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A supramolecular structure based on copper complex of 2,3-pyridinedicarboxylic acid and 1,3-bis(3-aminopropyl) tetramethyldisiloxane chlorohydrate

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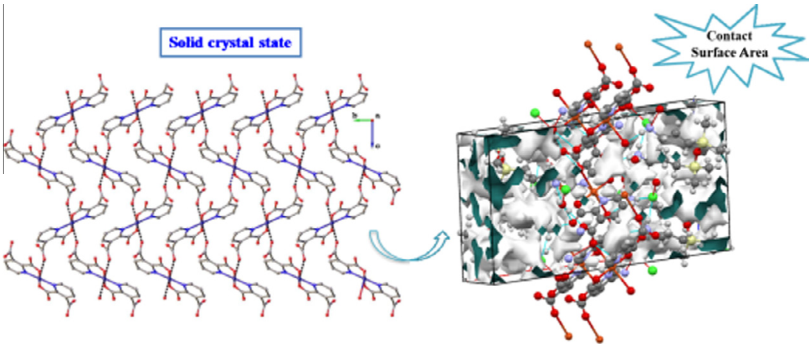
HIGHLIGHTS

- 3D supramolecular architecture built up on the basis of two complex entities was obtained.
- X-ray crystallography revealed the obtained crystalline compound to have an ionic structure.
- Complex structure preserves at heating in solid state and recovers from solution after solvent removal.
- Theoretical estimation revealed the sorption suitability for small molecules only.

GRAPHICAL ABSTRACT



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ABSTRACT

Having in mind the synthesis of a cooper complex with the product of condensation between an anhydride and a siloxane diamine as a new polydentate ligand, 2,3-pyridinedicarboxylic anhydride (PDCA) was treated first with 1,3-bis(3-aminopropyl)tetramethyldisiloxane (AP_0) and then with cooper chloride in alcoholic solution. However, according to single-crystal X-ray crystallography and IR spectroscopy, the reaction resulted in an ionic compound with the charge balance in agreement with the formation of $\mathbf{[H_2AP_0]_2[Cu(PDC)_2]{\cdot}Cl_2{\cdot}2H_2O}$ species, where PDC is a double deprotonated 2,3-pyridinedicarboxylic acid. The thermal and moisture behaviors of the complex were studied by thermogravimetrical analysis and dynamic vapor sorption, respectively. The stability of the supramolecular structure with temperature and in methanol solution was studied by ATR-FTIR analysis.

Introduction

The coordination compounds built on transition metal and multicarboxylate ligands are intensely studied due to their large potential applications. They can form extended supramolecular structures with various architectures and topologies by self-assembling of metal–organic units via hydrogen bonds and π–π interactions. The key in the designing of the desired structure is the proper selection of the metal ion and ligand. Polycarboxylic ligands are good candidates because they can function both as proton donor and as acceptor in the hydrogen bond depending on the number of the deprotonated carboxylic groups [1]. Pyridine dicarboxylic acids have proved to be interesting and important ligand because they exhibit various coordination modes [2–7]. Due to the manifold N- and O-donors of pyridine dicarboxylic ligands, these can form

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with metals versatile structural motifs, which finally aggregate to generate various supramolecular architectures with interesting properties [8]. As one of the dicarboxylate ligands, 2,3-pyridinedicarboxylic acid has drawn extensive attention [8–10]. This acid often acts as a bidentate chelating ligand through the nitrogen atom and one oxygen atom of the carboxylic group to form a discrete complex [11] and 2-D layer [12].

In this paper, our intention was to react 2,3-pyridinedicarboxylic anhydride with a siloxane diamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, and to complex the product with a copper salt, $CuCl_2$. Similar reactions between dicarboxylic acids and amine in general lead to amic acids or mixture of these with cyclic imides [13]. Due to its high reactive groups, 1,3-bis(3-aminopropyl)tetramethyldisiloxane is an important silicone derivative useful for the incorporation of the siloxane sequences in a large range of the siloxane–organic copolymers having amide [14,15], imide [16–18], or imine [19–25] internal functional groups. The last functional group mainly is very useful for the metal complexation. The presence of the highly flexible tetramethyldisiloxane moiety might confer them higher conformational flexibility useful in catalysis [26] and besides its high hydrophobicity also to increase the solubility in common organic solvents and lower the thermal transitions of the complexes thus improving their processability. The biocompatibility and physiological inertness of the siloxane is an advantage in future use of the resulted derivatives in biomedical field. The reaction product separated as a crystalline phase was characterized by spectral (FTIR and UV–Vis) methods and single crystal X-ray diffraction. The stability of the supramolecular structure with temperature as well as in methanol was studied by FTIR while the capacity of gas storage was theoretical estimated on the basis of crystallographic data.

Experimental

Materials

2,3-pyridinedicarboxylic anhydride, PDCA, (purum, ⩾98%, m.p. 136–139 °C), copper(II) chloride dihydrate, $CuCl_2{\cdot}2H_2O$ (ACS reagent, ⩾99%, m.p. 100 °C) and N,N-dimethylformamide, DMF (⩾99.8, b.p. 153 °C, density 0.944 g/mL) were purchased from Sigma-Aldrich, while 1,3-bis(3-aminopropyl)tetramethyldisiloxane, $[H_2N(CH_2)_3(CH_3)_2Si]_2O$, AP_0 (b.p. = 142 °C/11.5 mmHg, $d_{20}^{4} = 0.901$), was acquired from Fluka AG. Solvents: methanol p.a. (d^{20} = 0.792 g/mL), chloroform p.a. (d^{20} = 1.48 g/mL), were received from Chemical Company (Romania).

Measurements

Given the purpose of the paper, the following techniques were used:

FTIR spectroscopy was chosen for a primary structural characterization; because the compound was isolated as a single crystal, the structure presumed on the basis of IR spectrum could be confirmed by single-crystal X-ray diffraction. Due to the presence of supramolecular bonds emphasized by above techniques, it was of interest to study the thermal stability of the structure by using thermogravimetric analysis and ATR-FTIR spectroscopy, stability in solution (in a polar solvent, e.g., methanol) also monitored by ATR-FTIR spectroscopy, and behavior against moisture studied by water vapor sorption in dynamic mode.

Infrared spectra were recorded using a Bruker Vertex 70 FTIR spectrometer having integrated OPUS operation and evalution software, in the transmission mode (KBr pellets) between 4000 and 400 cm^{-1} at room temperature with a resolution of 2 cm^{-1} and accumulation of 32 scans. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded using a Bruker Vertex 70 FTIR spectrometer equipped with a zinc selenide (ZnSe) ATR crystal. Registrations were performed on liquid samples (0.020 g complex in 1 mL methanol) in ATR mode in the 600–4000 cm^{-1} in the room temperature −140 °C range at with a resolution of 4 cm^{-1} and accumulation of 32 scans.

The thermogravimetric (TG) – differential thermogravimetric (DTG) analysis was performed on a STA 449 F1 Jupiter NETZSCH equipment running under Proteus Software. The measurements were made in the temperature 20–700 °C range under a nitrogen flow (50 mL min^{-1}) using a heating rate of 10 °C min^{-1}. Alumina crucible was used as sample holder.

Water vapor sorption (DVS) capacity of the sample has been determined in dynamic regime in the relative humidity (RH) range 0–90% by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK). The sample was placed in a special container and dried at 25 °C in flowing nitrogen (250 mL/min) until it reaches a constant weight at RH < 1%. Then, the relative humidity (RH) was gradually increased from 0 to 90%, in 10% humidity steps, each step having a pre-established equilibrium time between 10 and 20 min so as the sorption equilibrium to be achieved every time. When RH decreased, desorption curves were recorded.

X-ray crystallography

Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo Kα radiation. Single crystals were positioned at 40 mm from the detector and 186 frames were measured each for 10 s over 1° scan. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [27]. The structure was solved by direct methods using Olex2 [28] software with the SHELXS structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-97 [29]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. All H atoms attached to carbon were introduced in idealized positions (d_{C-H} = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of the riding atom. The positional parameters of OH and NH hydrogen atoms were found from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. The molecular plots were obtained using the Olex2 program. Table 1 provides a summary of the crystallographic data together with refinement details for compounds **1**. CCDC 1002444 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Procedure

In a round bottom flask were loaded 1.073 g (7.2 mmol) of PDCA, 1 mL (0.897 g, 3.6 mmol) AP_0 and 10 mL of DMF. The mixture was stirred at room temperature for 1 h and then heated for 5 h at 140 °C after which left in rest at room temperature. The next day, the reaction mixture was distilled in vacuum to remove the solvent and other volatile fraction, eventually. The rest solid was dissolved in 12 mL methanol and then a solution consisting in 0.613 g (3.6 mmol) copper chloride and 6 mL methanol was added over it. The new resulting mixture was stirred for 5 min at room temperature and then was allowed to crystallize. Formation of blue prismatic crystals was observed after about two years. These were separated by filtration washed with methanol, dried in air and further analyzed (compound **1**), the rest being a complex mixture, amorphous, difficult to separate. Yield 1.153 g (32%).