Out with Acetonitrile: Water-assisted Accelerated-Aging Synthesis of CuI-Pyrazine Hybrid Materials

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Abstract: CuI and pyrazine form three hybrid materials, [(CuI)\(_2\)(pyrazine)] (Yellow), [(CuI)\(_2\)(pyrazine)\(_2\)] (Orange), and [(CuI)(pyrazine)] (Red). In this work, Red was prepared using a green synthetic method, water-assisted accelerated-aging synthesis, for the first time. The syntheses were performed under ambient conditions with only water and no organic solvents. Depending on the reaction conditions, the other two hybrid materials can be formed as well: Orange was formed immediately after dry grinding CuI and pyrazine, while Yellow can be formed from Red and excess amount of CuI at mildly elevated temperatures. The impacts of temperature and types and amounts of liquid added to the aging mixture on the accelerated-aging synthesis were studied, and mechanisms of the synthesis and interconversions between the three CuI-pyrazine hybrid materials were proposed.

Introduction:

Inorganic-organic hybrid materials are intimate mixtures of two or more components, some are inorganic and others are organic, assembled in such a way as to have properties different from any of the component alone. The most famous subclass of inorganic-organic hybrid materials is, perhaps, the metal-organic frameworks, which are a class of solid materials containing extended framework structures constructed from metal cation centers linked by organic ligands. Traditional syntheses of hybrid materials rely heavily on bulk use of organic solvents and/or energy intensive conditions\(^1-4\). The use of bulk solvents and high energy use associated with syntheses of hybrid materials increases the cost and environmental footprint of these compounds and reduce their viability on an industrial scale, and according to the 12 Principles of Green Chemistry\(^5\), the use of such organic solvents should be avoided or minimized due to their cost and toxicity, and energy efficiency of the syntheses should be improved. So far, several different synthetic methods have been developed to reduce energy usage, including sonochemical\(^6-8\), electrochemical\(^8,9\), and microwave-assisted\(^10-13\) synthesis. Synthetic methods have also been developed to avoid or minimize the usage of organic solvents, including syntheses that use water as the solvent\(^14-18\), or solvent-free syntheses such as mechanochemical\(^19-29\) and accelerated-aging\(^30-34\) syntheses. In a mechanochemical synthesis, chemical reactions are induced by grinding of a metal salt and linker in a ball mill. Adding a small amount of solvent and ionic compound such as (NH\(_4\))\(_2\)SO\(_4\) have both been found to speed up the synthesis, and result in more crystalline products\(^21,23\). Accelerated-
Aging synthesis for MOFs and other hybrid materials has been shown to form quality products using little to no solvent near ambient conditions. In an accelerated aging synthesis, the reactants are neatly ground, typically with additives which accelerate the reaction, then are left under various conditions to react. UV irradiation, microwaving, and controlled humidity have all been used to accelerate these reactions in the solid phase, as well as mildly elevated temperatures, and adding a small amount of solvent or ionic compound.

Copper Iodide (CuI) hybrid materials are constructed from CuI and organic ligands occupying one or more of the four coordination sites on Cu(I), having the general formula of (CuI)$_x$L$_y$ (where L = organic ligand). CuI/organic hybrids can exist as discrete compounds, such as the Cu$_4$I$_4$py$_4$ cluster, or as coordination polymers with CuI based building blocks linked by organic ligands. With the coordination flexibility and luminescent properties of Cu(I) complex, coordination polymers constructed with CuI aggregates possess significant structural diversity and unique physical properties. For example, they have been previously investigated for their excellent photoluminescent properties, potential as photocatalysts, and as hole-transporting materials in perovskite solar cells. With different bridging organic ligands, various CuI architectures, such as rhombus dimer connectors, zig-zag chains and staircase chains, have been constructed, which extend the crystal engineering of Cu(I) halides from discrete oligomers to coordination polymers with one, two and three-dimensional structures.

CuI and pyrazine form three hybrid materials with extended structures (Figure 1), $[(\text{CuI})_2(\text{pyrazine})]$ (Yellow), which is constructed by extended (CuI)$_x$ staircase chains linked by the coordinating organic ligands, pyrazine, and packed in a zig-zag fashion; $[(\text{CuI})_2(\text{pyrazine})_2]$ (Orange), which is constructed by (CuI)$_2$ rhombus-shaped dimers that are connected by the ligands to form 2-D sheets, and $[(\text{CuI})(\text{pyrazine})]$ (Red), which is constructed by 1-D CuI chains linked by the ligands to form 2-D sheets. Both Yellow and Red have been synthesized in solution, as well as hydro/solvothermally. Orange was synthesized using mechanochemical synthesis or by heating dry CuI and pyrazine at appropriate molar ratio.
Figure 1. Structures of the three CuI-pyrazine (abbreviated as pz in the figure) hybrid materials, \([(\text{CuI})_2(\text{pz})_2]\) (Yellow), \([(\text{CuI})_2(\text{pz})]_2\) (Orange), and \([(\text{CuI})(\text{pz})]\) (Red). Atoms are represented by spheres of different colors: purple: iodine; blue: copper; gold: carbon; light blue: nitrogen, and white: hydrogen.

Since CuI is insoluble in most solvents with the exception of acetonitrile,\textsuperscript{53} solvent-free syntheses such as mechanochemical and accelerated-aging syntheses are good options of green syntheses for CuI-hybrid materials. In this study, an accelerated-aging synthesis which uses minimal water as the sole additive was developed for the first time for CuI-pyrazine hybrid materials. The results of the syntheses are affected by the molar ratio of the starting materials, amount of water added, types of solvent added, and temperature. This method eliminates the need for acetonitrile in the synthesis of these compounds and can be performed in one beaker under ambient conditions using simple techniques. Further, possible mechanisms of interconversions between the Yellow, Red, and Orange hybrid materials are proposed based on the results of the syntheses.

Methods:

Materials: The pyrazine (>99%) and Copper (I) Iodide (>98%) were purchased from EMD Millipore Corporation. All reagents were used as is without further purification.
Synthesis of CuI-pyrazine hybrid materials by water-assisted accelerated aging: In a typical synthesis, a mixture of CuI and pyrazine at a certain molar ratio (2:1, 1:1, 1:2, or 1:3; all with 1 mmol CuI and the amount of pyrazine adjusted accordingly) were neatly ground in an agate pestle and mortar for approximately 30 seconds per sample then transferred to a 10 mL beaker. The reactants were well mixed with a small amount (45 μL/4 mmol mixture of reactants) of distilled water, then the beaker was sealed by adding a small amount of water around the rim of a rubber stopper and turning it into the beaker, then wrapping it with parafilm. The water added to the rim was only to seal the beaker and did not get mixed into the reaction mixture. All samples were aged at room temperature for a week.

Study of different reaction conditions on the accelerated-aging synthesis: We hypothesize that the aging temperature, the type of liquid added, and the amount of liquid added to the aging mixture can all affect the accelerated-aging synthesis. The following experiments were performed to study each of their effects on the synthesis. The CuI: pyrazine = 1:3 molar ratio (1 mmol CuI and 3 mmol pyrazine) was used to prepare all the aging mixtures in the following experiments. To study the effect of temperature, two mixtures were prepared by adding 45 μL of water to the grounded mixture (same procedure as described in the previous paragraph), and one of them was aged at 313(±5)K while the other at 323(±5)K on hot plates for approximately 5 hours. To study the effect of the type of liquid added to the aging mixture, a mixture was prepared by adding 45 μL CH$_3$CN, instead of water, to the grounded starting materials, and was aged at room temperature for one week. To study the effect of the amount of water added to the aging mixture, two mixtures, with 18 μL (45 μL/2.5) water added to one and 112 μL (45 μL × 2.5) water added to the other, were both aged at room temperature for one week. In addition, to study if adding solvent can lead to any further reaction in the products after the synthesis was complete, 1 mL CH$_3$CN was added to the product from the CuI: pyrazine = 1:3 sample aged in 45 μL water at room temperature for 1 week.

Study of phase transitions and reaction intermediates during the accelerated-aging synthesis: nine CuI: pyrazine = 1:3 mixtures in 45 μL water were prepared. Four of them were each aged at room temperature for 1 hr, 2 hrs, 3 hrs, and 4 hrs, respectively, and the other five were aged at 323(±5) K for 10 min, 20 min, 30 min, 1 hr, and 2 hrs, respectively. The samples aged for different amounts of time were further characterized to identify the phases formed during the aging process.

Structural analysis: All products were washed with acetone and centrifuged to remove any unreacted ligand before structural characterization. Structural characterizations were conducted by powder X-ray diffraction (PXRD) on a Rigaku Ultima X-ray diffractometer with Cu Kα (λ = 1.54056 Å) radiation from a sealed tube X-ray source (40 kV, 40 mA). PXRD patterns were scanned with a step size of 0.02° over the 2θ angular range from 10° to 60° and dwell times of 0.4 s for each step.

Results and discussion:

Water-assisted accelerated-aging syntheses with different CuI-to-pyrazine molar ratios
In all syntheses, the mixture of starting materials started visibly orange when mixed by mortar and pestle, then remained orange when 45 μL water was added (Figure 2a). After aging for a week, the color of the mixture changed from orange to red-orange, with some mixtures redder than others (Figure 2b). As shown in Figure 2b, of all the syntheses at room temperature with 45 μL of water per 4 mmol of reactant added, a CuI to pyrazine ratio of 1:3 resulted in the most vibrant red color. PXRD results (Figure 2c) show that the only hybrid compound in the product of this reaction is crystalline Red, which is consistent with the vibrant color. Syntheses conducted under the same conditions but with other molar ratios resulted in mixtures with a homogeneous orange color. PXRD results show that the hybrid compound in each product is still only crystalline Red, so the orange color is likely due to the unreacted CuI (white) mixed with the Red in the products. Based on the PXRD patterns, unreacted CuI was present in the products of all syntheses, but the height of the most intense peak of CuI (peak a in Figure 2c) compared to the most intense peak of Red (peak b in Figure 2c) decreases as the amount of pyrazine in the starting materials increases, which indicates that the excess amount of pyrazine drives the synthetic reaction further to the right and forms more product.

![Image of syntheses and PXRD patterns](image-url)

**Figure 2** (a) left: CuI: pyrazine = 1:3 right after grinding; right: CuI: pyrazine = 1:3, right after 45 μL water was added (before aging). (b) Products of water-assisted accelerated-aging syntheses: each sample was aged in 45 μL water/4 mmol starting materials at room temperature for one week. The starting materials in each sample has different CuI: pyrazine molar ratios, as indicated in the figure. (c) PXRD patterns of each of the products in (b), and the calculated PXRD patterns of [(CuI)(pyrazine)] (Red) and CuI. Peaks a and b are the most intense peak of CuI and Red, respectively.
Effects of reaction conditions on the accelerated-aging syntheses of CuI-pyrazine hybrid materials

Different reaction conditions, including temperature, the amount of liquid added to the aging mixture, and the type of liquid added to the aging mixture may all affect the accelerated-aging synthesis. Since the CuI: pyrazine = 1:3 mixture yielded the largest amount of Red in the product when aged in 45 μL water at room temperature, we chose that molar ratio for all of the experiments to study the impacts of each reaction condition.

Temperature was found to influence both the speed of the accelerated-aging syntheses with higher temperatures resulting in faster reactions, and the products of the syntheses. For syntheses with CuI: pyrazine = 1:3 mixtures (in 45 μL water) at elevated temperatures, the color of the reaction mixture stopped changing in 2 hours and in 30 minutes, respectively, at 313 K and 323 K. The final colors of the reaction mixtures are shown in Figure 3a. However, elevated temperatures also resulted in a mixture of Yellow and Red in the products, with more Yellow in the product from the mixture aged at higher temperature, as shown by the PXRD results in Figure 3b.

Figure 3 (a) Products of mixtures with CuI: pyrazine = 1:3 and 45 μL water added, aged at 313 K and 323 K for approx. 5 hours. (b) PXRD patterns of the two products in (a), compared to the calculated patterns of \([\text{CuI}](\text{pyrazine})\) (Red), \([\text{CuI}]_2(\text{pyrazine})\) (Yellow), and CuI.

When the mixture with CuI: pyrazine = 1:3 molar ratio was aged at room temperature for one week in 45 μL CH₃CN instead of water, the product has a similar color as the product from the accelerated-aging synthesis performed in 45 μL water (Figure 4a). PXRD results show that the
only hybrid material in the product was **Red**. Also, as shown by the relative heights of the most intense peak for CuI (Peak a in Figure 4b) to the most intense peak for **Red** (Peak b in Figure 4b) in the PXRD results, compared to the product from the accelerated-aging synthesis performed in 45 μL water, the product from aging in CH$_3$CN has a much smaller amount of unreacted CuI left, which indicates that the synthesis reaction was further driven to the side of products with the assist of CH$_3$CN. Since both CuI and pyrazine are soluble in CH$_3$CN, as opposed to water where only pyrazine is soluble, the concentration of CuI is higher in CH$_3$CN than in water, which drives the equilibrium to the right (i.e. the products’ side).

It has been reported that when the synthesis was performed in CH$_3$CN solution, **Yellow** was the product regardless of the molar ratio between CuI and pyrazine. It is likely that in the accelerated-aging synthesis, the amount of CH$_3$CN added was too small compared to solution synthesis, thus **Yellow** was not formed like in solution synthesis.

![Figure 4](image.png)

**Figure 4** (a) Products of accelerated aging synthesizes, with the molar ratio of CuI: pyrazine = 1:3, and aged in 45 μL water (left) and 45 μL CH$_3$CN (right) at room temperature for one week. (b) PXRD results of the two products in (a), and the calculated PXRD patterns of **Red** and CuI. Peaks a and b are the most intense peaks of CuI and **Red**, respectively.

When the mixture with CuI: pyrazine = 1:3 molar ratio was aged at room temperature for one week in different amount of water (18 μL, 45 μL, and 112 μL), the products all have similar colors (Figure 5a). The PXRD results of the three products (Figure 5b) are also similar with peaks for **Red** and unreacted CuI. Based on the height of the most intense peak for CuI (Peak a in Figure 5b) relative to that of the most intense peak for **Red** (Peak b in Figure 5b), adding more water in the aging mixture resulted in slightly more unreacted CuI in the product. Since CuI only dissolves
minimally in water, it is likely that adding more water leads to a decreased concentration of pyrazine, which shifts the equilibrium of the synthesis reaction to the left (i.e. the reactants’ side).

Figure 5 (a) Products of accelerated-aging syntheses, with the molar ratio of CuI: pyrazine = 1:3, and aged in 18 μL (left), 45 μL (middle), and 112 μL (right) water at room temperature for one week. (b) PXRD results of the products in (a), and the calculated patterns of Red and CuI. Peaks a and b are the most intense peaks of CuI and Red, respectively.

When 1 mL CH₃CN was added to the product of the CuI: pyrazine = 1:3 mixture that was aged in 45 μL water at room temperature for 1 week, before the addition of CH₃CN, there was only Red in the sample with unreacted CuI. After the addition of CH₃CN, the sample turned yellow almost immediately, and PXRD result showed that the majority of the sample was Yellow and there was only a small amount of Red left (Figure 6). Since the product before the addition of CH₃CN contained both Red and unreacted CuI, it is likely that after the addition of CH₃CN, the following reaction occurred:

\[
([\text{CuI}](\text{pyrazine}))ₙ (\text{Red}) + \text{CuI} \rightarrow [(\text{CuI})₂(\text{pyrazine})]ₙ (\text{Yellow}) \quad \text{(Reaction 1)}
\]

Since Red and unreacted CuI coexist for an extended period of time without transitioning into Yellow, Reaction 1 is likely very slow under ambient conditions. Because CuI is soluble in CH₃CN, when 1 mL CH₃CN was added, it increased the diffusion rate such that the rate of Reaction 1 was significantly increased, thus the formation of Yellow was observed.
Figure 6 (a) left: product from a mixture of CuI: pyrazine = 1:3, aged in 45 μL water at room temperature for 1 week; right: the same product after the addition of ~1 mL CH₃CN. (b) PXRD results of the two products in (a), compared to the calculated patterns of [(CuI)(pyrazine)] (Red), [(CuI)₂(pyrazine)] (Yellow), and CuI.

Phase transitions during the accelerated-aging syntheses at room temperature and elevated temperature

To study the phase changes during the aging processes, CuI: pyrazine = 1:3 samples in 45 μL water were also aged at room temperature for 1 hr, 2 hrs, 3 hrs, and 4 hrs, as well as at 323(±5) K for 10 min, 20 min, 30 min, 1 hr, and 2 hrs. The samples aged for different amount of time were characterized by PXRD. As shown in Figures 7a and 7b, Orange formed immediately after CuI and pyrazine were grinded with mortar and pestle before water was added (i.e. before aging). For the sample aged at room temperature, Red started to appear after aging for 3 hrs, but Orange still persists after 4 hours of aging. PXRD pattern of the same sample showed no Orange peaks and only Red peaks (and unreacted CuI) after aging at room temperature for 1 week, which indicates that Orange completely transitioned to Red during the 1 week period. By contrast, as shown in Figures 7c and 7d, for the sample aged at 323 K, Red was already present after aging for 10 minutes. After aging for 20 minutes, Orange has completely disappeared leaving only Red and unreacted CuI in the sample. Red remained to be the only product in samples aged for 30 min and 1 hr but after aging for 2 hrs Yellow appeared in the sample. These results indicate that an elevated temperature speeds up the formation of Red, however it also facilitated the formation of Yellow, which will be formed if the sample remains at the elevated temperature for a longer period of time.
(2 hours or more). Given that an elevated temperature also increases diffusion rates of reactant particles, it is likely that at an elevated temperature, the rate of Reaction 1 has increased significantly, thus the transition from Red to Yellow was observed.

Figure 7 (a) Products from mixtures of CuI: pyrazine = 1:3 in 45 μL water, aged at room temperature for (left to right) 1h, 2h, 3h, 4h, and 1 week. (b) PXRD results of the products in (a), compared to the calculated patterns of [(CuI)₂(pyrazine)]₂ (Orange), [(CuI)(pyrazine)] (Red), and CuI. (c) Products from mixtures of CuI: pyrazine = 1:3 in 45 μL water, aged at 323(±5) K for (left to right) 10 min, 20 min, 30 min, 1 h, and 2 h. (d) PXRD results of products in (c), compared to the calculated patterns of [(CuI)₂(pyrazine)]₂ (Orange), [(CuI)(pyrazine)] (Red), [(CuI)₂(pyrazine)] (Yellow), and CuI.

Relative stabilities and interconversions of the three CuI-pyrazine hybrid materials
Different synthetic methods and conditions lead to different CuI-pyrazine hybrid materials. Previously, it has been observed that Yellow is produced in acetonitrile solution synthesis regardless of the metal to ligand ratio. Cappuccino et. al. found that all three hybrid materials can be synthesized using mechanochemical synthesis by ball-milling CuI and pyrazine at the appropriate molar ratios, and with a small amount of acetonitrile added (except in the case of Orange which must be ground dry). In this study, we have successfully synthesized Red using an accelerated-aging synthesis with water as the only solvent added (i.e. no organic solvent). We have also observed that when CuI and pyrazine is ground, Orange formed immediately. After aging for 1 week at room temperature, Orange will convert to Red. At a slightly elevated temperature, or with 1 mL CH$_3$CN added to the product of the accelerated-aging synthesis, the diffusion rates increased, which significantly increased the rate of Reaction 1, and Red was observed to further convert into Yellow.

Based on literature and our results, we propose possible explanations for the formation and interconversion of these three hybrid materials under different conditions, as shown in Figure 8. The potential energy of the starting materials has been set as zero (black circle), and the depth below the black circle indicates the difference in potential energy between the starting materials and each hybrid material. Reaction mechanisms for two different syntheses are proposed in Figure 8: synthesis in CH$_3$CN solution, and accelerated-aging synthesis.

In a CH$_3$CN solution synthesis, when CuI is dissolved in CH$_3$CN, it forms [(Cu$_2$I$_2$)(NCCH$_3$)$_4$], which consists of Cu$_2$I$_2$ dimers. Since the dimers are in solution, they can diffuse rapidly in solution, aggregate, and form the staircase motif same as in Yellow before the individual dimers are linked by pyrazine, which is why Yellow is observed in CH$_3$CN solution synthesis regardless of the metal to ligand ratio. The quickness of the formation of Yellow in a CH$_3$CN solution synthesis indicates that the activation barriers for that synthesis should be low.

By contrast, in an accelerated-aging syntheses with only water or a minimal amount of CH$_3$CN added, none (or very little) of the same dimer structure formed in a CH$_3$CN solution of CuI can be formed, instead, two pyrazine molecules replace two iodine on the tetrahedrally coordinated Cu in CuI and form Cu$_2$I$_2$ dimers linked by pyrazine. Due to limited diffusion of the dimers, they are locked into place by pyrazine forming Orange. This is consistent with our observation that in the accelerated-aging synthesis, the product that formed immediately after grinding CuI and pyrazine was Orange. The quickness of formation of the Orange indicates a small activation barrier between it and the starting materials.

In an accelerated-aging synthesis, the conversion of the reactants directly to Red has not been observed, which indicates the starting materials have to go through Orange to reach Red. The formation of Orange before Red indicates that Orange is the kinetic product and must therefore have a potential energy closer to the starting materials than Red according to the Oswald step rule. The spontaneity of the conversion from Orange to Red indicates that Red has a lower potential energy than Orange, and the slowness of the conversion (at least 3 hours at room temperature) compared to the formation of Orange (immediate) indicates the activation barrier between Orange and Red is higher than that between the starting materials and Orange.
We have observed that Red and unreacted CuI can coexist for a long period of time, and the conversion from Red to Yellow (Reaction 1) was only observed with an increased diffusion rate, which indicates that Reaction 1, and thus the conversion between Red and Yellow, has a high activation barrier. Given that this reaction is spontaneous, and the Yellow formed was stable and did not convert back to Red when the diffusion rates were slowed back down, we propose that Yellow is the thermodynamic product of this system, but its formation is strongly dependent on the diffusion of CuI which should be improved either when the CuI is solvated or when the structure is heated to achieve the level of diffusion required for the staircase motif to be formed.

Figure 8 Relative potential energies and activation barriers of interconversions between different hybrid materials. Pyrazine is abbreviated as “pyz” in this figure. Structures of Orange, Red, and Yellow are included in the figure: purple: iodine; blue: copper; gold: carbon; light blue: nitrogen, and white: hydrogen.

Conclusion
CuI and pyrazine form three hybrid materials, [(CuI)$_2$(pyrazine)] (Yellow), [(CuI)$_2$(pyrazine)$_2$] (Orange), and [(CuI)(pyrazine)] (Red). In this work, we have developed a water-assisted accelerated-aging synthesis of the hybrid material, Red, which is a green synthetic method that can be performed under ambient conditions using no organic solvent. When the diffusion rate is higher, Red can further convert into Yellow. We have found that the accelerated-aging synthesis is affected by the temperature, and the type and quantity of liquid added to the aging mixture. An elevated temperature speeds up the aging process to form Red, but also increases the diffusion rates of the reactant particles, such that the Red formed is further converted into Yellow. The types and amounts of liquid added to the aging mixture change the concentrations of the reactants, which shifts the equilibrium of the synthesis reaction.

Based on our results and literature results, we have also proposed reaction mechanisms for the accelerated-aging synthesis, synthesis of Yellow in CH$_3$CN solution, and interconversions between the three CuI-pyrazine hybrid materials. The proposed reaction mechanisms are summarized in Figure 8. In CH$_3$CN solution, CuI forms a dimer structure, and due to the high diffusion rates in solution, they can easily aggregates into the staircase motif in Yellow, thus Yellow always forms in CH$_3$CN solution. In a water-assisted accelerated-aging synthesis, CuI forms a rhombus-shaped dimer structure with the pyrazine ligand, and due to the slow diffusion rate, the dimers stay separate and connected only by pyrazine ligands, thus forming Orange. Orange is not stable and converts into Red under ambient conditions over time. The conversion from Red to Yellow is very slow, and can only be observed with increased diffusion rates of reactant particles; however, the conversion is spontaneous and Yellow does not spontaneously convert back to Red, which indicates that Yellow is the most thermodynamically stable among all three hybrid materials.

The accelerated-aging synthesis developed in this work presents a very promising route to the large-scale production of Red without the use of organic solvents and with minimal energy use, as well as Yellow which can be produced by heating Red at mildly elevated temperature in the presence of excess CuI. Furthermore, the study of the impacts of temperature and solvents on the synthesis can be used to further optimize the synthesis, as well as providing insights on the mechanisms of the synthesis and the interconversions between the three hybrid materials.

References

(3) Schukraft, G.; Petit, C. In Sustainable Nanoscale Engineering; Elsevier: 2020, p 139-162.


(57) Barth, E. R.; Golz, C.; Knorr, M.; Strohmann, C. Crystal structure of di-μ-iodido-bis [bis(acetonitrile-κN) copper (I)]. Acta Crystallographica Section E: Crystallographic Communications 2015, 71, m189-m190.