Synthesis, Crystal Structures and Properties of Three New Tetrathiomolybdates with Organic Ammonium Cations

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Three new tetrathiomolybdates ($pipH_2$)[MoS_4] (**1**), ($trenH_2$)[MoS_4]·H_2O (**2**) and [$(prop)_4N]_2$-[MoS_4] (**3**) (pip = piperazine, tren = tris(2-aminoethyl)amine and prop = *n*-propyl) were synthesized and characterized by elemental analysis, infrared spectroscopy, single crystal X-ray crystallography, and thermoanalysis. All compounds were prepared by the base promoted cation exchange method, *i.e.* by the reaction of the ammonium salt of $[MoS_4]^{2-}$ with the corresponding organic amine or organic ammonium hydroxide. In the compounds **1** and **2** the organic amines pip and tren are diprotonated and they are linked to the tetrahedral $[MoS_4]^{2-}$ dianions through weak hydrogen bonding interactions. The strength and number of these hydrogen bonds affect the Mo-S bond lengths and a relatively long Mo-S bond of 2.2114(8) Å is observed in **1** while the longest Mo-S bond in **2** is 2.1951(5) Å. In compound **3** no S···H-N interactions are possible and the Mo-S bond lengths scatter in a more narrow range compared to those in compounds **1** and **2**. The thermal behavior was investigated using differential thermal analysis and thermogravimetry. On heating compound **1** decomposes in two closely related steps while **2** loses first the crystal water followed by the decomposition of the tetrathiomolybdate. The final products are amorphous molybdenum sulfides. The decomposition of compound **3** yields a very porous material with sponge-like morphology.

Key words: Thiomolybdates, Crystal Structures, Thermal Properties, Optical Properties