

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

NICKEL ALUMINATE SPINEL BY THERMAL DECOMPOSITION OF POLYNUCLEAR MALATE COMPLEXES

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Nickel aluminate was obtained by the thermal decomposition of three malates coordination compounds: $[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_4\text{O}_5)_2(\text{OH})_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, $[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_8\text{O}_3\text{N}_2)_4](\text{NO}_3)_8 \cdot 14\text{H}_2\text{O}$ and $(\text{NH}_4)_2[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_4\text{O}_5)_3(\text{OH})_4] \cdot 3\text{H}_2\text{O}$. These compounds were characterized by elemental chemical analysis, IR and UV-VIS spectra and thermogravimetric studies. The nickel aluminates obtained by the decomposition of these compounds were characterized by X-ray diffraction. The crystallite size ranges between 10–17 nm.

INTRODUCTION

Nickel aluminate spinel is a very important material due to its high-temperature stability and specific catalytic properties.¹⁻⁴ The preparation conditions and the calcination treatment have significant influence on the final structure and texture of the nickel aluminate spinel. This spinel can be prepared by many methods.⁵⁻¹⁰ The most general method involves solid-state reaction of metal oxides that are mechanically mixed in the form of finely divided powders.^{5,6} Some variants of the soft chemistry are also used: the coprecipitation method,⁸ the microemulsion sol-gel synthesis,^{7,10} the microwave heating,⁹ and so on. In the last years, the thermal decomposition of the polynuclear coordination compounds has been reported as a straight forward preparation process to produce homogeneous, very fine, crystalline powders.¹¹⁻¹⁷

The aim of the present study is to explore the possibilities to use the polynuclear coordination compounds with malate anions as ligands, as precursors for nickel aluminate spinel.

EXPERIMENTAL

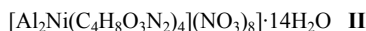
1. Synthesis of precursors

All chemicals were of reagent grade quality.



An aqueous solution containing the salts of metal ions ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is added dropwise to a solution of malic acid (the metal : ligand ratio is $2\text{Al}(\text{III}) : 1\text{Ni}(\text{II}) : 4\text{C}_4\text{H}_4\text{O}_5^{2-}$). The reaction mixture is stirred vigorously, at 80 °C, on a water bath, until a green-light compound is formed (pH ~ 2-3). The compound is filtered, washed with water and dried on P_4O_{10} .

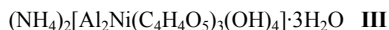
Anal. Calcd./Found: Al%:7.98/8.29; Ni%:8.71/9.06; C%:14.18/14.24; N%:4.14/3.94; H%:3.54/3.59; Ox.%:26.06/26.17



The same procedure as for compound **I** is used, but during the precipitation, the pH is adjusted until pH = 4.5-5 with an ammonium hydroxide solution 12.5%. A green compound is formed. After 24 h, this compound is filtered, washed with water and dried on P_4O_{10} .

Anal. Calcd./Found: Al%:3.86/3.60; Ni%:4.22/3.94; C%:13.73/13.82; N%:16.02/15.96; H%:4.29/4.58; Ox.%:12.66/13.06

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To the reaction mixture prepared by mixing stoichiometric quantities of aqueous solutions of the metallic salts and malic acid (2Al(III) : 1Ni(II) : 4C₄H₄O₅²⁻), 60 mL ethanol are added under constant stirring. The pH of this solution is adjusted until 4.5-5 with a 1:1 solution NH₄OH 25% / ethanol. A green-light compound is formed. After 24 h, this compound was filtered, washed with ethanol and dried on P₄O₁₀.

Anal. Calcd./Found: Al%:8.13/7.79; Ni%:8.84/8.51; C%:21.58/21.70; N%:4.19/4.15; H%:4.05/4.10; Ox. %:26.54/26.54.

2. Characterization

The polynuclear complex compounds were characterized by **elemental chemical analysis**: the metal content was determined by atomic absorption technique; the carbon, nitrogen and hydrogen content were performed by microcombustion.

IR spectra (400-4000 cm⁻¹) were recorded with a BIO – RAD FTIR 125 type spectrophotometer, in KBr pellets.

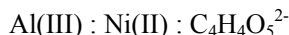
Diffuse reflectance spectra (400-1000 nm) were recorded at room temperature on a specord M-40 spectrophotometer, using MgO as standard.

The thermal measurements (TG, DTG, DTA) were performed using a Q-1500 Paulik-Paulik–Erdey derivatograph, in a static air atmosphere, with α-Al₂O₃ as the inert reference compound.

The crystalline phases in the calcinated powders were identified by **XRD powder methods** using a Rigaku-Multiflex X-Ray diffractometer (Cu K_α radiation).

RESULTS AND DISCUSSION

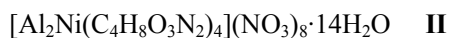
Data on the polynuclear coordination compounds of Al(III) and a 3d transition metal containing as ligands anions of hydroxycarboxylic acids are scarce.¹⁸⁻²¹ In the last 15 years, the studies concerning the formation of such species were related to the discovery that Al(III) ions are involved in biological processes.^{22,23} This is the reason why our purpose was to study the possibilities to isolate and to characterize some heteropolynuclear coordination compounds from the system:



The synthesis was carried out for a 2Al(III):1Ni(II):4C₄H₄O₅²⁻ ratio, as function of the pH-value of the reaction medium. In aqueous solution, at low value of pH (~2) one obtains compound **I**:

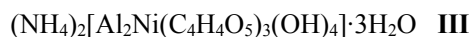


while at higher value of pH (4.5-5) compound **II** is formed:



We have also investigated the effect of the ethanol addition to the reaction mixture before the adjustment of the pH solution with an ammonia/ethanol mixture (1:1), up to the same pH ≈ 4.5-5.

The complex compound:



is isolated.

To establish the coordination of the ligands to the metallic ions, IR spectra were recorded for these compounds in the 400-4000 cm⁻¹ range (Table 1). All these spectra exhibit a strong, very wide band at ~ 3200-3400 cm⁻¹ assigned to the formation of hydrogen bonds in water. Furthermore, these spectra suggest that the malate anions are coordinated to the metal ions through both the COO⁻ and C-OH groups. The band due to the free carboxylic group (~1730 cm⁻¹) in the free acid is split, in all these compounds, into two strong bands characteristic for the coordinated carboxylic groups (ν_{OCOasym} at 1630 cm⁻¹ and ν_{OCOSym} at 1380 cm⁻¹). Also, the band assigned to ν_(C-OH) at ~1120 cm⁻¹ in the spectrum of the free acid is shifted towards lower frequencies ~1102 cm⁻¹ in all these spectra, suggesting the coordination by these groups.

In the spectrum of compound **II**, the band due to the free acid is not clear because is completely overlapped with that due to amide (-CO-NH₂), (~1760 cm⁻¹) which is formed by the reaction between the malic acid and NH₃ and confirmed by the presence of the NH vibration band (~3032 cm⁻¹). IR spectra recorded for the compounds **I** and **II**, also evidenced the presence of the NO₃⁻ ion (ν_{NO₃⁻} ~1382 cm⁻¹, 804 cm⁻¹ and 700 cm⁻¹).

Table 1
The IR spectra for malic acid and for compounds **I**, **II** and **III**

Malic acid	I	II	III	Assignment
~3400vs	3403vs	3135-3040br, s	3392vs	v(H ₂ O), v(OH)
		3132s	3204vs	v(NH) _{amide}
		3032s		v(NH ₄ ⁺)
1730vs	----	1760w	----	v(CO)
1650m	1635vs	1597m	1612vs	v(OCO) _{asym}
				v(CO) _{amide}
1440m	----	----	----	v(CO) + δ(OH)
1420m	----	----	----	δ(CH ₂) _{bond}
----	1381s	1382vs	1385vs	v(OCO) _{sym} ; v(NO ₃ ⁻) _{asym} ;
				v(NH ₄ ⁺)
1295m	----	----	----	
1270w	----	----	----	
1230w	----	----	----	
1195m	----	----	1205m	v(CC) _{asym}
1120w	1104m	1100w	1102m	v(C-OH)
1100w	1046w	1045w	1047w	
		993w	993w	
960m	----	----	959w	
935m	893w	897w	895m	
----	824w	830m	857m	v(H ₂ O), v(NO ₃ ⁻) _{sym}
760w	----	----	----	δ(COOH)
670m	720w	716w	719m	v(NO ₃ ⁻)
----	576m	530w	568w	v(MO)

vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder

[Al₂Ni(C₄H₄O₅)₂(OH)₂](NO₃)₂·8H₂O **I**

[Al₂Ni(C₄H₈O₃N₂)₄](NO₃)₈·14H₂O **II**

(NH₄)₂[Al₂Ni(C₄H₄O₅)₃(OH)₄]·3H₂O **III**

The band appearing at ~3204 cm⁻¹ in the spectrum of compound **III** is due to the presence of NH₄⁺ ion (vNH₄⁺ outer sphere). The band appearing in the range 570-600 cm⁻¹, in all these spectra can be assigned to the M-O stretching vibration.

The electronic spectra evidenced that the nickel ions exhibit an octahedral environment.²⁴ The absorption bands observed in these spectra, are presented in Table 2. In Fig. 1, the electronic spectrum recorded for the compound **II** is shown. The spectrum of the [Al₂Ni(C₄H₈O₃N₂)₄](NO₃)₈·14H₂O **II** evidences two bands, at ~670 nm and ~400 nm which may be assigned to (v₂) (³T_{1g}(F) ← ³A_{2g}) and (v₃) (³T_{1g}(P) ← ³A_{2g}), respectively, for Ni(II) (d⁸)ion in an octahedral high spin environment.

Table 2
Absorption bands in the electronic spectra of compounds **I**, **II** and **III**

Transition	I (nm)	II (nm)	III (nm)
(v ₂) ³ T _{1g} (F) ← ³ A _{2g}	660	670	668
(v ₃) ³ T _{1g} (P) ← ³ A _{2g}	400	400	390

Al₂Ni(C₄H₄O₅)₂(OH)₂] (NO₃)₂·8H₂O **I**

[Al₂Ni(C₄H₈O₃N₂)₄](NO₃)₈·14H₂O **II**

(NH₄)₂[Al₂Ni(C₄H₄O₅)₃(OH)₄]·3H₂O **III**

Given the aim of this study, the obtaining of nickel aluminate spinel–NiAl₂O₄, the thermal stability of these compounds is studied, in order to establish the optimum conditions for the obtaining of NiAl₂O₄. The three compounds underwent a multiple step decomposition in the temperature range 60-450 °C (Fig. 2a-c).

The experimental loss of mass recorded by TG measurements is 73.83/87.26/73.32% (compound **I**, **II**, **III**) in comparison with the theoretical values 73.94/87.34/73.47%. The first step (65-178 °C/79-170 °C/72-181 °C, **I/II/III**) assigned to the dehydration and/or the deamination, is followed by a decomposition process (in one step for the compounds **I** and **III** and in two steps for the compound **II**) corresponding to the ligands break-down decomposition, accompanied by NO_3^- decomposition (**I**, **II**). At ~ 450-500 °C, the crystalline lattice of the nickel aluminate is formed, but the crystallites size is very small. For this reason, a treatment of 1h/800 °C is applied.

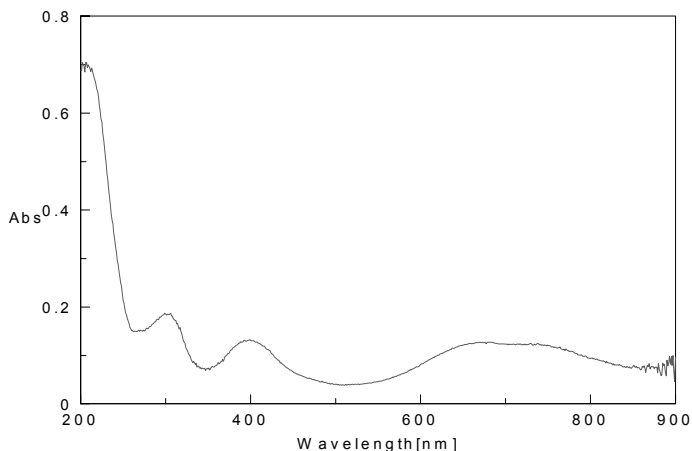


Fig. 1 – Diffuse reflectance spectrum of $[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_8\text{O}_3\text{N}_2)_4](\text{NO}_3)_8 \cdot 14\text{H}_2\text{O}$ compound.

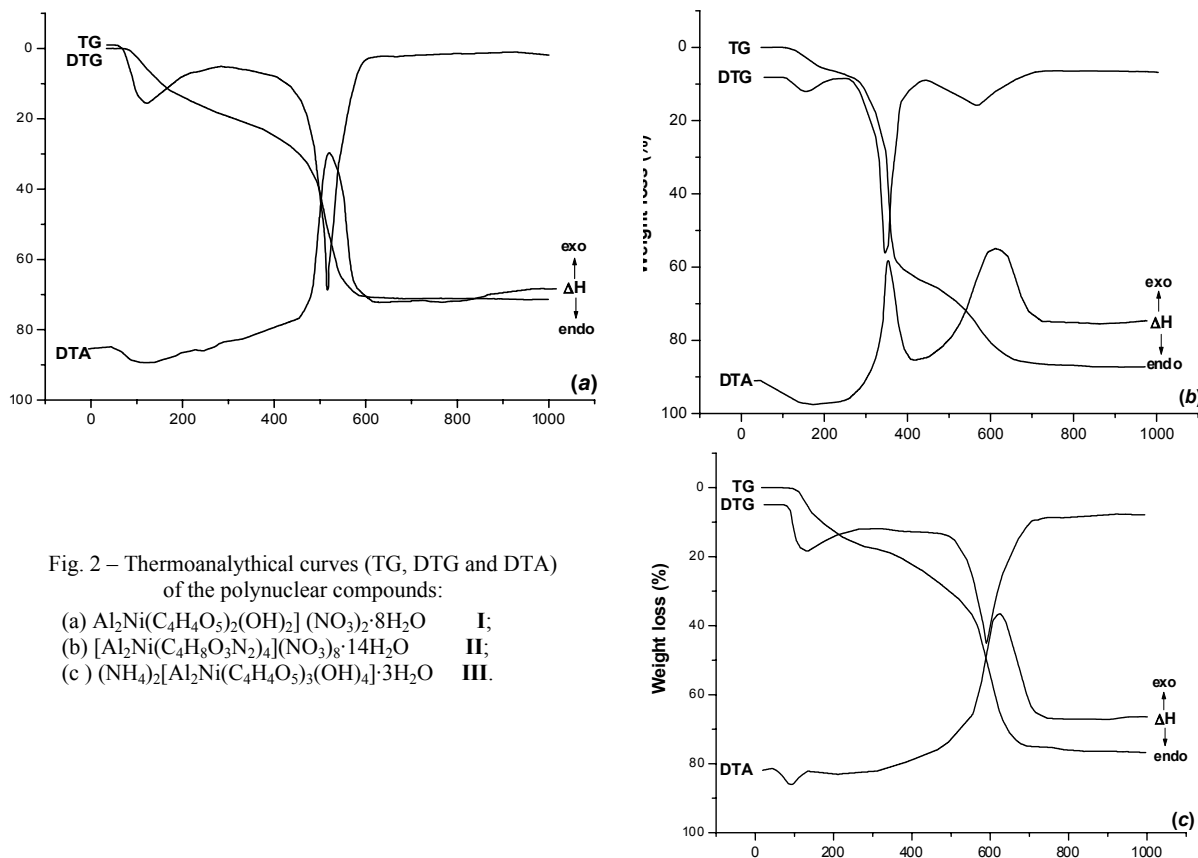


Fig. 2 – Thermoanalytical curves (TG, DTG and DTA) of the polynuclear compounds:

- (a) $\text{Al}_2\text{Ni}(\text{C}_4\text{H}_4\text{O}_5)_2(\text{OH})_2(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ **I**;
 (b) $[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_8\text{O}_3\text{N}_2)_4](\text{NO}_3)_8 \cdot 14\text{H}_2\text{O}$ **II**;
 (c) $(\text{NH}_4)_2[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_4\text{O}_5)_3(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ **III**.

The X-ray diffraction patterns of the samples evidenced the spinel nickel aluminate phase, only. For example, in Fig. 3 is presented the X-Ray diffraction pattern recorded for the NiAl_2O_4 spinel obtained by the decomposition of the compound **III**. The crystallite size of the particles ranges between 10–17 nm.

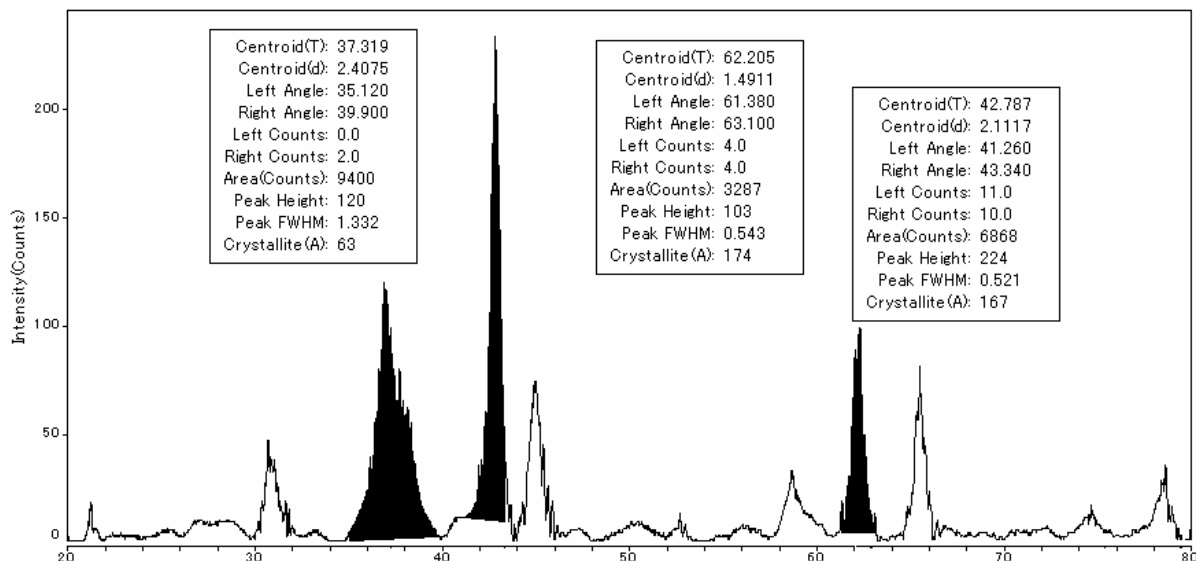


Fig. 3 – XRD pattern of NiAl_2O_4 obtained by thermal decomposition of the $(\text{NH}_4)_2[\text{Al}_2\text{Ni}(\text{C}_4\text{H}_4\text{O}_5)_3(\text{OH})_4]\cdot 3\text{H}_2\text{O}$ compound.

CONCLUSIONS

The thermal decomposition of the complex compounds of Ni(II) and Al(III) with malate anions as ligands is a promising method for the obtaining of spinel nickel aluminates. The crystallization of the spinel occurs at low temperature method, 450 °C. After a treatment of 1 h/800 °C, the well-crystallized single phase spinel is observed.

The average particle size of the aluminates ranges between 10-17 nm.

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