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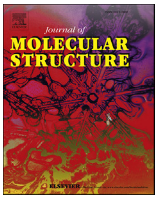

Synthesis, structural characterization, IR- and Raman spectroscopy, magnetic properties of new organically templated metal sulfates with 4-aminopyridinium

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ABSTRACT

Crystal structures of the series of twelve 4-aminopyridinium templated metal sulfates: $(C_5H_7N_2)_2[Me^{II}(H_2O)_6](SO_4)_2$ (Me^{II} = Cu (**1**), Co (**2**), Mg (**3**), Zn (**4**), Fe (**5**), Mn (**6a**)), $(C_5H_7N_2)_2[Me^{II}(H_2O)_4(SO_4)_2]\cdot 4H_2O$ (Me^{II} = Mn (**6b**), Cd (**7a**)), $(C_5H_7N_2)_2[Mn^{II}(H_2O)_4(SO_4)_2]$ (**6c**), $(C_5H_7N_2)_2[Cd(H_2O)_4(SO_4)_2]$ (**7b**), $(C_5H_7N_2)[Al(H_2O)_6](SO_4)_2\cdot 4H_2O$ (low (**8lt**) and room temperature (**8rt**) phases) and $(C_5H_7N_2)[Fe^{III}(H_2O)_4(SO_4)_2]$ (**9**) were determined by single-crystal X-ray diffraction. Compounds **1-6a** are isostructural, crystal structure consists of $[Me(H_2O)_6]^{2+}$ octahedra, 4-aminopyridinium cations (**4ap**) and sulfate anions. Crystal packing in **1-6a** series is characterized by alternating **4ap** and inorganic layers. In the structure of **1** Cu^{2+} coordination environment is axially deformed due to Jahn-Teller effect to tetragonal bipyramidal. Compounds **6** (**a**, **b**) and **7a** at ambient conditions dehydrate to produce isostructural complexes **6c** and **7b**, respectively. In structures of **6c**, **7b** and **9** sulfate anions are involved in slightly distorted octahedral metal coordination composed of six O atoms from four water molecules and two sulfate anions. Room temperature phase of **8** is characterized by disorder of **4ap** around center of inversion. Continuous phase transition at ≈185 K leads to the cell doubling and ordering of **4ap**. All of the structures are governed by an extensive three-dimensional hydrogen bond networks, as well as $\pi-\pi$ interactions visualized by Hirshfeld surface analysis. Moreover, selected compounds were characterized by the IR and Raman spectroscopy and magnetic measurement studies.

1. Introduction

Chemistry of organically templated metal sulfates (**otms**) has received increasing attention during the past two decades, which is mainly caused by their fascinating structural diversities, potential applications as precursors for oxides and catalysis, ion exchange, and also by their magnetic and luminescent properties [1–7]. A lot of research efforts are concerned with the design and prediction of new structures and materials. They include some otms with open-framework structure, which are reported to possess interesting ferroelastic and ferroelectric properties [3,8,9]. Much research has been done on the synthesis of transition and alkaline earth metal based otms with copper [4,6], cobalt [1,10], magnesium [11,12], manganese [13], cadmium [14,15], iron(II) [2,16], zinc [17], nickel [18] and aluminium [3]. The synthesis of organically templated materials often involves the employment of hydrothermal or solvothermal conditions in the presence of protonated organic amines that play the role of structure directing agents or templates. The main interactions between the organic templates and inorganic components are realized through hydrogen bonding and van der Waals forces, which are significantly weaker if compared to the ionic or covalent bonds. Nevertheless, these interactions are sufficient to provide the construction and stabilization of frameworks in these materials. Moreover, these non-covalent interactions between the organic cations and inorganic anions along with the electrostatic forces are the main factors responsible for the structural diversity of these compounds. 4-Aminopyridinium (**4ap**) cation is well known as a template in series of inorganic-organic hybrids with various halogen salts, which were found to exhibit interesting magnetic, magneto-electric and elastic properties [19–24]. To the authors best knowledge, very few reports can be found in literature that discuss crystal structure and physical properties of hybrid materials with different aminopyridinium sulfates. Even less information can be found concerning the

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synthesis and crystal structures of **4ap** sulfates and hydrogensulfates [25,26]. In case of double metal and 4ap sulfates, only one representative is known up to now, namely $(C_5H_7N_2)_2[Ni^{II}(H_2O)_6](SO_4)_2$ [27]. In current paper we report for the first time on synthesis, crystal structure and physical properties of a series of twelve new metal sulfates templated by **4ap**, with following compositions: $(C_5H_7N_2)_2[Me^{II}(H_2O)_6](SO_4)_2$ (Me^{II} = Cu (**1**), Co (**2**), Mg (**3**), Zn (**4**), Fe (**5**), Mn (**6a**)), $(C_5H_7N_2)_2[Me^{II}(H_2O)_4(SO_4)_2]\cdot 4H_2O$ (Me^{II} = Mn (**6b**), Cd (**7a**)), $(C_5H_7N_2)_2[Cd(H_2O)_4(SO_4)_2]$ (**7b**), $(C_5H_7N_2)_2[Mn^{II}(H_2O)_4(SO_4)_2]$ (**6c**), $(C_5H_7N_2)[Al(H_2O)_6](SO_4)_2\cdot 4H_2O$ ((**8rt**) and (**8lt**)), $(C_5H_7N_2)[Fe^{III}(H_2O)_4(SO_4)]$ (**9**). Moreover, single crystals of $(C_5H_7N_2)_2[Ni^{II}(H_2O)_6](SO_4)_2$ (**10**) were grown to complement the previous studies with magnetic and IR spectroscopy measurements.

2. Experimental details

All solvents and reagents are commercially available and were used without further purification. The synthetic procedure, similar for all compounds, involved a direct reaction between aqueous solutions of 4-aminopyridine and metal sulfates. The resulting solution was then neutralized by adding 30% sulfuric acid solution drop by drop. The crystallization of title compounds was achieved by slow evaporation of the solvent at room temperature during the period of several weeks. Single crystals of complexes **1**–**9**, sufficient for a good data collection, were selected under a polarized light microscope and glued onto a thin glass fibre by two-part epoxy adhesive. Crystal structure determination by X-ray diffraction data was performed on a KUMA Diffraction KM-4 four-circle single crystal diffractometer, equipped with a CCD detector, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature (at 100 K for **6b**, **7a** and **8lt**). The lattice parameters were calculated on the basis of all reflection positions. Temperature dependence of lattice parameters for **8** was measured on cooling from room temperature to 80 K performing a data collection every 10 K. Data collection and reduction were made using CrysAlis CCD and CrysAlis RED programs [28]. The crystal structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELX-2014 crystallographic software package [29]. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms of the amines were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed geometrically. The hydrogen atoms of the water molecules were located from difference Fourier maps and were refined with O–H distances equal to 0.84 Å and $U_{iso}(H) = 1.5\ U_{eq}(O)$. Details on the single-crystal XRD data collection, reduction and structure parameters for complexes **1**–**9** are gathered in Tables 1 and 2. Selected bond distances are listed in Tables S1–13 and hydrogen bonding parameters are given in Tables S14–S26. Powder XRD diffraction patterns were obtained with an X'Pert PRO PANalitycal diffractometer equipped with Cu Kα (λ = 1.5418 Å) radiation at room temperature. Data was collected in the range of $5° \leq 2\theta \leq 70°$. The experimental XRD powder patterns of the bulk samples show no evidence of impurities and are in good agreement with those simulated on the basis of the single crystal structures. As apparent, it serves as a firm confirmation of the phase purity of the bulk samples (Fig. S1–S10). Infrared spectra of powdered samples (in Nujol oil with KBr windows) were recorded at room temperature with a Bruker IFS-88 spectrometer over the wavenumber range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. Room temperature FT-Raman spectra were measured in the 3600–80 cm^{-1} range using Bruker FRA-106 attachment with 4 cm^{-1} spectral resolution, averaging 256 scans. Magnetization and magnetic susceptibility measurements were performed on powdered single crystals packed in gelatine capsules in 1.8–300 K temperature interval and in magnetic fields up to 5 T using a Quantum Design MPMS-7 SQUID magnetometer. Differential Scanning Calorimetry (DSC) analysis was performed using Perkin-Elmer DSC-7 calorimeter equipped with a CCA-7 low temperature attachment. Microscopy analysis was performed with a Philips SEM 515 microscope equipped with an EDAX 9800 spectrometer (30 kV, linear resolution 5 nm).

3. Results and discussion

3.1. Synthesis

The synthetic procedures were, for the most part, carried out for all the systems in a similar manner. Continuous magnetic stirring was applied throughout the whole syntheses. For the preparation of compounds **1**-**5**, **6** (**a**, **b**, and **c**), **7** (**a** and **b**) and **10** 0.2353 g (2.5 mmol) of 4-aminopyridine was dissolved in water (5 ml). After that, aqueous solutions of metal sulfates (1.25 mmol, 5 ml) were added to the initial solution, followed by an intensive stirring of the mixture at 40 °C for a few minutes. Then, a 30% solution of H_2SO_4 was added dropwise until a clear solution was formed (until a complete dissolution of the precipitate and disappearance of turbidity). In case of compounds **6a** and **6b**, the resultant solution was additionally filtered to eliminate a small fraction of precipitate and then left at room temperature. For the phase **6c** the aqueous filtrate was heated to the temperature 70–90° C and left for several hours. Phase **7b** was obtained in the same manner as phase **6c**. The final values of pH were 3.5, 7, 3.5, 3.5, 3, 4, 6 and 6 for **1**, **2**, **3**, **4**, **5**, **6** (**a**, **b** and **c**), **7** (**a** and **b**) and **10**, respectively. Compounds **8** and **9** were prepared by direct reaction between the solutions of 4-aminopyridine (2 mmol) and metal sulfate (2 mmol) in distilled water (10 ml). By the addition of 30% sulfuric acid, the pH was adjusted to 6.5 and 3.5 for **8** and **9**, respectively.

3.2. Description of the structure of compounds 1-9

The reported compounds crystallize in six types of the crystal structures: type **I** structures of $(C_5H_7N_2)_2[Me^{II}(H_2O)_6](SO_4)_2$ (Me^{II} = Cu (**1**), Co (**2**), Mg (**3**), Zn (**4**), Fe (**5**), Mn (**6a**)) composition, type **II** – $(C_5H_7N_2)_2[Me^{II}(H_2O)_4(SO_4)_2]\cdot 4H_2O$ (Me^{II} = Mn (**6b**), Cd (**7a**)), type **III** – $(C_5H_7N_2)_2[Cd(H_2O)_4(SO_4)_2]$ (**7b**), type **IV** – $(C_5H_7N_2)_2[Mn^{II}(H_2O)_4(SO_4)_2]$ (**6c**), type **V** – $(C_5H_7N_2)[Al(H_2O)_6](SO_4)_2\cdot 4H_2O$ ((**8lt**) and (**8rt**)) and type **VI** – $(C_5H_7N_2)[Fe^{III}(H_2O)_4(SO_4)_2]$ (**9**).

3.2.1. Structure of compound series 1-6a

Crystal structures of compounds **1**–**6a** (type **I**) are composed of **4ap** cations, which were formed through a proton transfer from the sulfuric acid to pyridine nitrogen atom of 4-aminopyridine, isolated sulfate anions and $[Me(H_2O)_6]^{2+}$ (Me^{II} = Cu (**1**), Co (**2**), Mg (**3**), Zn (**4**), Fe (**5**), Mn (**6a**)) octahedra (Fig. 1). In compound **1** the Cu^{2+} cation is positioned on the inversion center and is surrounded by six O atoms of six water molecules with the Cu–O bonds of 1.9778(13), 2.0364(14) and 2.2483(17) Å, forming a distorted tetragonal bipyramid, $[Cu(H_2O)_6]^{2+}$, which is markedly elongated to both apices due to the Jahn-Teller effect of the Cu^{2+} cation. The coordination polyhedra around the metal centers in **2**-**6a** are also formed by six aqua ligands, but in a slightly distorted octahedral geometry with similar *Me*–O bond lengths: 2.0577(12)–2.1081(15), 2.0516(12)–2.0671(14), 2.0740(12)–2.1170(14), 2.0864(17)–2.1401(18) and 2.1629(12)–2.1871(15) Å for compound **2**, **3**, **4**, **5** and **6a**, respectively. Crystal packing is characterized by diverse network of hydrogen bonding interactions (Fig. 2). The crystal structures of **1**-**6a** are isotypic with the Ni analogue [27]. The