

Synthesis and Structural Characterization of [Me₄N]₂[W₂O₂(μ-S)(η²-S₂)₄]·MeCN, a Novel Oxo-thiotungstate(VI)

A. B. M. Shamsur Rahman, H. Boller, and K. O. Klepp*

Department of General and Inorganic Chemistry, Johannes Kepler University Linz,
Altenbergerstrasse 69, A-4040 Linz, Austria

* Reprint requests to Prof. Dr. Kurt O. Klepp. Phone & Fax: +43 732 2468 800.

E-mail: kurt.klepp@jk.uni-linz.ac.at

Z. Naturforsch. **54 b**, 1318–1322 (1999); received April 19, 1999

Crystal Structure, IR Data, Chalcogenides, Complex Sulfides, Tungsten Compounds

Orange red crystals of the new compound [Me₄N]₂[W₂O₂(μ-S₂)(η²-S₂)₄]·MeCN were obtained from the reaction of a solution of [Me₄N]₂[WOS₃] in MeCN with solid AuCN at room temperature. They are monoclinic, space group P2₁/n, with $a = 9.264(2)$, $b = 17.736(3)$, $c = 18.742(5)$ Å, $\beta = 95.19(1)^\circ$; $Z = 4$. The crystal structure was determined from single crystal diffractometer data (MoK α -radiation) and refined to $R = 0.050$ (2955 reflections, 221 variable parameters). It is characterized by binuclear complex anions [(S₂)₂O₂WSWO(S₂)₂]²⁻ with close to C₂ symmetry. Each metal center is surrounded by two end-on coordinating disulfide groups at distances ranging from 2.37 to 2.42 Å which together with a bridging sulfur atom ($\bar{d}_{W-S} = 2.445$ Å) occupy the equatorial positions of a pentagonal bipyramid whose apices are defined by a terminal oxygen atom ($\bar{d}_{W-O} \sim 1.725$ Å) and one sulfur atom of the neighboring component at a distinctly larger distance ($\bar{d}_{W-S} \sim 2.82$ Å).

Infrared spectra of the complex (KBr powder) showed $\nu(W-O)$ and $\nu(W-S)$ of bridging W-S-W at 931 (vs) and 454 (m) cm⁻¹, respectively, $\nu(W-S)$ of the WS₂ unit appeared in the range between 465 and 438 cm⁻¹. The mass spectrum of the anion showed the molecular mass at m/z 688 for [W₂O₂S₉]⁻ as well as peaks for other fragments.