Synthesis, Identification and Thermal Behaviour of $[Al(C_4O_4)(OH)(H_2O)_4]_n$

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Abstract

A powder of $[Al(C_4O_4)(OH)(H_2O)_4]_n$ was obtaind by slow vaporation of nonahydrated aluminum nitrate and 3,4-dihydroxy-3-cyclobutene-1,2-dione acid in water/ethanol ratio of 1/3. The structure was determined from IR spectroscopy, elemental analyses and powder X-ray diffraction. Diffractogram indexation using Dicvol demonstrated the cell parameters: a = 10.0325 (Å), b = 8.1577 (Å), c = 11.9406 (Å), α = 89.999 (°), β = 95.836 (°), γ = 89.920 (°), V = 972.18 (Å^3) and crystallize in the triclinic crystal system, confirming isotypic phase with catena-((μ-Squarato)-tetra-aqua-hydroxy-gadolinium reported by Soumava Biswas et al(2013). Thermal gravimetric (TGA) and differential analyses (DSC) of the title compound were performed in an oxygen environment, up to 800 °C. The final decomposition product undergoes sequential phenomena in the temperatute ranging from 450°C to 800°C.

Keywords: -X-rays diffraction; IR spectroscopy; soft chmistry: TGA-DSC; Aluminium complex.

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1. Introduction

3,4-Dihydroxy-3-cyclobutene-1,2-dione acid [1-4] is one of the most often reported ligands in numerous research studies. A wide range of compounds have been designed with this ligand, many of which have vital uses. For instance, the family of hydroxo metals hydrate of this ligant with different formula $[M(OH)(C_4O_4)(H_2O)2]_2 2H_2O$, M is a trivalent chemical element, sructured in 0D dimension. This class of materials which were first produced by West and Niu in

1963 has good stability and magnetic characteristics [5-9]. The auto-stimulation of the chemical agents engaged in the contacts between the $C_4O_4^{2-}$ ligant and the trivalent cation during the formation of this molecule results in a variety of compounds belonging to the same family, where Fe, Cr, V were used as metalic cation without any complexity in reproduction.

$[Fe_3(OH)_3(C_4O_4)(C_4O_4)_{0.5}]_n$ is a three dimensional porous Coordination polymer For advanced applications, this material exhibits an anti-ferromagnetic characteristic with inclined rotation and long-range magnetic order at low temperatures [10]. The same research team reported that this material exhibits the ability to convert tetrazines into oxadiazole derivatives at room temperature using a heterogeneous catalytic approach [11].

Nevertheless, it should be mentioned that utilizing a metal cation from the lanthanide family in the production of materials can result in a wide range complexes. In 2013 SOUMARA Biswas and co-workers have synthesized a new 2D compound with Gadolinium $[Gd(C_4O_4)(OH)(H_2O)_4]_n$ which exibit a magnetocaloric effect. It can be used for magnetic refrigeration in a process known as cryogenic adiabatic degaussing, which is the highest of all MOF reported until the end of 2013 [12].

In this paper, we report mainly on the synthesis and identification of a new isomorph of $[Gd(C_4O_4)(OH)(H_2O)_4]_n$ using aluminium cation (Al^{3+}). The thermal decomposition in oxygen media leads to aluminium oxyde at 320 °C.

2. Materials and méthods

All of the chemicals used were commercially purchased (Sigma-Aldrich). The IR spectrum was captured between 4000 and 400 cm^{-1} using an FTIR-8300 CH-HMADZU spectrophotometer on a KBr pellets. Elemental analysis was carried on ZEISS EVO 15 Scaning Electron Microscope with ZEISS smart EDX. X-ray powder diffraction measurement was carried out at room temperature on the AXRD Benchtop powder diffractometer using CuKα radiation. The crystal lattice search was carried out with the Dicvol 06 program [13-14] implemented in FullProf. The program used for molecular charts is a mercury program [16]. The utilized number for the crystallographic data file (.cif) was 1194867. after having designed and optimized the geometry of the molecule by the hyperchem software [17], the formula weight was generated by the ChemSketch software [18]. Thermogravimetric analyses were performed to record simultaneous TG, DSC curves in the temperature range 20–800 °C under Oxygen atmosphere, using a LINSEIS TGA PT 1000 thermobalence.

3. Synthesis de $[Al(C_4O_4)(OH)(H_2O)_4]_n$

Aluminium hexahydrate nitrate $Al(NO_3)_3.6H_2O$ (0,1875 g) in water (10 ml) solution was added to a 3,4-Dihydroxy-3-cyclobutene-1,2-dione acid $H_2C_4O_4$ (0,62 g) in water/ethanol (1/3) (20 ml) solution. After a few drops of solution ((NaOH) 0,01g) in 15 ml of distilled water were added, the mixture was agitated for 5 minutes at 60°C. The clear solution formed has been

stirred at room temperature for 24 hours. A transparent colorless powder is formed then filtred and washed with water befor being dried. According to elemental analysis the composition found was: C(16.11%) H(3.77%) Co(20.75%) O(59.47%).

4. Caracterization of $[Al(C_4O_4)(OH)(H_2O)_4]_n$

4.1. IR Spectra caracterization

IR spectra of $[Al(C_2O_4)(OH)(H_2O)_4]_n$ given in Fig. 2 is found to show considerable similarities to those reported by west [5] and Brouca [19]. It exhibits the characteristic bands of each of the most significant functional groups related to the compound under study. The strong band of water (O-H) groups at 3301.9 cm^{-1} is ascribed to strong hydrogen bonds between the hydroxyl groups, which cause shifts in the wave number toward the low value. A strong water massif band can be found about 3031.9 cm^{-1}, as well as a sharp band around 1820 cm^{-1} that is due to υ(C=O). The carbon ring measures around 1620,1 cm^{-1} is for υ(C-O) and 1527,5 cm^{-1} is for υ(C-C), and 1114.8–1107.1 cm^{-1} assigned to a υ(C-C) [19-21], while υ(Al-O) is responsible for the band at 894.9 cm^{-1} indicating that the C=O group participates in the coordination with the Al^{3+} ion.

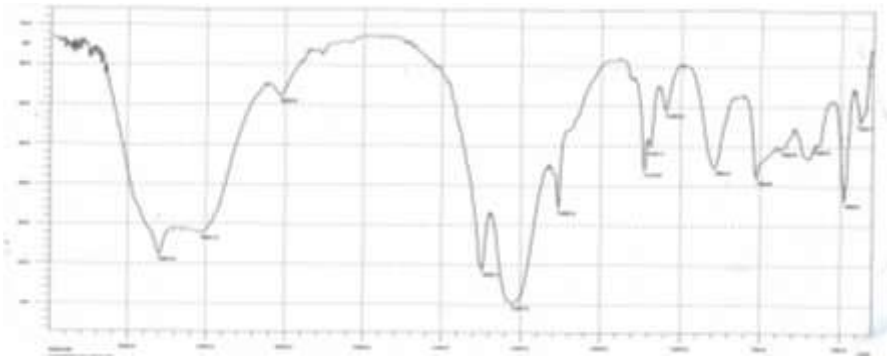


Figure 1: Ir spectra for $[Al(C_2O_4)(OH)(H_2O)_4]_n$

4.2. Powder X-ray diffraction analysis

Figure 2 schows the powder X-ray diffractogram generated for the studied simple. The indexing results of the phase related to diffraction peaks recorded out using Dicvol are listed in table 1. The result of the calculated cell parameters is in good agreement with those enregistred for $[Gd(C_2O_4)(OH)(H_2O)_4]_n$ [10] table 1. The merit factors value were M(25) = 13.6 et F(25) = 14.2(0.0067, 261) confirms the good quality and homogeneity of the product obtained.

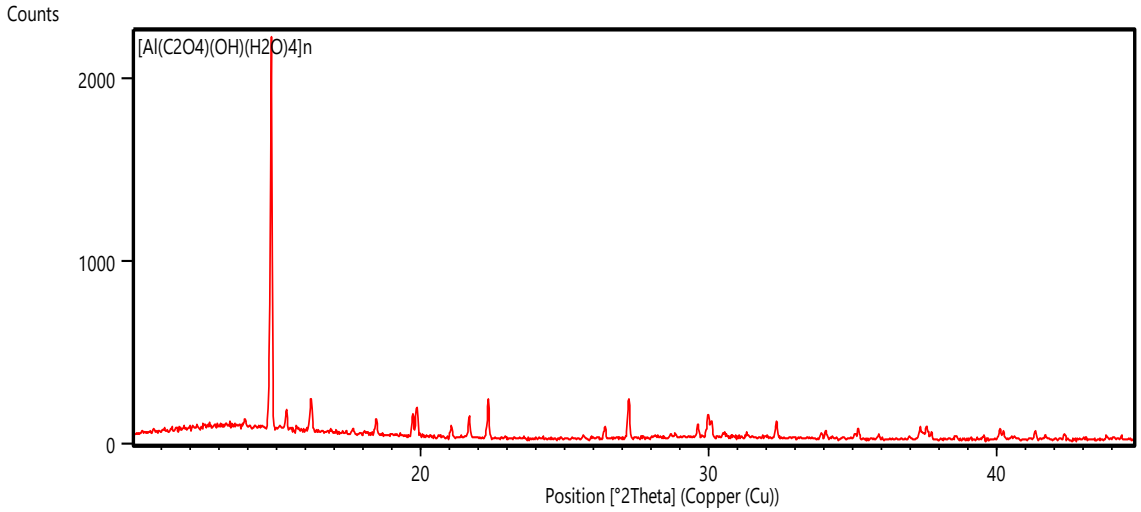


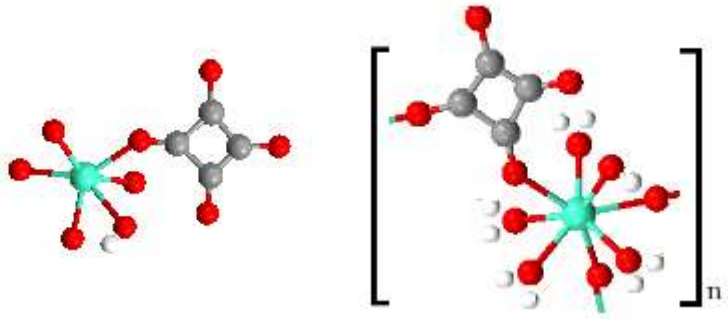
Figure 2: Experimental powder diffraction pattern of [Al(C2O4)(OH)(H2O)4]n the powder pattern

Based on the verification of the values obtained with those included in previous studies, we conclude the accuracy of the proposed chemical formula named catena-((μ-Squarato)-tetra-aqua-hydroxy-gadolinium, where gadolinium is substituted by aluminium so that the synthetized is catena-((μ-Squarato)-tetra-aqua-hydroxy-aluminium.

Table 1 : Indexing cell parameters of x-ray diffraction pattern for $[Al(C2O4)(OH)(H2O)4]_n$ synthesized and $[Gd(C2O4)(OH)(H2O)4]_n$ [10]

	a (Å)	b (Å)	c (Å)	α	β	γ	V (Å^3)	system e
$[Al(C_4O_4)(OH)(H_2O)_4]_n$	10.032	8.157	11.940	89.999	95.836	89.920	972.18	triclinic
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	11.898	8.1956	10.076	90	96.396	90	976.455	triclinic
formula weight for $[Al(C_4O_4)(OH)(H_2O)_4]_n$					263.115 g/mol			

The crystal structure with single X-rays diffraction of catena-((μ-Squarato)-tetra-aqua-hydroxy-gadolinium was already reported [10]. The asymmetric unit consists of an aluminum atom, a squarate anion $(C_4O_4)^{2-}$, an anion (OH^-) and four molecule of water figure 3- a, while, the central atom for each molecule unit is surrounded by eight oxygen atoms, three come from the squaric ligand, four from the water molecule and one from the hydroxyde ion, this system forms an antiprism around the central atom figure 3- b.



a b

Figure 3: asymetric unit and the molecule of $[Al(C2O4)(OH)(H2O)4]_n$

4.3. Thermal behavior of $[Al(C_2O_4)(OH)(H_2O)_4]_n$

The TGA curve presented in the figure 4 represents the variation of the molar mass parameter as a function of the temperature parameter. This curve is coupled to the DSC exothermic process graph. This system reveals weight loss caused by a set of crystallization water elimination chemicals followed by subsequent decomposition.

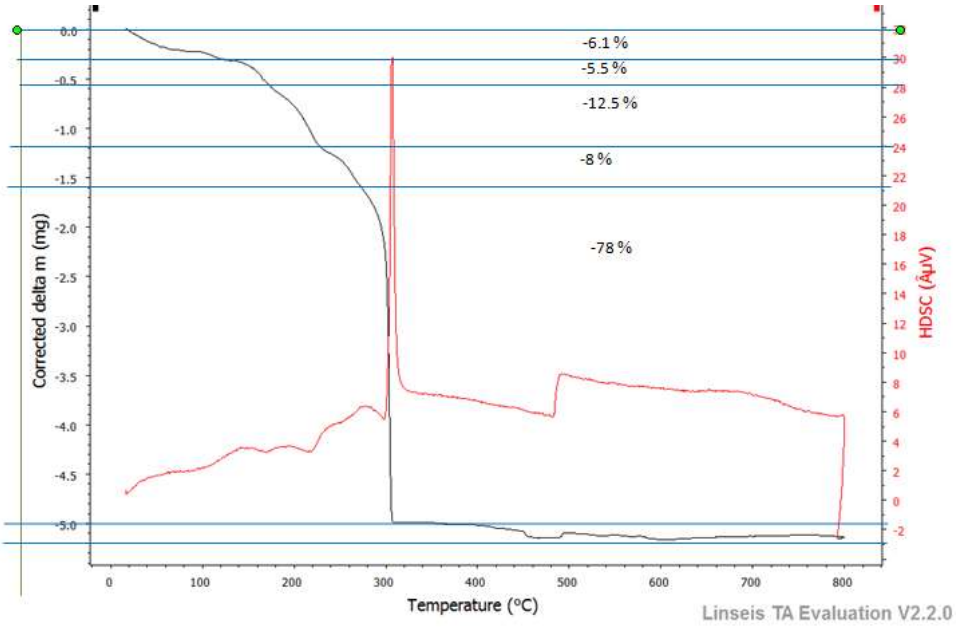


Figure 4: Thermogravimetric analysis (TGA) and DSC signal curves of $[Al(C_4O_4)(OH)(H_2O)_4]_n$

The thermal behaviour of $[Al(C_2O_4)(OH)(H_2O)_4]_n$ is shown in figure 4 On heating the compound from ambiant to 800 °C five loss mass steps are observed in the TG curves. The compound was estimated to maintain the stability of the crystalline lattice up to 20 °C. The first weight-loss region concerns the simultaneous release of one hydroxyd ion were the compound has lost 6.1 % of its global weight. The second, third and fourth degradation step concerns rapid and successive loss of mass characteristic of dehydration of coordination water molecules 5.5 %, 12.5 % and 8 % respectively accompanied with cross linking events in the DCS curves (Fig. 4) in temperature range 40 °C – 270 °C. The next stage with a strong exothermic peak on the DSC curve (DSC_{max} = 320 °C) is associated with decomposition of $C_4O_4^{2-}$ ions which is followed by a well deffind plateau observd between 320 °C -800 °C where nemourous phenomena hapened. In temperature range 320 °C – 450 °C shows thermal decomposition with formation of volatile reaction products. The breakdown of the $C_4O_4^{2-}$ anion produces CO which reacts with the oxygenated gas present in the CO2-producing medium. In the temperature range 450°C - 500°C produces an oxidation of aluminium with

5. Conclusion

Aluminium (II) complexe with 3,4-Dihydroxy-3-cyclobutene-1,2-dione acid has been synthesized. The new complex member of the family of $[Gd(C_2O_4)(OH)(H_2O)_4]_n$ with aluminium was investigated by X-ray powder diffraction analysis, FT-IR spectroscopy and elemental analysis. The thermal decomposition of [Al(C2O4)(OH)(H2O)4]n has finally been investigated, and the final residue undergoes a number of phenomena in a significant heat plateau.

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