Journal of Molecular Structure 963 (2010) 267–273

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and structural characterization of Keggin polyoxometalate compounds with argininium(2+) cations

F.M. Santos [a], P. Brandão [a], V. Félix [a], A.M.V. Cavaleiro [a,*], E. de Matos Gomes [b], M.S. Belsley [b]

[a] Universidade de Aveiro, Departamento de Química, CICECO, 3810-193 Aveiro, Portugal
[b] Universidade do Minho, Departamento de Física, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:
Received 22 September 2009
Received in revised form 29 October 2009
Accepted 2 November 2009
Available online 6 November 2009

Keywords:
Polyoxometalate
Keggin
Heteropolyacid
L-Arginine

ABSTRACT

New organic–inorganic hybrid compounds, with formula $(H_2Arg)_3[PM_{12}O_{40}]_2{\cdot}4H_2O$ and $(H_2Arg)_4[SiM_{12}O_{40}]{\cdot}nH_2O$ (n = 0–1), where Arg = *L*-arginine and M = Mo, W, were prepared and characterized by analytical, spectroscopic, and X-ray diffraction techniques. Thermal analysis was performed to study their thermal stability. The crystal structure of $(H_2Arg)_3[PMo_{12}O_{40}]_2{\cdot}15H_2O{\cdot}EtOH$ (triclinic, space group $P1$, Z = 1) was determined by X-ray diffraction. The chiral H_2Arg^{2+} cations and the Keggin anions are involved in hydrogen bonding interactions which lead to the formation of an infinite three-dimensional network. This study adds new members to the important family of argininium/inorganic anions hybrid salts. To our best knowledge these are the first compounds of diprotonated arginine and Keggin-type polyoxoanions and also the first crystal structure determination of an argininium(2+) compound with an inorganic anion of the polyoxometalate family.

1. Introduction

L-Arginine (Arg) is an aminoacid that occurs widely in biological substances. It is also the most basic of the natural aminoacids, since it contains a terminal guanidyl group, in addition to the α-amino group. It can easily form salts through the reaction with acids, such as phosphoric, hydrofluoric and hydrochloric acids [1], which generally crystallize in non-centrosymmetric space groups, such as $P2_12_12_1$, $P2_1$ or $P1$ [1–3], due to the presence of the chiral carbon atom. These properties make *L*-arginine a natural candidate for the development of new materials since chirality plays an ever increasing role in various fields, namely catalysis, where chiral selectivity is a major goal, biomedical applications, where many biological activities involve chiral selectivity, and in materials science, where the development of accentric materials is a requirement for some optical applications.

One of the most attractive fields of current material research is nonlinear optics (NLO), due to its applications in areas like frequency shifting, signal processing, optical modulation, optical switching and others for the developing technologies in telecommunications and signal processing [4]. Considerable interest has gathered around *L*-arginine derivatives for applications in NLO ever since the properties of one of its salts, $(HArg)H_2PO_4{\cdot}H_2O$, commonly referred as *L*-arginine phosphate (LAP), were first reported by Xu et al. [2,5]. The search for new argininium salts led to the preparation and crystal structure determination of many compounds with inorganic anions and either $HArg^+$ or H_2Arg^{2+} cations. In particular, the argininediium cation has been found in several crystals formulated $(H_2Arg)X_2$, with X = F^- [6], Cl^- [3,6], Br^- [3,6], NO_3^- [6–9], IO_3^- [6,10], $H_2AsO_4^-$ [11] and $H_2PO_4^-$ [6,12,13] (a few of them hydrated).

Polyoxometalates (POMs) have attracted significant attention due to their potential application in various fields, such as catalysis, medicine, optics, electronics and magnetic materials, owing to their diverse chemical, structural and electronic properties [14]. Many POMs have been used as building blocks to construct a variety of organic–inorganic solid-state hybrid materials, following several strategies, namely the use of entities capable of acting as charge compensating cations in the synthesis of salt-like compounds and the synthesis of organically functionalized polyoxometalate clusters. Examples of the former are compounds with polyoxometalates and cationic porphyrins [15], propane sulfonate functionalized organic cations [16], surfactants [17], organic radical ions [18] and transition metal or lanthanide complex cations or coordination polymers with organic ligands [19]. Several procedures have been used for derivatization of polyoxometalates [20].

Reported association of POMs with aminoacids are a result of either (i) functionalization of the heteropolyanions with the aminoacids [21] or (ii) electrostatic and/or hydrogen bonding interactions [22]. For different purposes, materials have been prepared with the Keggin heteropolyanions ($[XM_{12}O_{40}]^{n-}$, M = Mo, W, X = P, Si, B) and several aminoacids, namely with glycine [23–26], tyrosine [27], ornithine [28], alanine [25], histidine [24], lysine [24,29], proline [30], cysteine [31] and also with aminoacidate copper complexes [32]. Only a few had their crystal structure deter-

* Corresponding author. Tel.: +351 234 370734; fax: +351 234 370084.
E-mail address: anacavaleiro@ua.pt (A.M.V. Cavaleiro).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.11.002

mined [28,30a,32a]. Compounds with *L*-arginine were referred by Hill and co-workers, that presented results on the *in vitro* antiviral activities of several compounds with Keggin anions and aminoacids, including three organic–inorganic hybrids formulated $(ArgH^+)_nH_{4-n}[SiW_{12}O_{40}]$, $(ArgH^+)_nH_{5-n}[BW_{12}O_{40}]$, and $(Arg{\cdot}H^+)_n$-$Na_{7-n}[PTi_2W_{10}O_{40}]$ [33]. To our knowledge, no other reports with Keggin anions and *L*-arginine have been published.

The research on argininium salts continues to be an interesting subject both in respect to the discovery of new crystalline supramolecular architectures (assemblies) and to the study of their properties, and this prompted us to investigate the compounds resulting from reaction of Arg and heteropolyacids. The compounds here reported have the general formula $(H_2Arg)_3[PM_{12}O_{40}]_2{\cdot}4H_2O$ and $(H_2Arg)_2[SiM_{12}O_{40}]{\cdot}nH_2O$ (M = Mo, W, n = 0–1). They were obtained through the reaction of the Keggin heteropolyacids with an acidic solution of *L*-arginine and studied by several techniques. Single crystal X-ray diffraction analysis of solvated $(H_2Arg)_3[PMo_{12}O_{40}]_2$ revealed the presence of the chiral *L*-argininediium di-cations. This study adds new members to the family of argininium hybrid salts with inorganic anions. Compounds with polyoxometalates and the argininium(2+) cation (H_2Arg^{2+}) have not been reported before.

2. Experimental

2.1. Reagents and synthetic procedures

All chemicals were reagent grade and used as received from the suppliers, including the heteropolyacids (HPA) $H_3[PM_{12}O_{40}]{\cdot}nH_2O$ and $H_4[SiM_{12}O_{40}]{\cdot}nH_2O$, n = 13–28, M = Mo, W.

2.1.1. Syntheses of the compounds

An aqueous solution of *L*-arginine in 1 M HCl was added with stirring to an aqueous solution of the chosen heteropolyacid in a molar ratio Arg/HPA equal to the anion charge (3 or 4 for P and Si anions, respectively). A precipitate immediately appeared which was filtrated, washed with ethanol and dried in a desiccator. The compounds with Mo were shown to be slightly photosensitive and, as such, were protected from light.

Crystals of $(H_2Arg)_3[PMo_{12}O_{40}]_2{\cdot}15H_2O{\cdot}EtOH$ with sufficient quality for single X-ray diffraction, were obtained by slow evaporation of the mother liquor.

*$(H_2Arg)_3[PMo_{12}O_{40}]_2{\cdot}4H_2O$ (**1**)* – Anal. (%): Found (calcd.) for $C_{18}H_{56}Mo_{24}N_{12}O_{90}P_2$: C, 5.08 (5.09), H, 1.09 (1.33), N, 3.95 (3.96), hydration H_2O, 2.2 (1.7), total weight loss %TG, 16.8 (15.3). IR (cm^{-1}): ν_{as}(P–O_a) 1063 (vs), ν_{as}(Mo–O_d) 960 (vs), ν_{as}(Mo–O_b–Mo) 869 (vs), ν_{as}(Mo–O_c–Mo) 783 (vs).

*$(H_2Arg)_3[PW_{12}O_{40}]_2{\cdot}4H_2O$ (**2**)* – Anal. (%): Found (calcd.) for $C_{18}H_{56}N_{12}O_{90}P_2W_{24}$ C, 3.40 (3.40), H, 0.79 (0.89), N, 2.65 (2.64), hydration H_2O, 1.7 (1.13), %TG, 10.4 (12.0). IR (cm^{-1}): ν_{as}(P–O_a) 1079 (vs), ν_{as}(W–O_d) 980 (vs), ν_{as}(W–O_b–W) 893 (s), ν_{as}(W–O_c–W) 800 (vs).

*$(H_2Arg)_4[SiMo_{12}O_{40}]{\cdot}H_2O$ (**3**)* – Anal. (%): Found (calcd.) for $C_{12}H_{34}Mo_{12}N_8O_{45}Si$: C, 6.52 (6.58), H, 1.37 (1.56), N, 5.05 (5.12), hydration H_2O, 0,9 (0.82), %TG, 17.8 (18.4). IR (cm^{-1}): ν_{as}(Si–O_a) 952 (vs), ν_{as}(Mo–O_d) 903 (vs), ν_{as}(Mo–O_b–Mo) 864 (m), ν_{as}(Mo–O_c–Mo) 789 (vs).

*$(H_2Arg)_4[SiW_{12}O_{40}]$ (**4**)* – Anal. (%): Found (calcd.) for $C_{12}H_{32}N_8O_{44}SiW_{12}$: C, 4.47 (4.47), H, 0.88 (1.00), N, 3.48 (3.47), %TG, 11.3 (11.9). IR (cm^{-1}): ν_{as}(Si–O_a) 921 (vs), ν_{as}(W–O_d) 970 (vs), ν_{as}(W–O_b–W) 887 (med), ν_{as}(W–O_c–W) 794 (vs).

2.2. Instrumentation and methods

C, H, N elemental analyses were performed on a Leco CHNS-932 apparatus. Thermogravimetric measurements were carried out between 30 and 600–700 °C at 5 °C min^{-1} on a TGA-50 Shimatzu thermobalance. The values of the total weight loss (%TG) were calculated assuming decomposition to a mixture of oxides at the end of the experiment.

The diffuse reflectance spectra were recorded on a Jasco V-560 spectrophotometer using MgO as reference. Samples were tested as bulk and diluted with MgO in a ratio of 4:6. The electronic absorption measurements were made on the same equipment, using dmso and aqueous solutions of approximately 0.005 mol dm^{-3}. The infrared absorption spectra were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets.

^1H and ^{31}P NMR spectra in deuterated dimethylsulfoxide, dmso-d_6, were carried out in 5 mm tubes on a Bruker AMX 300 spectrometer. Chemical shifts are reported against TMS and 85% aqueous H_3PO_4, respectively.

Powder XRD at room temperature data were collected on a X'Pert MPD Philips diffractometer, using Kα(Cu) radiation with a curved graphite monochromator, a fix incident area of 10 mm^2, and a flat plate sample holder, in a Bragg–Brentano para-focusing optics configuration. Intensity data were collected by the step counting method (step 0.02° and time 5s) in the range $3° < 2\theta < 60°$.

Optical second harmonic generation was measured on polycrystalline samples using the standard Kurtz and Perry technique [34]. The fundamental beam of a Q-switched Nd:YAG laser with a 1064 nm wavelength, energy of approximately 20 mJ, pulse duration of roughly 7 ns and a 10 Hz-repetition rate was weakly focused to a spot size of approximately 1 mm diameter on the samples. The material was particle sized using a set of standard microsieves (Retsch) having mesh width between 50 μm and 120 μm. The sample cell consisted of a microscope slide with a depression of 3 mm diameter and 0.5 mm thickness covered with a flat microscope slide. Both compounds generated second harmonic signal but after exposure to the laser beam they burn and consequently no reliable measurements could be made.

2.3. Single crystal X-ray diffraction

Crystal data of $(H_2Arg)_3[PMo_{12}O_{40}]_2{\cdot}15H_2O{\cdot}EtOH$: M_r = 4465.30, Triclinic, space group $P1$, Z = 1, a = 13.2802(3), b = 13.2864(3), c = 16.1167(4) Å, V = 2499.29(10) $Å^3$, α = 65.89(0), β = 77.83(0), γ = 76.11(1)°, ρ(calcd) = 2.983 Mg m^{-3}, μ = 3.067 mm^{-1}. 110898 reflections were collected and subsequently merged to 56606 unique reflections with a R_{int} of 0.0297.

The single crystal X-ray data was collected on a CCD Bruker APEX II at 150(2) K using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The crystal was positioned at 35 mm from the CCD and the frames were measured using a counting time of 20 s. Data reduction including a multi-scan absorption correction was carried out using the SAINT-NT from Bruker AXS. The diffraction data are consistent with both $P1$ and $P\bar{1}$ triclinic space groups. The structure solution and refinement were attempted in both spaces groups, but the structure refinement was successful in the first one. In addition, the mean of Abs($E^2 - 1$) (0.811) was consistent with the non-centrosymmetric space group. The atomic positions of the molybdenum atoms were determined by direct methods using SHELXS-97 [35]. Subsequently, the C, O, N and P atomic positions were found from successive difference Fourier Maps. The structure was refined through full-matrix least squares with SHELXL-97 [36] on F^2. Anisotropic thermal parameters were used for all non-hydrogen atoms. The N–H, O–H and C–H hydrogen atoms of the argininium cations and the ethanol solvent molecule were introduced in the refinement at calculated positions giving thermal parameters equivalent 1.2 times those of the atom to which were attached. The hydrogen atoms of the water molecules were not revealed from the last Fourier difference maps and they were not included in the structure refinement. The absolute config-