LANTANUM AND COPPER HETEROPOLYNUCLEAR COMPOUNDS WITH OXALATE

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The following oxalate-bridged heteropoynuclear complexes $[CuLa_2(ox)_4(H_2O)_6]$ **(1),** $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ **(2)** and $[Cu_4La(ox)_{5.5}(H_2O)_8]_n$ have been synthesised and characterised. The bonding and stereochemistry of the complexes have been characterised by IR, EPR, electronic spectroscopy and conductivity measurements. The results concerning the thermal behaviour of complexes are presented. The ligand behaves as bridge for all complexes and also as chelate for complex (**1**).

Introduction

In the last few years, there has been a great deal of interest in the synthesis of complexes with polyatomic bridging ligands as oxalate anion and his derivatives. Such complexes posses interesting magnetic properties [1÷3] and can be used for preparation of mixed oxides [4÷6] or fine particles oxide ceramic materials [7÷9].

Our continuing interest in preparation of mixed oxides led us to explore the possibility to synthesise the oxalate-bridged polynuclear complexes which could generate mixed oxides by thermal decomposition. Thus, as we reported [10], the complexes of cobalt and different lantanides with oxalate generated such species.

In this paper we have extended the study to complexes of La(III) and Cu(II) with formula $[CuLa_2(ox)_4(H_2O)_6]$ **(1),** $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ (**2**) and $[Cu_4La(ox)_{5.5}(H_2O)_8]_n$ (**3**). The complexes were formulated as heteropolynuclear species on the basis of analytical, thermal and spectral data.

Experimental

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. *EPR spectra* were recorded on microcrystalline samples at room temperature with a Varian E-9 spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl (g=2.0036). *The conductivities* of 10^{-3} M methanol solutions of the compounds were measured with a Radelkis OK-120/1 (Hungary) conductivity bridge, at room temperature. *Thermal decomposition* was studied with a MOM (Budapest) derivatograph, type Paulik-Paulik-Erdey, in a static air atmosphere with a sample weight of 25 mg over the temperature range 20-800^oC at a heating rate of 10^oCmin^{-1}.

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Metal salts (Merck) were of analytical grade. The chemical analysis was performed by usual micromethods.

Preparation of the complexes (1) ÷ (3)

Compound $[CuLa_2(ox)_4(H_2O)_6]$ (**1**): To a solution of $La(NO_3)_3 \cdot 6H_2O$ (0.87g, 2 mmoles) and $Cu(NO_3)_3 \cdot 3H_2O$ (0.24g, 1 mmole) in water (25 cm^3) was slowly added oxalic acid (0.38g, 3 mmoles). The reaction mixture was then refluxed 6h until results a sparingly soluble, blue coloured product. The compound was filtered off and washed several times with a small volume of water and air dried. Analysis found: Cu, 7.4; La, 34.5; C, 10.6 %; requires for $CuLa_2C_8H_{12}O_{22}$: Cu, 7.9; La, 34.7; C, 12.0 %; Λ_M(DMF) = 8 $\Omega^{-1}cm^2mol^{-1}$ at 25^0C.

Compound $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ (**2**) : To a solution of $La(NO_3)_3 \cdot 6H_2O$ (0.43g, 1 mmole) and $Cu(NO_3)_3 \cdot 3H_2O$ (0.48g, 2 mmoles) in water (25 cm^3) was slowly added oxalic acid (0.51g, 4 mmoles). The reaction mixture was then refluxed 6h until results a sparingly soluble, blue coloured product. The compound was filtered off and washed several times with a small volume of water and air dried. Analysis found: Cu, 19.8; La, 22.4; C, 12.5 %; requires for $Cu_2LaC_7H_8O_{18}$: Cu, 19.6; La, 21.5; C, 13.0 %; Λ_M(DMF) = 0.5 $\Omega^{-1}cm^2mol^{-1}$ at 25^0C.

Compound $[Cu_4La(ox)_{5.5}(H_2O)_8]_n$ (**3**): To a solution of $La(NO_3)_3 \cdot 6H_2O$ (0.43g, 1 mmole) and $Cu(NO_3)_3 \cdot 3H_2O$ (0.96g, 4 mmoles) in water (25 cm^3) was slowly added oxalic acid (0.51g, 4mmoles) The reaction mixture was then refluxed 8h until results a sparingly soluble, blue coloured product. The compound was filtered off and washed several times with a small volume of water and air dried. Analysis found: Cu, 25.1; La, 13.4; C, 12.6 %; requires for $Cu_4LaC_{11}H_{16}O_{30}$: Cu, 24.9; La, 13.6; C, 12.9 %; Λ_M(DMF) = 14 $\Omega^{-1}cm^2mol^{-1}$ at 25^0C.

Results and discussion

In this paper, we report the preparation and physico-chemical characterisation of three new heteropolynuclear complexes $[CuLa_2(ox)_4(H_2O)_6]$ **(1),** $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ (**2**) and $[Cu_4La(ox)_{5.5}(H_2O)_8]_n$ (**3**).

By thermogravimetric analysis it was proved that all the water present in the molecule of the complexes was lost in two steps in range 60÷200^{o}C. This fact proves that coordinated water only is present in these compounds.

The oxidative degradation of the compounds is performed in three or four steps, in range 230 - 780 ^{o}C with a mixture of metal oxides as a final residue. The TG, DTG and DTA curves of the thermal degradation of compound (**2**) in air are showed in Fig. 1. The experimental mass loss is in good agreement with the theoretical value for all complexes as is showed in Tables 1÷3.

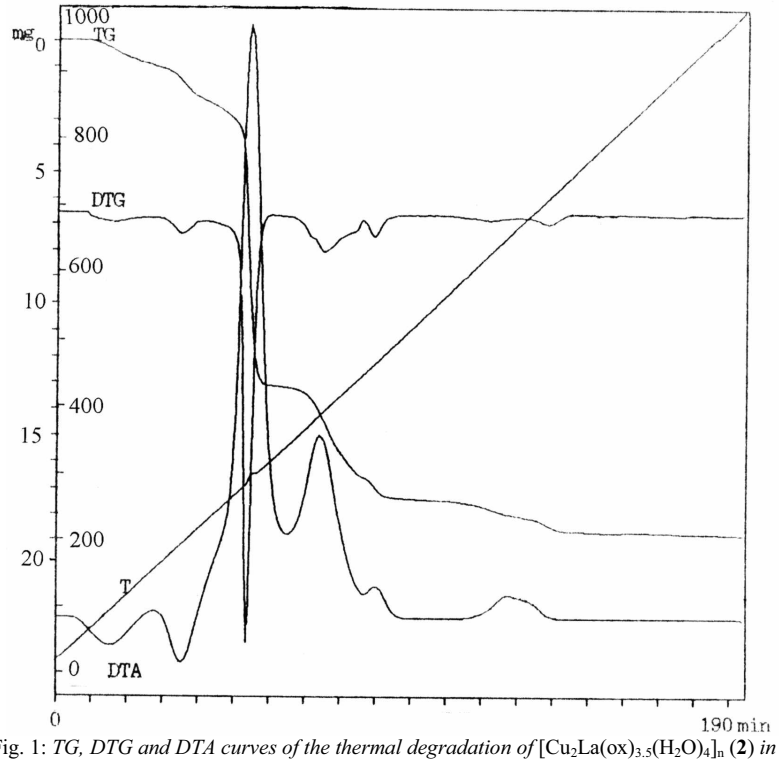


Fig. 1: *TG, DTG and DTA curves of the thermal degradation of* $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ (**2**) *in air.*

Table 1. Thermoanalytical data of the compound $[CuLa_2(ox)_4(H_2O)_6]$ (1)

Decomp. step	T_i-T_f (°C)	$T_{max(DTG)}$ (°C)	Mass loss (%) Found	Calculated	Thermal effect	Assignment
1	50-140	116	4.1	4.1	endo	$CuLa_2(ox)_4(H_2O)_4$
2	170-210	180	8.0	8.2	endo	$CuLa_2(ox)_4$
3	230-340	280	13.2	12.8	exo	$CuLa_2(CO_3)_4$
4	360-500	380	15.7	15.1	exo	$CuLa_2\ O_3(CO_3)$
5	580-780	720	4.8	5.0	exo	$CuO + La_2O_3$

Table 2. Thermoanalytical data of the compound $[Cu_2La(ox)_{3.5}(H_2O)_4]_n$ (2)

Decomp. step	T_i-T_f (°C)	$T_{max(DTG)}$ (°C)	Mass loss (%) Found	Calculated	Thermal effect	Assignment
1	60-130	95	5.5	5.6	endo	$Cu_2La(ox)_{3.5}(H_2O)_2$
2	150-210	180	5.6	5.6	endo	$Cu_2La(ox)_{3.5}$
3	260-310	290	15.3	15.2	exo	$Cu_2La(CO_3)_{3.5}$
4	360-420	390	4.6	4.6	exo	$Cu_2LaO_{2.5}(CO_3)$
5	420-500	480	3.4	3.4	exo	$Cu_2LaO_3(CO_3)_{0.5}$
6	650-750	710	3.4	3.4	exo	$1/2(4CuO + La_2O_3)$

Table 3. Thermoanalytical data of the compound $[Cu_4La(ox)_{5.5}(H_2O)_8]_n$ (3)

Decomp. step	T_i-T_f (°C)	$T_{max(DTG)}$ (°C)	Mass loss (%) Found	Calculated	Thermal effect	Assignment
1	70-130	110	7.1	7.1	endo	$Cu_4La(ox)_{5.5}(H_2O)_4$
2	150-210	180	7.2	7.1	endo	$Cu_4La(ox)_{5.5}$
3	250-285	275	15.0	15.1	exo	$Cu_4La(CO_3)_{5.5}$
4	290-340	320	6.3	6.5	exo	$Cu_4LaO_{1.5}(CO_3)_4$
5	360-470	420	6.6	6.5	exo	$Cu_4LaO_3(CO_3)_{2.5}$
6	640-740	680	10.5	10.8	exo	$1/2(8CuO + La_2O_3)$

The conductivity measurements in methanol have indicated that all complexes behave as nonelectrolytes in this solvent [11].

The most important IR absorption bands for the sodium oxalate and for the isolated complexes (**1**) ÷ (**3**) are given in the Table 4.

Table 4. Absorption maxima (cm^{-1}) and assignments for sodium oxalate and complexes (1) - (3)

Na_2ox	(**1**)	(**2**)	(**3**)	Assignments
–	3440s	3420s	3400bs	ν(OH)
–	1690vs	-	-	
1640vs	1640vs	-	–	ν_{ass} (COO)
–	1620vs	1620vs	1620vs	
-	1440s	-	-	
1355s	1370s	1365s	1360s	ν_{sym} (COO)
1316s	1315s	1320s	1320s	
740s	830m, sh 800m	830m	830m	δ(OCO)

The IR spectrum of compound (**1**) is more complex than the spectra of the complexes (**2**) and (**3**) in the ranges characteristic to the ν_{ass}(COO) and ν_{sym}(COO) vibrations.

The intense bands which appears at 1620, 1370, 1320 and respectively 830 cm^{-1} indicate the presence of oxalate anion as bridging bichelate in all complexes [12,13].

The additional bands which appear at 1690, 1640, 1440 and 800 cm^{-1} for the complex (**1**) is a proof of the oxalate ion functioning also as chelate [12].

The presence of water molecules in all compounds could be responsible for the appearance of a large strong band in the 3400÷3500 cm^{-1} range, assigned to ν(OH) stretching vibrations [14].

Electronic spectral data of the complexes (**1**)÷(**3**) are presented in Fig. 2. The electronic spectral data revealed an octahedral stereochemistry for Cu(II) in all complexes [15]. The electronic spectra of complexes are similar and show a broad band centred at 13160 cm^{-1} and shoulders at low energies.

The EPR spectrum of complexes show a wide and isothrope signal (g_i=2.171, a_T=37.6 mT) characteristic for this ion in a distorted octahedral geometry [16,17].

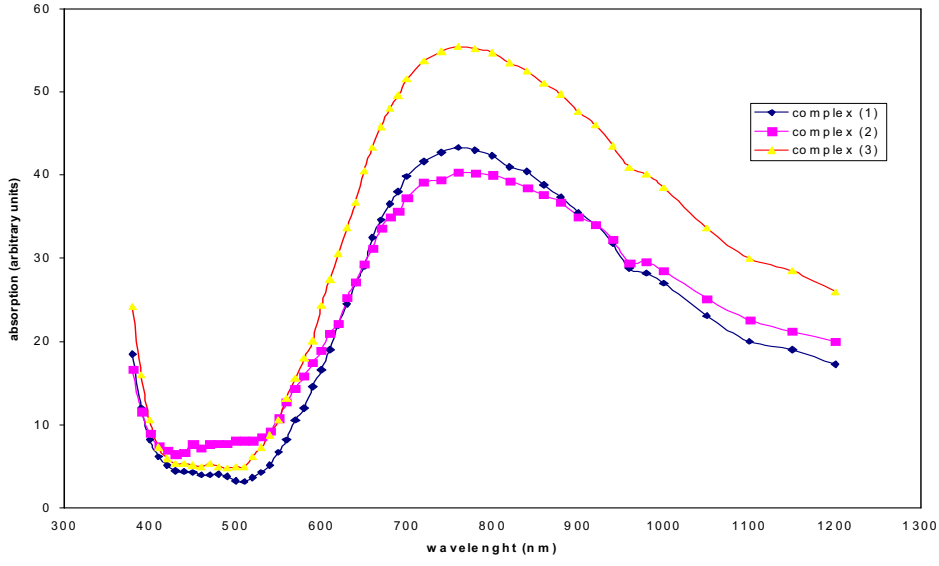
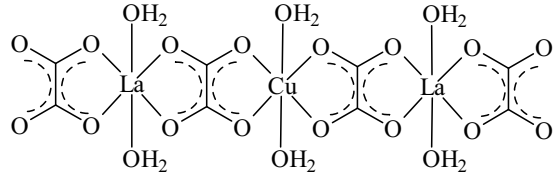
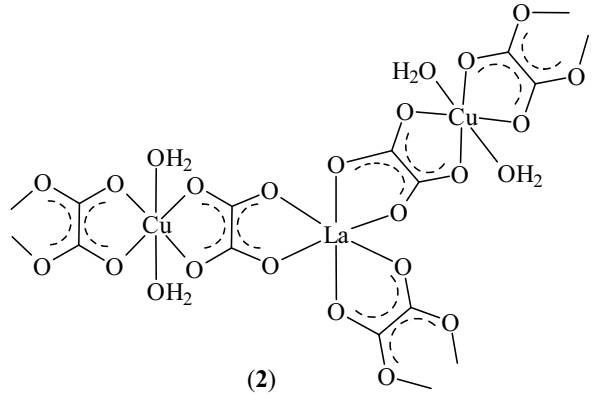


Fig.2: Electronic spectra of the complexes (1)-(3)

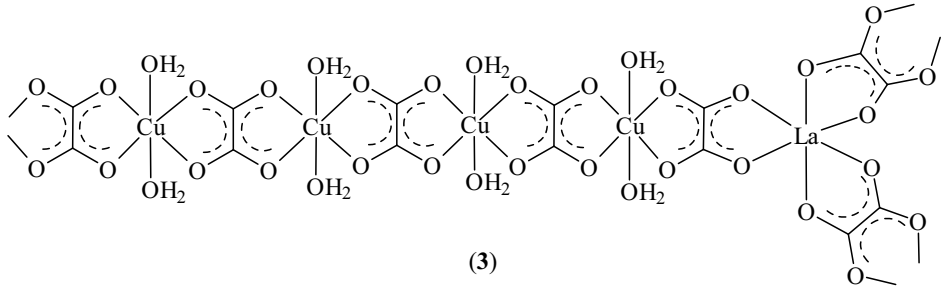
By correlating the data of chemical analysis, thermal behaviour, IR, electronic and EPR spectra, the proposed formula for the new complexes are the following:



(**1**)



(**2**)



(**3**)

Conclusions

Three new La(III) and Cu(II) heteropolinuclear complexes have been synthesised by reaction of metallic nitrates with oxalic acid.

The complexes were formulated as polinuclear species on the basis of chemical analysis, molar conductivity measurements, thermal behaviour, electronic, IR and EPR spectral data.

In all complexes the Cu(II) adopt distorted octahedral stereochemistry. The oxalate acts as bridge and as chelate respectively in the case of complex (**1**).

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