

Electronic Supplementary Information on

Surprising Discoveries on the Way to an Old Compound: Four Transient Iodido Antimonates

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Crystallographic Details

Details of Crystal Structure Refinement

Compound **1** crystallizes in the form of elongated, highly sensitive rectangular prisms that lose acetonitrile immediately upon removal from the mother liquor, even when stored under silicon oil. This is evidenced by an independent motion of the crystals when viewed under an optical microscope, ostensibly as solvent molecules found in channels along the *c* axis are expelled. Solvate acetonitrile molecules disordered about these channels can be identified during crystal structure refinement, as shown in Figure S1, but could not be modelled in a completely satisfactory manner and their electron density was thus described with a solvent mask to stabilize the refinement. Additionally, a number of ISOR restraints on carbon atoms had to be used to obtain reasonable anisotropic displacement parameters.

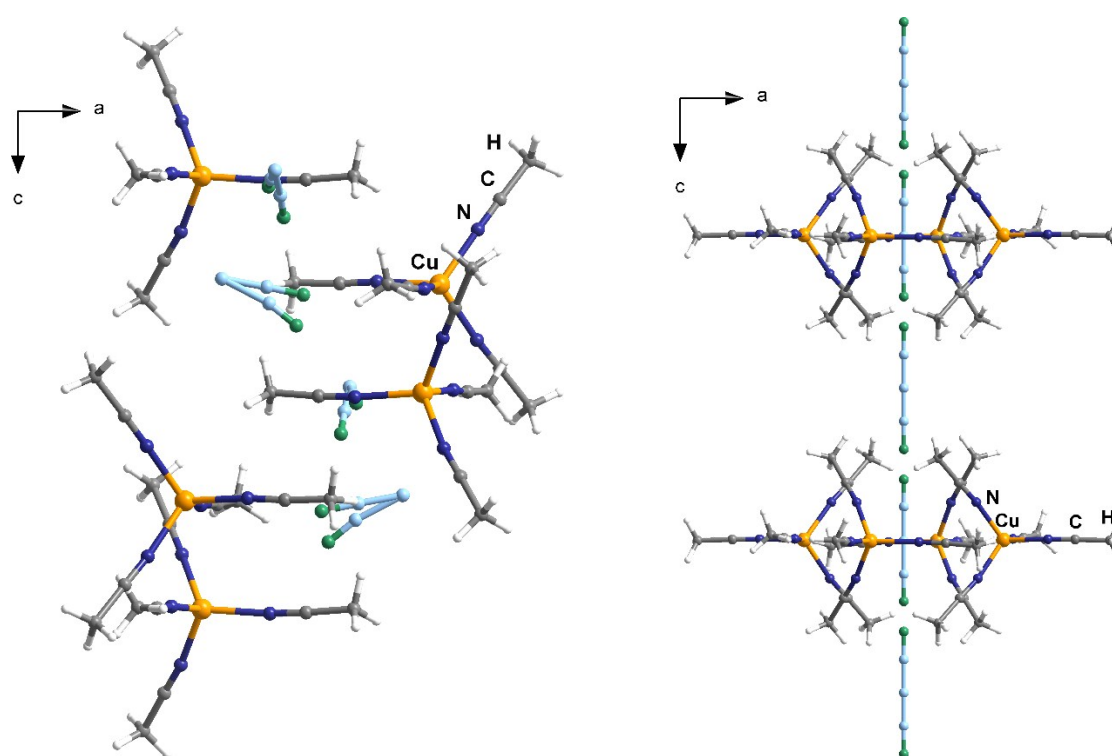


Figure S1: Excerpt of the crystal structure of **1**, with disordered acetonitrile molecules in channels along the *c* axis shown in pale green and light blue. As can be seen, the molecules located directly along the axis cannot be fully modelled within the given crystallographic symmetry.

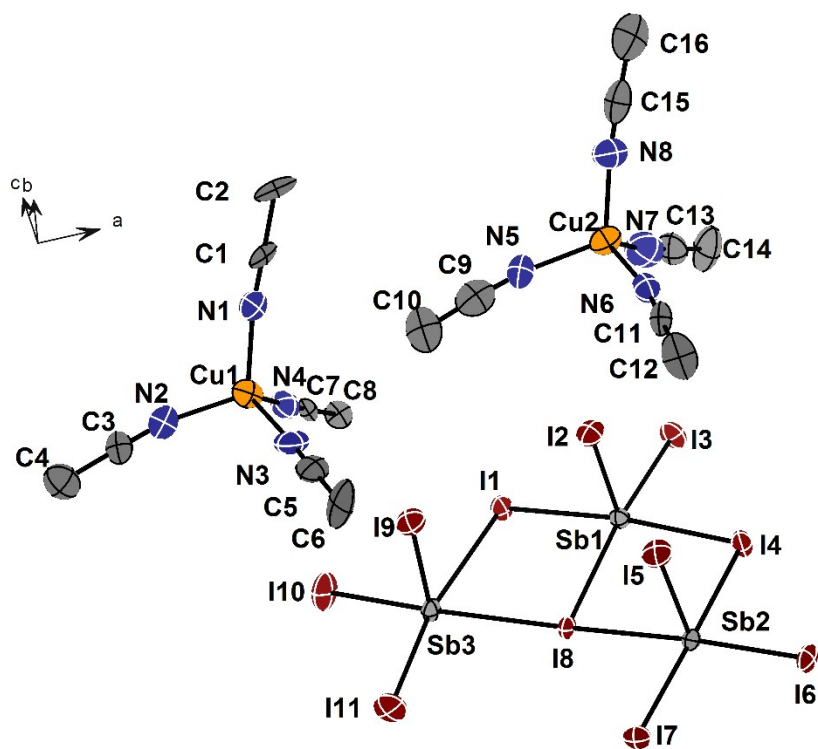


Figure S2: Asymmetric unit of **1**, ellipsoids at 80% probability.

Compound **2** crystallizes in the form of thin planks that also rapidly lose acetonitrile upon removal from the mother liquor. In this case the solvate molecules could be modelled. The compound crystallizes in the non-centrosymmetric space group $P2_1$ (No. 4) and was refined as an inversion twin with BASF 0.38956 and a Flack parameter of 0.39(8). A number of ISOR restraints on carbon and nitrogen atoms had to be used to obtain reasonable anisotropic displacement parameters.

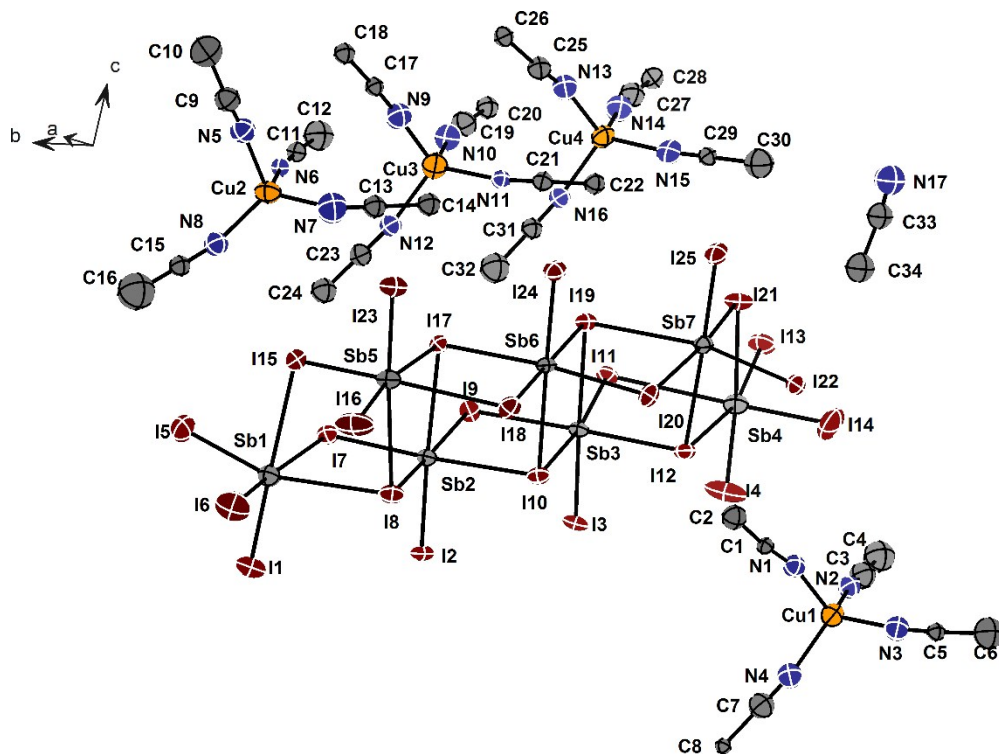


Figure S3: Asymmetric unit of **2**, ellipsoids at 80% probability.

Compound **3** crystallizes in the form of red blocks. The compound crystallizes in the non-centrosymmetric space group $P1$ (No. 1) and was refined as an inversion twin with BASF 0.23340 and a Flack parameter of 0.23(5). A number of ISOR and DFIX restraints on carbon and nitrogen atoms had to be used to obtain reasonable anisotropic displacement parameters and bond length. The crystal structure can also be solved and refined in the more common space group $P\bar{1}$ (No. 2), yet this leads to a disordered arrangement of the acetonitrile ligands that cannot be accurately modelled while keeping the inversion symmetry, as also shown in Figure 8 in the main manuscript.

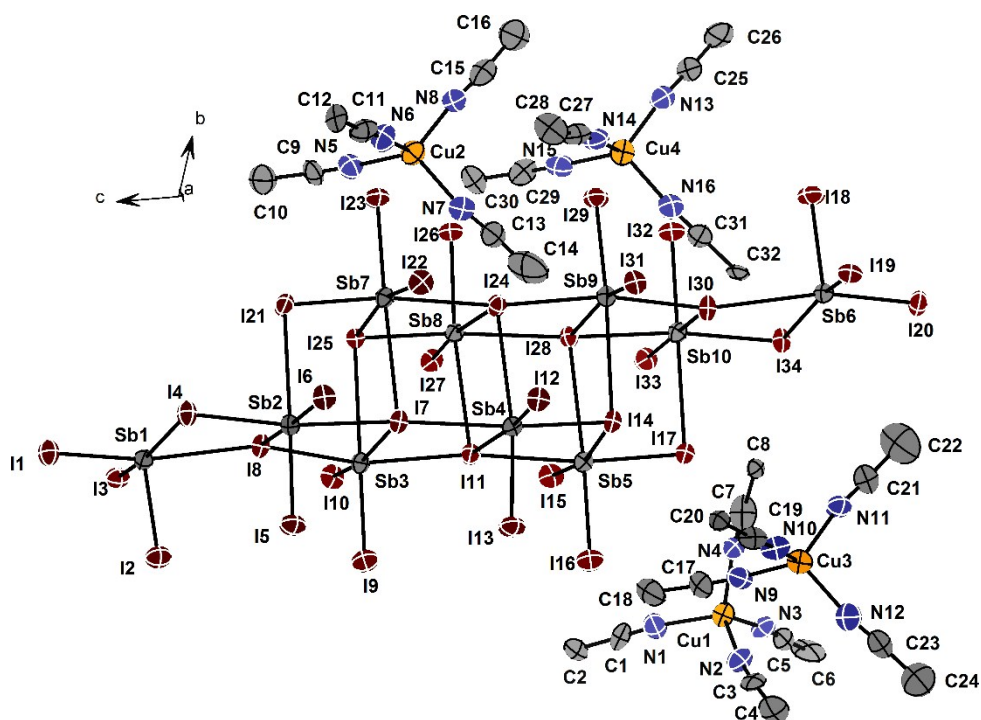


Figure S4: Asymmetric unit of **3**, ellipsoids at 80% probability.

Compound **4** crystallizes in the form of heavily intergrown red rods.

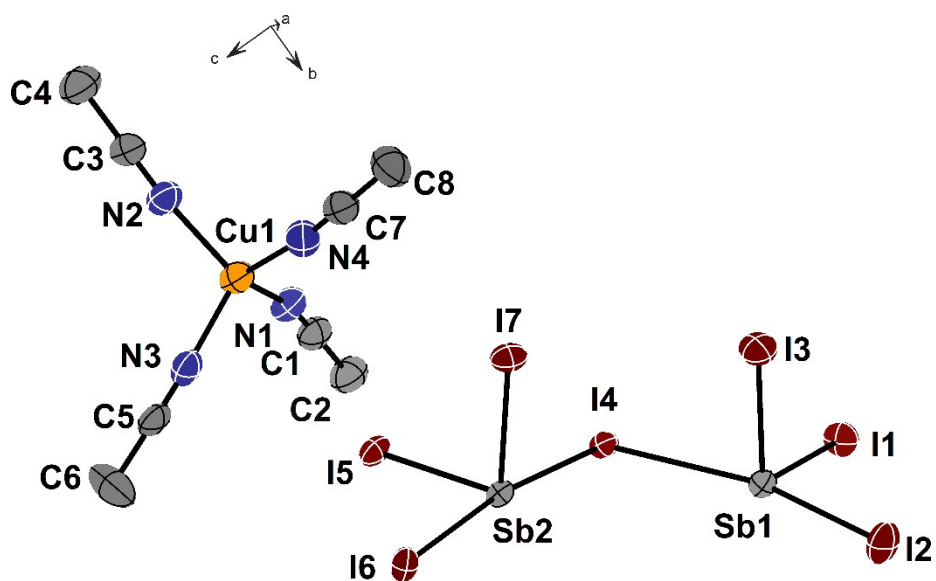


Figure S5: Asymmetric unit of **4**, ellipsoids at 80% probability.

Details of Crystal Structure Analysis

Table S1: Bond length and angles in compounds **1-4** and $[\text{Cu}(\text{MeCN})_4][\text{Sb}_3\text{I}_{11}]_2$,^[1] all distances in Å, all angles in °.

	1	2	3	4	$[\text{Cu}(\text{MeCN})_4][\text{Sb}_3\text{I}_{11}]_2$
Sb-I_{terminal}	2.774- 2.870	2.743- 2.837	2.738- 2.797	2.758- 2.811	2.782
Sb-I_{μ₂}	2.844- 3.455	2.823- 3.549	2.798- 3.496	2.849- 3.460	3.207
Sb-I_{μ₃}	-	3.024- 3.456	2.885- 3.523	3.002- 3.437	3.356
Sb-I_{μ₄}	3.217- 3.395	-	3.102- 3.466	-	-
Cu-N	1.965- 2.011	1.937- 2.045	1.939- 2.009	1.982- 1.996	1.985-2.080
cis-I-Sb-I	82-97	78-99	82-98	79-99	86-96
N-Cu-N	103-117	104-116	98-117	105-113	106-113

As shown in Table S1, a wide range is observed for the length of Sb-I_{μ₂} bonds in **1-4**. This can be explained by a strong trans-effect,^[2] where Sb-I_{μ₂} distances are longer when trans to a shorter bond, e.g. Sb-I_{terminal} and shorter when trans to a longer bond, e.g. Sb-I_{μ₄}. A similar effect is also observed for Sb-I_{μ₃} bonds, especially in **3**, where all four types of Sb-I bonds are present. Additionally, the need to accommodate fairly condensed motifs featuring μ₃ or μ₄ bridging iodine atoms enhances these structural distortions and also results in deviations from the ideal cis-I-Sb-I angle of 90°.

While Cu-N distances are fairly uniform, N-Cu-N angles show some deviation from the ideal angle of 109.5° to accommodate the interlocked packing of the $[\text{Cu}(\text{MeCN})_4]^+$ units.

Bond length and angles are similar in the literature reference compound $[\text{Cu}(\text{MeCN})_4][\text{Sb}_3\text{I}_{11}]_2$, although, due to the high symmetry of the crystal structure, only a single distance is observed for each category of Sb-I bonds.

References.

[1] S. Pohl, R. Lotz, W. Saak, D. Haase. *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 344.

[2] H.-L. Sheu, J. Laane. *Inorg. Chem.*, 2013, **52**, 4244.