

# Gemischte Alkalimetall-Oxidosulfidomolybdate $A_2[\text{MoO}_x\text{S}_{4-x}]$

( $x = 1, 2, 3$ ;  $A = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ ).

## Synthesen, Kristallstrukturen und Eigenschaften

Mixed Alkali Oxidosulfidomolybdates  $A_2[\text{MoO}_x\text{S}_{4-x}]$  ( $x = 1, 2, 3$ ;  $A = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ ).

Synthesis, Crystal Structure and Properties

Anna J. Lehner, Korina Kraut und Caroline Röhr

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21,  
79104 Freiburg, Germany

Reprint requests to Prof. Dr. C. Röhr. E-mail: caroline@ruby.chemie.uni-freiburg.de

*Z. Naturforsch.* **2012**, *67b*, 127 – 148; received January 16, 2012

Mixed sulfido/oxidomolybdate anions  $[\text{MoO}_x\text{S}_{4-x}]^{2-}$  ( $x = 1, 2, 3$ ) have been prepared by passing  $\text{H}_2\text{S}$  gas through a solution of oxidomolybdates. The alkali salts of  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{NH}_4^+$  precipitate as crystalline salts from these solutions depending on the pH, the polarity of the solvent, the educt concentrations and the temperature. Their structures have been determined by means of X-ray single-crystal diffraction data. All trisulfidomolybdates  $A_2[\text{MoOS}_3]$  ( $A = \text{NH}_4/\text{K}/\text{Rb}/\text{Cs}$ ) are isotypic with the tetrasulfido salts, exhibiting the  $\beta\text{-K}_2[\text{SO}_4]$  type (orthorhombic, space group  $Pnma$ ,  $Z = 4$ ; for  $A = \text{Rb}$ :  $a = 940.62(4)$ ,  $b = 713.32(4)$ ,  $c = 1164.56(5)$  pm,  $R1 = 0.0281$ ). In contrast, the disulfidomolybdates exhibit a rich crystal chemistry, forming three different structure types depending on the preparation conditions and the size of the  $A$  cation: All four cations form salts crystallizing with the  $(\text{NH}_4)_2[\text{WO}_3\text{S}_2]$  structure type (monoclinic, space group  $C2/c$ ,  $Z = 4$ , for  $A = \text{Rb}$ :  $a = 1144.32(11)$ ,  $b = 732.60(4)$ ,  $c = 978.99(10)$  pm,  $\beta = 120.324(7)^\circ$ ,  $R1 = 0.0274$ ). For the three alkali metal cations a second polymorph with a new structure type (monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ) is observed in addition (for  $A = \text{Rb}$ :  $a = 674.83(2)$ ,  $b = 852.98(3)$ ,  $c = 1383.10(9)$  pm,  $\beta = 115.19(1)^\circ$ ,  $R1 = 0.0216$ ). The cesium salt also crystallizes with a third modification of another new structure type (orthorhombic, space group  $Pbcn$ ,  $Z = 4$ ,  $a = 915.30(6)$ ,  $b = 777.27(7)$ ,  $c = 1120.02(7)$  pm,  $R1 = 0.0350$ ). Only for  $\text{K}$ , an anhydrous monosulfidomolybdate could be obtained ( $\text{K}_2[\text{MoO}_4]$  structure type, monoclinic, space group  $C2/m$ ,  $Z = 4$ ,  $a = 1288.7(3)$ ,  $b = 615.7(2)$ ,  $c = 762.2(1)$  pm,  $\beta = 109.59(1)^\circ$ ,  $R1 = 0.0736$ ). The intramolecular chemical bonding in the molybdate anions is discussed and compared with the respective vanadates. Hereby aspects like bond lengths, bond strengths and force constants derived from Raman spectroscopy, are taken into account. Especially for the polymorphic disulfido salts, in-depth analyses of the local coordination numbers and the packing of the ions are presented. The gradual bathochromic shift of the crystal color with increasing  $S$  content and increasing size of the counter cations  $A$  and molar volumes (for the polymorphic forms), respectively, is in accordance with the increase of the experimental (UV/Vis spectroscopy) and calculated (FP-LAPW band structure theory) band gaps.

*Key words:* Oxidosulfidometallates, Thiooxomolybdates, Molybdates, Crystal Structure