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

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Dedicated to Prof. Dr. Wilhelm Preetz on the occasion of his 70th birthday

Three new tetrathiomolybdates (pipH₂)[MoS₄] (1), (trenH₂)[MoS₄]·H₂O (2) and [(prop)₄N]₂-[MoS₄] (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 [MoS₄]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 [MoS₄]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