B169 The Application of Single Crystal X-Ray Diffraction to Solve the Crystal Structure of the Complex Produced by the Gold (III) Chloride Microcrystal Test for Cocaine

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After attending this presentation, attendees will have gained an understanding of the crystal structure of cocaine and its gold (III) chloride complex, how this structure was determined using single crystal X-Ray diffraction techniques, and potential implications for the microcrystal testing of cocaine.

This presentation will impact the forensic community and/or humanity by demonstrating providing essential information regarding the molecular structure and interactions within the cocaine-gold chloride crystal.

The microcrystal test using chloroauric acid for the identification of cocaine has been used for over 120 years. Microcrystal testing is inexpensive and does not require sophisticated instrumentation beyond the light microscope. However, microcrystal testing has recently been criticized as being subjective and relying heavily upon the training and experience of the analyst. While the morphology and optical properties of the resulting crystals have been studied and documented, very little structural information has been available on the molecular level. Single crystal and powder X-Ray diffraction are ideal techniques for determining the chemical composition of crystals containing highly diffractive heavy metals, such as the cocaine-gold chloride complex.

Crystals suitable for single crystal X-Ray diffraction were grown very slowly at room temperature using evaporative concentration of a mixture of dilute aqueous cocaine hydrochloride and dilute acidified gold (III) chloride reagent. The resulting crystals were elongated gold colored parallelepiped rods.

The unit cell consists of a one to one ratio of four protonated cocaine ions and four anions of gold (III) chloride ($AuCl_4^-$). The orthorhombic cell dimensions are a = 7.7358(3) Å, b = 9.4543(5) Å, and c = 29.9093(13) Å [the numbers in parentheses are the errors in the last significant digits].

Several interesting features of the crystal structure are noted. One hydrogen bond and two close contacts exist, as shown by the X-Ray crystal structure. There is an intermolecular hydrogen bond between the hydrogen of the amine and the carbonyl oxygen of the benzoyl ester; a C-H...O close contact exists between the hydrogen of a methyl carbon and the methoxy oxygen in an adjacent molecule, and an intermolecular C-H...O close contact between a hydrogen of the phenyl ring and the methoxy oxygen. The crystal structure of the cocaine-gold chloride complex has been compared to the crystal structure of cocaine hydrochloride solved by Gabe and Barnes in 1963 and re-determined by Zhu et al. in 1999. In contrast, the crystal structure of cocaine hydrochloride exhibits hydrogen bonding between the hydrogen of the protonated nitrogen atom and the chloride ion and a slightly weaker H- bond between the same protonated nitrogen atom and the methoxy oxygen atom. Additionally, the gold chloride anion, which is planar in many structures, was found to be quite flexed in this one, with two opposing chlorides being 0.078 Å above the plane and the other two opposing chlorides being -0.081 Å below the plane.

Following ASTM 1968-98, the microcrystal test was performed on pure cocaine hydrochloride. The resulting crystal precipitate was filtered and dried before the powder X-Ray diffraction pattern was obtained. The powder diffraction pattern of the microcrystals was compared to the electronically-generated pattern obtained from the single crystal structure in order to confirm that the crystals were identical.

The purpose of this research is to gain an understanding of how the structure of the cocaine hydrochloride and its gold (III) chloride complex may play a role in the formation of crystals visualized by the traditional microcrystal test. This is an ongoing research project at Rutgers University with the cooperation of the New Jersey State Police Office of Forensic Sciences. Further crystallographic studies will focus on other related drug compounds and their respective microcrystal tests.

Cocaine, X-Ray Crystallography, Microcrystal Tests

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