

THE NEW FIELD OF TITAN CRYOMINERALOGY: SIX CONFIRMED CO-CRYSTALS AND COUNTING. Morgan L. Cable¹, Tuan H. Vu¹, Helen E. Maynard-Casely², Michael J. Malaska¹, Mathieu Choukroun¹ and Robert Hodyss¹, ¹NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Morgan.L.Cable@jpl.nasa.gov), ²Australian Nuclear Science and Technology Organisation, NSW, Australia.

Introduction: Titan, the largest moon of Saturn, contains a vast catalogue of organic molecules and is broadly considered to be a prebiotic chemical laboratory on a planetary scale. Photochemistry in the atmosphere, induced by solar radiation and fast-moving particles accelerated by Saturn's magnetosphere, initiates a chemical cascade which dissociates the main atmospheric components (N_2 and CH_4) and generates myriad small and large organic molecules. These molecules continue to react as they are transported through Titan's thick atmosphere, forming aerosol haze layers and ultimately depositing on the surface [1, 2]. Once there, these molecules have the opportunity to interact through various processes as they become integrated into the unique geology of Titan.

Many of the organic molecules on Titan's surface seem to have the capability to associate in a manner akin to minerals on Earth, forming molecular solids, co-crystals, and hydrates. These 'molecular minerals' exhibit unique physical and mechanical properties compared to their pure components, and may affect formation mechanisms and timescales of landscape evolution on Titan. Here, we focus on a subset of these molecular minerals: co-crystals.

A **co-crystal** is a unique crystalline structure comprised to two or more components in a set stoichiometric ratio, where no formal electronic modifications of the components occur. The constituents are instead associated via non-covalent interactions such as hydrogen bonding, interactions with π systems, and attractions due to van der Waals forces. In a cryogenic environment like the surface of Titan, weaker forces such as these could have a greater influence on molecular interactions and affect physical properties of surface materials to a higher degree than in the warmer conditions found on Earth. To date, six co-crystals have been characterized experimentally in Titan-like conditions, with modeling work suggesting a seventh (also the first ternary co-crystal). These molecular minerals are described in more detail below, as well as their implications for the cryomineralogy of Titan.

Benzene-Ethane Co-Crystal: This was the first reported co-crystal that was characterized under Titan surface conditions [3]. It forms readily at 90 K through simulated pluvial interactions or precipitation from a benzene-saturated hydrocarbon lake, and remains stable up to 160 K, 15 degrees above the point where liquid ethane evaporates [4]. X-ray powder diffraction

indicates a 3:1 benzene:ethane ratio (Fig. 1), where the benzene host crystal lattice reorganizes to accommodate the ethane guest molecules within channels in the structure maintained by a network of $C-H\cdots\pi$ interactions [5].

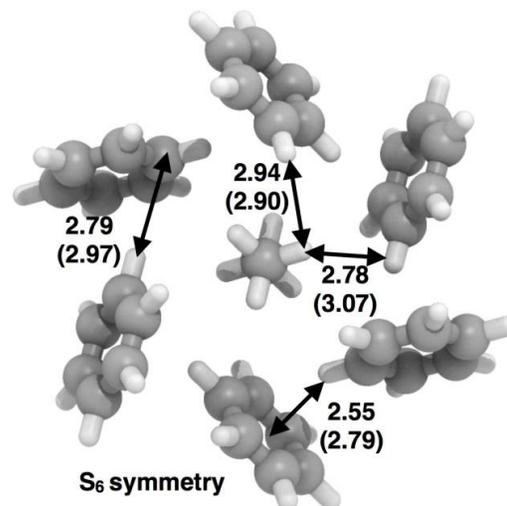


Figure 1. Crystal structure of the benzene-ethane co-crystal, with distances from the calculated gas-phase geometry in Å (experimentally determined distances are in parentheses). From Maynard-Casely et al. [5].

Acetylene-Ammonia Co-Crystal: This molecular mineral could form either via co-condensation in the atmosphere [6] or exposure of an ammonia-rich cryovolcanic surface deposit to acetylene-saturated methane/ethane liquids via fluvial or pluvial processes [7]. X-ray diffraction indicates significant anisotropic thermal expansion along the c -axis (loosely connected via π -stacking of acetylene) until the co-crystal destabilizes at 120 K [8].

Acetylene-Butane Co-Crystal: This co-crystal forms rapidly and remains intact up to 180 K, approximately 20 degrees higher than the point where acetylene sublimates [9]. Given that butane and acetylene are predicted to be the most abundant evaporite materials around Titan's lakes [10], this molecular mineral may be ubiquitous in these regions of Titan's surface.

Acetonitrile-Acetylene Co-Crystal: While previous work indicated these two molecules form a co-crystal [11], this was not demonstrated at Titan surface temperatures until recently [12]. The acetonitrile-acetylene co-crystal forms rapidly at Titan surface temperatures and is stabilized by strong $N\cdots H-C$ inter-

actions. These two abundant organic solids could come into contact either via co-condensation in the atmosphere (both condense at ~65-70 km altitude) or fluvial/pluvial transport (acetylene is soluble in liquid methane and ethane and could be washed by rain or rivers into areas rich in acetonitrile). As volatiles evaporate, a deposited layer of co-crystalline material could be formed that could be either intimately-associated co-crystal, or grains of acetonitrile cemented by interstitial precipitated acetylene (similar to calcite-cemented sandstone on Earth). Following uplift and erosion, such deposits could explain the labyrinth terrain of Titan, as well as the undifferentiated plains, which are believed to be the end-stage product of the labyrinth terrain.

Acetylene-Benzene Co-Crystal: This co-crystal was first reported following condensation at high pressure and temperatures ≥ 123 K [13] and was recently demonstrated to also readily form at Titan temperatures and pressures [14]. Given the propensity of both acetylene and benzene to form co-crystals with other, more abundant molecules on Titan's surface (butane and ethane, respectively), the presence of this molecular mineral might be indicative of a dry region of Titan's surface that has not undergone extensive pluvial/fluvial erosion.

Acetonitrile-Benzene Co-Crystal: A new co-crystal between acetonitrile and benzene was recently reported [15]. Diffraction measurements suggest a 1:3 ratio of acetonitrile to benzene, with a configuration very similar to the benzene-ethane co-crystal [5]. Interestingly, diffraction data collected following the addition of ethane at 100 K is inconsistent with either known binary co-crystal structures, suggesting the possibility of a new ternary mineral (or mixed phases).

Acetylene-Benzene-HCN Co-Crystal: Recent modeling work [16] suggests a ternary co-crystal comprised of acetylene, benzene and hydrogen cyanide (HCN) in a 1:2:1 stoichiometry would form spontaneously under Titan atmospheric conditions (all three species are predicted to condense within the same region of Titan's stratosphere). Predicted far-IR absorption bands of this ternary molecular mineral may be consistent with the 220 cm^{-1} haystack feature observed by Voyager and Cassini in Titan's stratospheric polar ice clouds [17]. Further experimental work is needed to confirm formation of this co-crystal and its unique spectroscopic characteristics.

Conclusions: The field of Titan cryomineralogy is growing rapidly, with six co-crystals confirmed experimentally to form and be stable under Titan-relevant conditions and a seventh ternary mineral possible based on modeling. Many of these co-crystals can form from solid-solid interactions and would form readily under Titan surface conditions, indicating that kinetics

would likely not inhibit formation of these molecular minerals on Titan.

Intermolecular interactions of co-crystals could change dissolution and reprecipitation timescales and equilibria, and therefore could affect the chemical erosion, transport, and deposition of molecules in terrains on Titan's surface. Many of these materials have order/disorder transitions that can lead to significant changes in volume, which might lead to unique geological features. Differences in physical or mechanical properties may also lead to chemical gradients, which life could potentially exploit [18]. Future in situ missions to Titan such as Dragonfly may be able to identify molecular minerals on Titan's surface via identification of enhanced thermal stability, unique stoichiometric ratios or other physical or chemical properties of surface materials [19].

Future work will involve further characterizing existing co-crystals, as well as searching for new molecular minerals.

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References: [1] Cable, M.L. et al. (2012) *Chem. Rev.*, 112, 1882-1909. [2] Hörst, S.M. (2017) *JGR Planets*, 122, 432-482. [3] Vu, T.H. et al. (2014) *J. Phys. Chem.*, 118, 4087-4094. [4] Cable, M.L. et al. (2014) *GRL*, 41, 5396-5401. [5] Maynard-Casely, H.E. et al. (2016) *IUCrJ*, 3, 192-199. [6] Boese, R. et al. (2009) *JACS*, 131, 2104-2106. [7] Cable, M.L. et al. (2018) *Earth Space Chem.*, 2 (4), 366-375. [8] Vu, T.H. et al. (2020) *J. Appl. Cryst.*, 53, 1524-1530. [9] Cable, M.L. et al. (2019) *Earth Space Chem.*, 3, 2808-2815. [10] Cordier, D. et al. (2013) *Icarus*, 226, 1431-1437. [11] Kirchner et al. (2010) *Chem. Eur. J.*, 16, 2131-2146. [12] Cable, M.L. et al. (2020) *Earth Space Chem.*, 4, 1375-1385. [13] Boese, R. et al. (2003) *Helv. Chim. Acta*, 86, 1085-1100. [14] Czaplinski, E. et al. (2020) *Planet. Sci. J.*, 1, 76. [15] McConville, C.A. et al. (2020) *Chem. Comm.*, 56, 13520-13523. [16] Ennis, C. et al. (2020) *Earth Space Chem.*, 4, 1195-1200. [17] Anderson, C.M. et al. (2018) *Space Sci. Rev.*, 214, 125. [18] Maynard-Casely, H.E. et al. (2018) *Am. Mineral.*, 103, 343-349. [19] Turtle, E.P. et al. (2017) *LPSC XLVIII* abstract no. 1958.