Synthesis, Spectroscopic and X-Ray Structure Characterisation of Bis(tetramethylammonium) and Bis(tetra-*n*-butylammonium) Tetrathiomolybdates

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The new tetraalkylammonium tetrathiomolybdates $(Me_4N)_2[MoS_4]$ (**1**) and $(nBu_4N)_2[MoS_4]$ (**2**) were prepared *via* a direct salt substitution using $(NH_4)_2[MoS_4]$ as starting material. Compound **1** crystallises in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with a = 8.9233(4), b = 15.5210(9) and c = 37.255(3) Å. Compound **2** crystallises in the orthorhombic space group $Fdd2$ with a = 28.9142(18), b = 35.7811(10) and c = 15.6774(17) Å. The structures of both compounds consist of slightly distorted $[MoS_4]^{2-}$ tetrahedra and tetraalkylammonium cations which are packed in different ways. Single crystals of $(Et_4N)_2[MoS_4]$ (**3**) were also investigated giving the lattice parameters a = 14.0346(7) and c = 12.5143(8) Å. A very strong disorder prevented a successful structure refinement and only the anion and one cation could be located. It is remarkable that the disorder of parts of the alkyl groups decreases with increasing chain length, in correlation with the IR and Raman vibrations of the $[MoS_4]^{2-}$ tetrahedron showing a slight shift to lower energy with increasing alkyl chain length. The most prominent IR band of $[MoS_4]^{2-}$ is broad but not split, indicating that the distortion of the tetrahedra is small.

Key words: Crystal Structure, Tetrathiomolybdates, IR and Raman Spectroscopy