

Structural and Computational Studies of 1-Methyl-2-thiocyto-sine and its Coordination Mode in a Dinuclear Platinum(IV) Complex [(PtMe₃)₂(μ-1-MeSCy-1κN³,1:2κ²S)₂][BF₄]₂

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Z. Naturforsch. **2010**, *65b*, 578 – 586; received January 20, 2010

X-Ray diffraction analysis of 1-methyl-2-thiocyto-sine (1-MeSCy, **1**) revealed that its crystals contain two structurally very similar independent molecules (A, B). These molecules are connected through a complex network of hydrogen bonds. Centrosymmetric di- and tetrameric units AA' and BAA'B', respectively, are formed through N–H···N hydrogen bonds (N4a···N3a' 3.019(4) Å, AA'; N4a···N3b 2.988(4) Å, BAA'B'), and the tetrameric units are connected through N–H···S hydrogen bonds. The arrangement of A and B molecules found in crystals of **1** was confirmed by DFT calculations up to tetrameric BAA'B' units, yielding similar equilibrium structures, and the energies of the N–H···N hydrogen bonds between A and A' and A and B were calculated to be about 10 kcal mol⁻¹. Reaction of 1-MeSCy (**1**) with [PtMe₃(Me₂CO)₃][BF₄] (**2**) led to the formation of the ionic dinuclear complex [(PtMe₃)₂(μ-1-MeSCy-1κN³,1:2κ²S)₂][BF₄]₂ (**3**) which was fully characterized by NMR (¹H, ¹³C, ¹⁹⁵Pt) and IR spectroscopy, ESI mass spectrometry and microanalysis. A single-crystal X-ray diffraction analysis of **3** confirmed the dinuclear structure of the complex. The complex cation consists of a central [Pt₂(μ-S)₂] core having bound the 1-methyl-2-thiocyto-sine ligands in a 1κN³,1:2κ²S coordination mode in a face-to-face arrangement, the thionucleobase ligands being present as the amino-thione tautomer.

Key words: Thionucleobases, Platinum Complexes, Hydrogen Bonding, Single-crystal X-Ray Diffraction Analysis, DFT Calculations