

Ag(I)-, Hg(II)- und Pt(II)-Komplexe von Maleonitril-thiakronenethern

Ag(I), Hg(II) and Pt(II) Complexes with Maleonitrile-thiacrown Ethers

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The synthesis and single crystal X-ray structures of eight Ag^I, Hg^{II}, and Pt^{II} complexes with the thiacycrown ethers maleonitrile-tetrathia-12-crown-4 (mn12S₄), maleonitrile-tetrathia-13-crown-4 (mn13S₄), and maleonitrile-pentathia-15-crown-5 (mn15S₅) (**1**) are reported. The ligand mn15S₅ was synthesized for the first time and characterized by X-ray diffraction. With silver(I) perchlorate and silver(I) tetrafluoroborate it forms the chiral complexes [Ag(mn15S₅)]ClO₄·CH₃NO₂ (**2**) and [Ag(mn15S₅)]BF₄·CH₃NO₂·0.25H₂O (**3**) with half-sandwich moieties. Ag^I is located in a distorted tetrahedral coordination environment, involving three sulfur atoms of the crown cycle and a fourth one of the adjacent half-sandwich moiety, forming a helical structure. The reaction of Hg(ClO₄)₂ with mn13S₄ yielded the dinuclear complex [Hg₂(mn13S₄)₃](ClO₄)₄ (**4**) containing two half-sandwich moieties with a third ligand molecule as a bridging unit. Mercury(II) chloride and mercury(II) iodide react with mn12S₄ and mn13S₄ to form complexes of the general composition [HgX₂(L)] (X = Cl, I; L = mn12S₄, mn13S₄): [HgCl₂(mn12S₄)] (**5**), [HgI₂(mn12S₄)] (**6**), [HgCl₂(mn13S₄)] (**7**) or [HgX₂(L)₂] (X = I; L = mn13S₄): [HgI₂(mn13S₄)₂] (**8**). Only one or two sulfur atoms of the ligand are involved in the complexation, and chain or ribbon structures are formed. In these compounds the HgX₂ units (X = Cl, I) are preserved, coordinated by sulfur atoms of bridging mn12S₄ or mn13S₄ ligands. In all complexes of this type, the metal atoms are not coordinated inside the cavity, but in an exocyclic mode, because the diameter of the macrocycle is too small.

Additionally, the PtCl₂ complex of mn12S₄ was investigated, where Pt^{II} is coordinated in an exocyclic mode forming the complex [PtCl₂(mn12S₄)] (**9**). Two of the four sulfur atoms of the macrocycle are bonded to the metal giving together with both chlorine atoms a square-planar coordination geometry. Together with a long-range interaction with a further sulfur atom of the macrocycle a square-pyramidal coordination environment is formed.

Key words: Silver Complexes, Mercury Complexes, Platinum Complex, Pentathiacrown Ether, Tetrathiacrown Ether, Maleonitrile, Crystal Structure