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Investigation of Aluminum aqueous chemistry with organophosphonate ligands

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Abstract

The reaction of Al(NO3)3 with N-(phosphonomethyl)iminodiacetic acid in aqueous solution at the optimum pH 4 affords a crystalline material, which represents a new Al-organophosphate species. The isolated crystalline material was characterized by elemental analysis, spectroscopic techniques (FT-IR, NMR) and X-ray crystallography. The new species contains aluminum ions in an octahedral environment and reflect chemical reactivity of that metal ion with phosphonate-containing substrates in biologically relevant fluids.

Keywords: Aluminum(III), N-(phosphonomethyl)iminodiacetic acid

1. Introducere

Aluminum was first recognized as a human neurotoxin in 1886. Recent studies in the chemistry of aluminum, indicates that this metal ion is a potential risk factor for neurodegenerative disorders such as Alzheimer's Disease (AD) [1], dialysis related osteomalacia [2], microcytic anemia [3], etc. The brains of the patients of AD showed the typical hallmark changes, such as senile plaques and neurofibrillary tangles, the densities of which correlated roughly with aluminum levels over the age period [4]. In biological systems, Al(III) is expected to complex with oxygen donor ligands. Carboxylate and phosphonate groups, inorganic phosphate, nucleotides, and polynucleotides meet this prerequisite. It is, therefore, important to investigate the aqueous chemistry of Al(III) in the presence of functional groups that represent substrates with the chemical environment in naturally occurring proteins, peptides or other low molecular mass substrates of the peripheral blood circulation and other biological fluids.

One such representative binder is the low molecular mass ligand N-(phosphonomethyl) iminodiacetic acid (NTAP). It is a mixed carboxylate-phosphonate binder with structural characteristics encountered in phosphorous containing functional groups in various biological substrates.

2. Materials and methods

In the framework of this work, the binary system of Al(III)-NTAP was investigated synthetically in aqueous media. Under specific stoichiometric and pH conditions, and in the presence of the appropriate base, Al(III) reacted with NTAP ultimately leading to the isolation of colorless crystals of the new species of, $(NH_4)_2[Al_2(N(CH_2PO_3)(CH_2COO)_2)_2(H_2O)_2]$ (1).

The synthesis of the crystalline material 1 took place in aqueous media (the water used was of nano-pure quality). The pH value and the base had a significant role for the isolation of 1. Therefore, the pH was adjusted to a value of ~5 by the addition of aqueous ammonia. The reaction mixture was stirred in a round flask and was subsequently placed in the refrigerator at 4 °C. The stoichiometric reaction for the synthesis of complex 1 is shown below:

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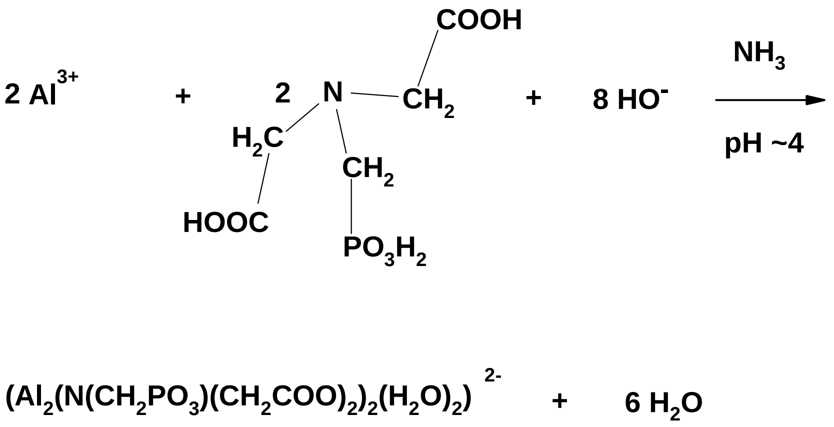

The characterization of the newly isolated species was accomplished with the use of analytical chemistry, crystallographic and spectroscopic techniques, such as FT-IR.

The FT-IR spectrum of crystalline material 1 in KBr is dominated by strong absorptions of the coordinated mixed carboxylate - phosphonate ligand in the carbonyl region. Specifically, the antisymmetric stretching vibrations νas (COO-) appear in the around 1642 cm-1, whereas the symmetric stretches νs(COO-) appear in the range 1433-1405 cm-1 for complex **1**.

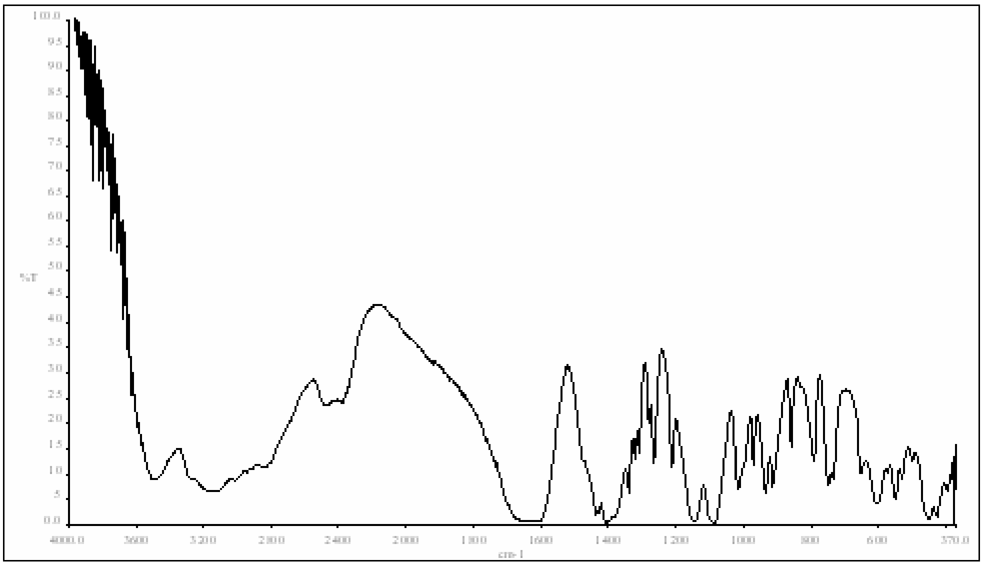

Figure 1: The FT-IR spectrum of $(NH_4)_2[Al_2(N(CH_2PO_3)(CH_2COO)_2)_2(H_2O)_2]$

X-Ray crystallography measurements provided the three dimensional structure of the investigated molecule. Complex **1** consists of a dinuclear assembly with two aluminium centers bearing two N-(phosphonomethyl) iminodiacetic acid (NTAP) ligands. Each Al(III) ion coordinates to one NTAP. Each N -(phosphonomethyl) iminodiacetic acid is fully deprotonated and is coordinated with four binding sites of Al. Furthermore, aluminum coordinates with two molecules of water. Thus, Al(III) and NTAP are coordinated in a distorted octahedral environment. Ammonia has a twofold role in this reaction.

Firstly, it adjusts the pH of the reaction mixture to deprotonate the NTAP in order to bind Al(III), and secondly it balances the charge of the arising complex.

Further characterization of the isolated complex 1 was accomplished through 13C-solution NMR and 1H-solution NMR.

3. Conclusions

The aqueous synthetic chemistry of the binary system Al(III)-organophosphonate ligand was investigated in an effort to comprehend the interaction of Al(III) with mixed carboxylate-phosphonate substrates. The data collected from the physio-chemical and spectroscopic measurements project a relevance between the chemistry of the system above and the aqueous chemistry of aluminum coordinated to low mass carboxylate-phosphonate molecules, encountered in proteins and peptides relevant to key biological functions in sensitive loci. The analysis of aluminum interactions with this type of targets, suggests crucial clues on the speciation of that metal ion with carboxylate-phosphonate substrates and its relevance to biotoxic effects relevant to processes involved in the formation of senile plaques in Alzheimer's disease.

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