*M. Daskalakis, et al. Scientifical Researches. Agroalimentary Processes and Technologies, Volume XI, No. 1 (2005), 49-52*

# STRUCTURAL SPECIATION STUDIES IN THE BINARY Al(III)-QUINIC ACID AQUEOUS SYSTEM

**M. Daskalakis,[1] C. Mateescu,[2] A. Salifoglou[3]**
[1] Department of Chemistry, University of Crete, Heraklion 71409, Greece.
[2]Faculty of Food Processing Technology, Banat University of Agricultural Sciences and Veterinary Medicine, Timisoara, Romania.
[3]Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, and Chemical Process Engineering Research Institute, Thermi, Thessaloniki 57001, Greece

## Abstract

*The importance of aqueous aluminum chemistry in biology relates to Al(III) involvement in many neurological disorders such as Alzheimer's disease (AD). The biotoxic role of this metal in neurodegeneration is widely researched nowadays with as yet ambiguous results. Therefore, the study of the aqueous chemistry of Al(III) with physiological ligands simulating proteins or peptides in the biological target area is important. An example of such a ligand is quinic acid. We have been able to synthesize, isolate and characterize the first Al(III)–quinic acid complex, $K[Al(C_7H_{11}O_6)_3]\cdot(OH)\cdot 5H_2O$, from aqueous media.*

***Key words:*** *aluminum, toxicity, quinic acid*

## Introduction

The presence of quinic acid in nature has been well established. It is present in the plant kingdom, where it constitutes a significant intermediate precursor in the synthesis of shikimic acid, which in turn is involved in the biosynthesis of various essential aminoacids and specifically the aromatic ones (Stryer, 1997). Quinic acid has two important structural features: a) it is an α-hydroxycarboxylic acid. In that respect, it is similar to carboxylic acids present in higher quantities than that in a real biological system and b) it belongs to a category of cyclic polyols, which function as calcium carriers in biological systems. A natural consequence of that is the tremendous impetus in studying the aqueous chemistry with biotoxic metal ions like

aluminum. That drive rides primarily on the chemical attributes of quinic acid of which most prominent appear to be the large number of functional groups that contain oxygen. The latter, known hard bases, constitute a natural target for the coordination of hard acids like the metal ion Al(III).

The rising interest, on the other hand, in the aqueous chemistry of Al(III) shown in the last decade or so reaches prominence with the continuing epidemiological studies showing active involvement of Al(III) in neurotoxic effects and neurodegenerative processes in which it is involved. The latter have been known to lead to biological dysfunctions and ultimately aberrant pathologies with detrimental health results. Among the commonly encountered paradigms of such pathophysiological conditions linked to Al(III) are the following neurodegenerative diseases: Alzheimer's disease (Crapper, 1976), osteomalacia (Kovalchik, 1978), microcytic anemia (Gitelman, 1989), and others.

The biotoxic role of aluminum in the case of Alzheimer's disease has been under close scrutiny, however, without any tangible evidence for a definitive cause and effect relationship between the two. It has been shown, though, that amyloid plaques and neurofibrillary tangles in Alzheimer's patients in the terminal stages of the disease are associated with high levels of Al(III) (Perl, 1985; McLachan, 1986). It is therefore very important that the aqueous structural speciation of Al(III) involved in binary and ternary systems with physiological substrates-ligands be studied, in an effort to comprehend a) the nature and distribution of soluble species arising from requisite interactions and b) the bioavailability of soluble species to which potential biotoxic effects can be ascribed. One of such systems under investigation in our labs is the binary Al(III)-quinic acid system.

## Experimental

The synthesis of the complex $K[Al(C_7H_{11}O_6)_3]\cdot(OH)\cdot 5H_2O$ was achieved in nanopure water at pH 4. The isolated crystalline product was characterized by elemental analysis, FT-IR spectroscopy, NMR and X-ray crystallography. The reaction leading to the formation and isolation of the title species is given concisely below:

$$Al(III) + 3\,C_7H_{12}O_6 \xrightarrow[pH\ 4]{KOH} [Al(C_7H_{11}O_6)_3] + 3H^+$$

## Results and Discussion

FT-IR spectroscopy was essential in pointing out the coordination of the quinic acid to the metal ion Al(III). Equally informative was X-ray crystallography. The structure shows that the species forming and eventually isolated is an octahedral Al(III) complex with three quinic acid moieties coordinated to it. More specifically, the three carboxylate groups of the corresponding ligands along with the three α-alkoxy moieties bind to Al(III) through formation of five-membered metallacycle rings.

The presence of potassium and hydroxide ions in the lattice of the title complex point out the charge consideration in the overall structural assembly of the species in question. The total charge of the complex is zero. Further evidence on the structure of the complex comes from NMR spectroscopy. The structure of the complex itself is shown in the ORTEP diagram below (Figure 1):

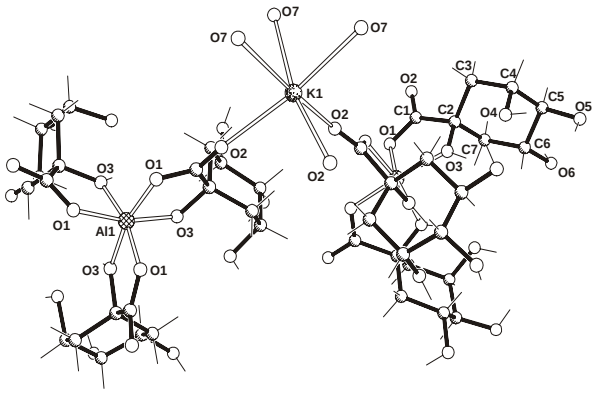


**Fig. 1.** ORTEP diagram of the $K[Al(C_7H_{11}O_6)_3]\ (OH)\cdot 5H_2O$ complex

On the basis of the initially designed reaction, a number of trials were made in the range from 3.5 to 4 and from 6.5 to 7. All of the reactions tried led ultimately to the formation and isolation of the same

product. The identity of the product was verified by FT-IR and X-ray crystallography. The isolation of the same product from variable pH specific reactions indicated the high thermodynamic stability of the complex under the experimental conditions investigated.

## Conclusions

The synthetic efforts developed in the binary aqueous Al(III)-quinic acid system denotes the underlying chemical importance of Al(III) biotoxicity. The structural attributes of the title complex $K[Al(C_7H_{11}O_6)_3]\cdot(OH)\cdot 5H_2O$ exemplifies key attributes of soluble species of Al(III) that might be involved in further potential toxic effects. Especially important is the absence of charge on the complex, which renders the species capable of expediently traversing cellular membranes and concomitantly participating in biological events of potential toxicity. Further work on the system itself through synthetic and solution speciation studies is expected to shed more light in this direction and help in the delineation of Al(III) biotoxicity.

## Acknowledgments

The authors would like to acknowledge the financial support of this project by the GSRT, Greece, for the bilateral collaboration between Greece and Romania.

## References

Crapper D. R., Krishnam S. S., Quittkat S. (1976). *Brain*, 99, 67.

Gitelman H. J., Hillel J. (1989). in "*Aluminum and Health: A Critical Review*.", Dekker, New York.

Kovalchik M. T., Kaehny W. D., Hegg A. P., Jackson J. T., Alfrey A. C. (1978). *J. Lab. Clin. Med.* 92, 712-20.

McLachan D. R. (1986). *Neurobiol. Aging,* 7, 525-532.

Perl D. P. (1985). *Envir. Health Persp.* 63, 149-153.

Stryer, L. (1997). *Biochemistry*. 2η έκδοση, University Press of Crete, Heraklion, Greece.