

MS30-P9 Na₃CoS₃: A new sulfido cobaltate with simple formula, but complex structure

Pirmin Stübtle¹, Jan Kägi¹, Caroline Röhr¹

¹ Albert-Ludwigs-Universität Freiburg, Germany

email: pirmin@pyrite.chemie.uni-freiburg.de

Alkali sulfido metallates have been extensively investigated by the Bronger group in the 1980s [1]. In the case of the sodium cobaltates, Na₆[CoS₄] containing isolated tetrahedra [2], and the chain compounds Na₂[CoS₂] [3] and Na₂[Co₂S₄][S] [4] are the only compounds obtained in these studies.

Applying an alternative synthetic route in directly reacting the pure transition metals and elemental sulfur with the alkali metals (or their previously prepared sulfides), the structure family of the respective ferrates has been substantially extended in the last years [5-6]. Accordingly, the new sulfido cobaltate(II) Na₃CoS₃, which forms dark grey xenomorphic crystals, was synthesized from the pure elements, with a small amount of CoS₂ and Na₆[CoS₄] as by-products, in melt flux reactions from a sulfur rich sample with the composition like e.g. Na:Co:S = 2.4:1:6.6 at a maximum temperature of 760 °C.

Contrary to the initial assumption based on the formula, the new compound does not contain Co(III), but is a quite complex sulfido cobaltate(II), which exhibits both sulfido and disulfido ligands besides each other. According to Na₁₂[Co₂S₇][Co₂S₅], the acentric orthorhombic structure (space group *Cmc*2₁) with a large unit cell (*a*=884.24(2), *b*=2177.38(5), *c*=1193.20(3) pm, *Z*=12), which has been determined by mean of single crystal X-ray data (*R*₁=0.0205), contains two different, both yet unknown sulfido cobaltate ions: The oligomeric anions [Co₂S₇]⁸⁻ are built up from two edges sharing [CoS₄] tetrahedra. In contrast to common disulfido metallates, one of the terminal sulfido ligands S²⁻ is substituted by a η¹-disulfido ligand S₂²⁻ ([Co₂S₅(S₂)]⁸⁻). Chains of [CoS₄] tetrahedra, which are alternatingly connected via edges and corners, form the second building block. Herein, the disulfido ions as μ²-ligands are connecting two corner-sharing tetrahedra. Similar anions are yet only observed in the selenido gallate Cs₂Ga₂Se₅ [7]. The seven different Na cations are arranged inbetween the layers at heights *x* = 1/4 and 3/4 (CN= 5 - 8).

[1] W. Bronger, *Angew. Chem. Int. Ed. Engl.* **20**, 52 (1981).

[2] K. Klepp, W. Bronger, *Z. Naturforsch.* **38b**, 12 (1983).

[3] K. O. Klepp, W. Bronger, *J. Less-Common Met.* **98**, 165 (1984).

[4] W. Bronger, C. Bomba, *J. Less-Common Met.* **158**, 169 (1990).

[5] M. Schwarz, C. Röhr, *Inorg. Chem.* **54**, 1038 (2015).

[6] M. Schwarz, M. Haas, C. Röhr, *Z. Anorg. Allg. Chem.* **639**, 360 (2013).

[7] D. Friedrich, M. Schlosser, A. Pfitzner, *Z. Anorg. Allg. Chem.* **640**, 826 (2014).

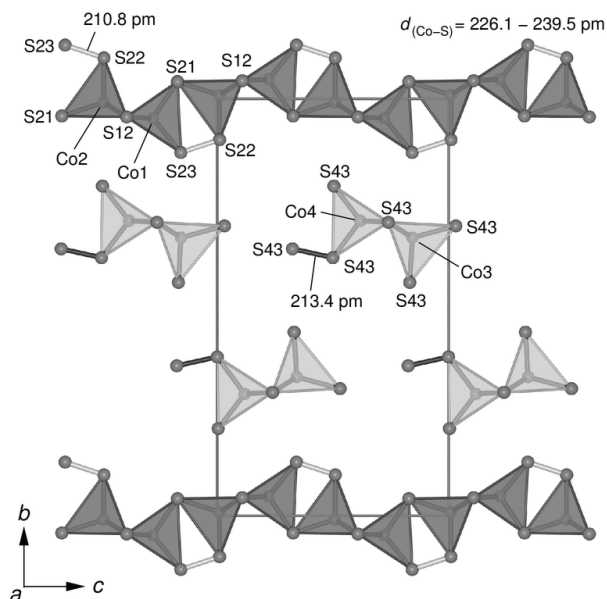


Figure 1. Arrangement of the two anions to form layers in the *b-c* plane. Chains Niggli formula: ${}^1_{\infty}[\text{CoS}_{2/2}\text{S}_{1/2}(\text{S}_2)_{1/2}]_2^{4-} = [\text{Co}_2\text{S}_5]^{4-}$. Dimere formula: $[\text{Co}_2\text{S}_5(\text{S}_2)]^{8-}$.

Keywords: sulfido cobaltates, thiocobaltates, disulfide, synthesis