based on the obtained data, we have proposed the following structures for the hexacoordinated complexes of the Cr^{3+}, Fe^{3+} and Zr^{4+} ions with L1 (Fig. 7).



M=Cr^{3+} and Fe^{3+}

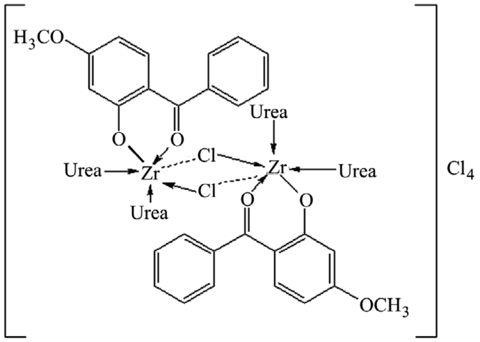


Fig. 7 The hexacoordinated structures of the synthesized complexes

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