

Synthesis and Crystal Structures of Silver Thianthrene Complexes with Weakly Coordinating Anions

Rachmat Triandi Tjahjanto and Johannes Beck

Institute of Inorganic Chemistry, Bonn University, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Reprint requests to Prof. Dr. J. Beck. Fax: +49 (228) 73 5660. E-mail: j.beck@uni-bonn.de

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Two novel silver complexes with thianthrene (TA) as a ligand have been synthesized in the poorly coordinating solvent liquid sulfur dioxide, using silver salts with weakly coordinating anions $[\text{BF}_4]^-$ and $[\text{SbF}_6]^-$. Both colorless compounds contain discrete molecular entities and SO_2 molecules included in the crystal structure. Selection of crystals and the diffraction data collection were performed at low temperatures (123 K). The tris(μ -thianthrene- $\kappa^2\text{S}$)disilver(I) bis(hexafluoroantimonate) sulfur dioxide solvate $[\text{Ag}_2(\text{TA})_3][\text{SbF}_6]_2 \cdot 5 \text{SO}_2$ (**1**) (monoclinic, $P2_1/c$, $a = 21.644(3)$, $b = 12.4216(4)$, $c = 21.934(3)$ Å, $\beta = 115.04(1)^\circ$, $Z = 4$) is made up of complexes bearing three TA units acting as bridging ligands with both S atoms towards two Ag^+ ions with $d(\text{Ag}^+ - \text{Ag}^+) = 2.911$ Å giving the $[\text{Ag}_2(\text{TA})_3]^{2+}$ unit approximately D_{3h} molecular symmetry. The bis(μ -thianthrene- $\kappa^2\text{S}$)disilver(I) bis(tetrafluoroborate) sulfur dioxide solvate $[\text{Ag}_2(\text{TA})_2][\text{BF}_4]_2 \cdot 3 \text{SO}_2$ (**2**) (monoclinic, $C2/c$, $a = 21.0045(6)$, $b = 7.4553(2)$, $c = 22.6024(6)$ Å, $\beta = 109.65(0)^\circ$, $Z = 4$) is made up of $[\text{Ag}_2(\text{TA})_2]^{2+}$ units with two bridging TA units coordinating two Ag^+ ions with $d(\text{Ag}^+ - \text{Ag}^+) = 2.925$ Å giving the complexes approximately D_{2h} molecular symmetry. Weak, secondary bonds between Ag^+ and the F atoms of the anions, such as $\text{Ag} \cdots \text{F} - \text{SbF}_5 = 2.862(4)$ Å in **1** or $\text{Ag} \cdots \text{F} - \text{BF}_3 = 2.773(2)$ Å in **2**, and with O atoms of SO_2 molecules link the complexes with the anions and the solvate molecules, respectively.

Key words: Silver Complexes, Sulfur Dioxide, Thianthrene Complexes,
Weakly Coordinating Anions, Crystal Structure