Title:
Mechanochemical synthesis of a mercury(II) metal-organic framework reveals a two-dimensional polymorph stabilized by weak interactions

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Abstract:
Solid-state mechanochemistry revealed a novel polymorph of the mercury(II) imidazolate framework, based on square-grid (*sql*) topology layers. Reaction monitoring and periodic density functional theory calculations show that the *sql*-structure is of higher stability than the previously reported three-dimensional structure, with the unexpected stabilization of a lower dimensionality structure explained by contributions of weak interactions, which include short C-H···Hg contacts.

Main text:
Metal-organic frameworks (MOFs)[1] are one of the most active, prolific areas of materials chemistry, due to a modular design that permits rational incorporation of diverse metal ions and suitably functionalized organic linkers into functional solid-state structures.[2] While a significant amount of effort has been put into developing materials with improved properties,[3] fundamental and systematic studies of how the stability and topology of MOFs are affected by component choice and structure have remained less developed.[4,5] Popular MOF designs have mostly focused on lighter main group (*e.g.* Li,[6] Mg,[7] Al[8]) and first row transition metals[9-13] with the exception of NbOFFIVE, UiO- and NU-type MOFs based on Nb, Zr or Hf.[14-17] Although recent work started exploring the benefits of heavier elements Ce, Th, U or Np[18-20] as framework nodes, properties and formation of MOFs with heavier, 6th period members of the periodic table remains largely unexplored.[21] Consequently, it is unknown to what extent such heavy elements are compatible with, and can bring novelty to, MOF designs. This is particularly relevant for topologically-flexible MOFs, such as zeolitic imidazolate frameworks (ZIFs)[22] and other metal azolates,[23] that are prone to polymorphism and can adopt a wide range of topologies depending on metal and linker choice.[24] Mercury (as Hg^{2+}) is particularly suitable for investigating the effect of heavy elements in ZIFs, as it is the heaviest accessible homologue of Zn^{2+}, the most extensively used node in ZIF design.[22-24] As ZIFs with Cd^{2+} have also been studied,[25] using a Hg^{2+} node offers a unique opportunity to explore MOF formation across an entire series of homologous transition metals. While MOFs of Hg^{2+} are not likely to be of practical value, due to toxicity of mercury, we see studies of such materials as necessary to fully understand the scope and limitations of MOF designs.

To date, there has been one report of a mercury-based imidazolate framework, a diamondoid (*dia*) topology mercury(II) imidazolate Hg(**Im**)₂.[26,27] The framework is isostructural to its cadmium analogue, both of which were made by precipitation from aqueous solution and structurally characterized from powder X-ray diffraction (PXRD) data (**Fig. 1a**) by Masciocchi *et al*. In 2006, Fernández-Bertrán *et al*. attempted the synthesis of Hg(**Im**)₂ mechanochemically,[28,29]

from HgO and imidazole (**HIm**), and established that manual grinding led to partial formation of a material with hexagonal symmetry, distinct from *dia*-Hg(**Im**)$_2$.
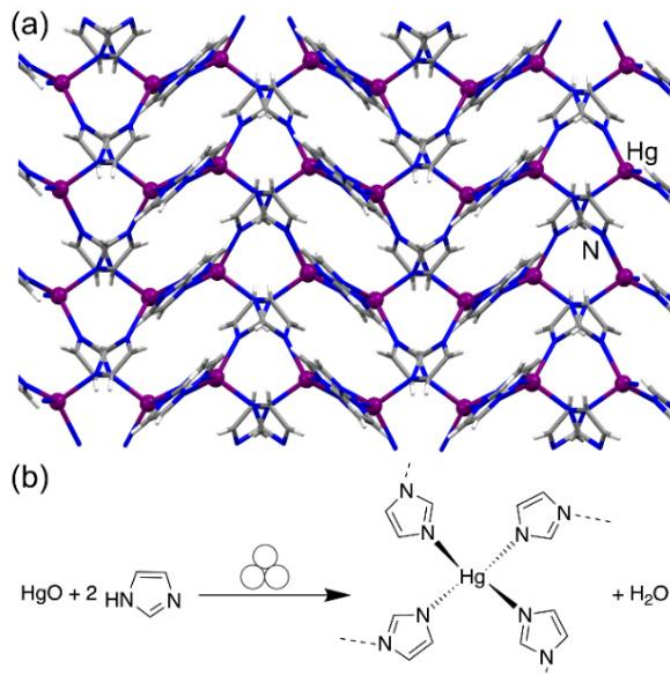

Fig. 1. (a) View of the crystal structure of *dia*-Hg(**Im**)$_2$ and (b) herein explored mechanochemical reaction. The symbol for mechanochemical reaction conditions has been adopted from ref. 28.

Intrigued by this potential difference in mechanochemical and solution-based routes to Hg(**Im**)$_2$, we re-investigated the mechanochemical reaction by ball milling HgO and HIm in a respective 1:2 stoichiometric ratio (**Fig. 1b**),[‡] a methodology previously shown highly successful in making zinc ZIFs.[24] Milling was performed in a 25 mL Teflon jar, using one ZrO$_2$ ball (3.25 grams weight, see ESI). Chemical reaction upon milling was evident by change in color of the reaction mixture from orange (due to HgO) to colorless. After 30 min milling, PXRD analysis revealed complete absence of Bragg reflections of reactants, indicating complete conversion (**Fig. 2a**). Unexpectedly, the product exhibited X-ray reflections that did not match either the *dia*-Hg(**Im**)$_2$ structure or the product of Fernández-Bertrán *et al*.
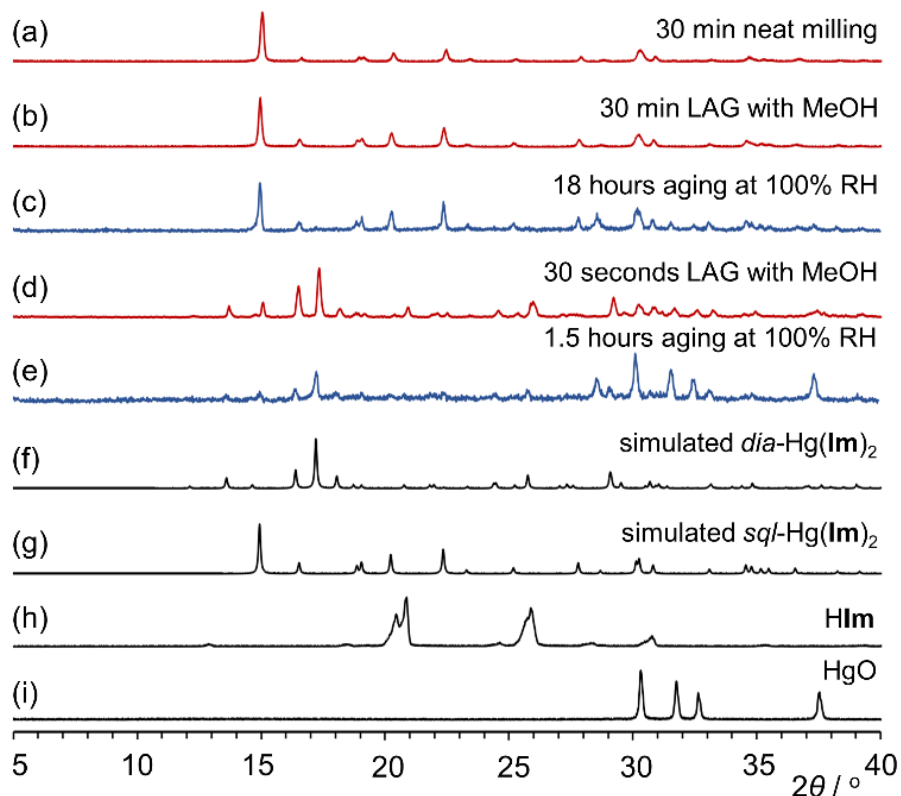
Fig. 2. Comparison of selected PXRD patterns for the reactions of HgO and H**Im**: (a) after 30 min neat milling; (b) after 30 min LAG with MeOH; (c) after 18 h aging at 100% RH; (d) after 30 seconds LAG with MeOH; (e) after 1.5 h aging at 100% RH; (f) simulated for *dia*-Hg(**Im**)$_2$ (CSD BAYPUN); (g) simulated for *sql*-Hg(**Im**)$_2$ and measured for: (h) H**Im**; (i) HgO.

The reaction was repeated by liquid-assisted grinding (LAG),[30] a method in which the reaction progress is accelerated and directed by small amounts of a liquid. The outcome of the mechanochemical reaction did not change upon LAG with different liquids, including methanol (MeOH, **Fig. 2b**), N,N-dimethylformamide (DMF), acetonitrile (MeCN) or water (see ESI). Thermogravimetric analysis (TGA) of the product revealed no weight loss until the decomposition temperature of ca. 200 °C, indicating that the material does not contain guest solvent.

Attempts to prepare the known *dia*-Hg(**Im**)$_2$ by following the reported solution synthesis were unsuccessful, yielding a microcrystalline powder with a PXRD pattern identical to that of the mechanochemically made material. The PXRD pattern of mechanochemically prepared material was readily indexed to an orthorhombic unit cell in space group $P2_12_12$, with a=9.4089(4) Å, b=7.6414(3) Å, c=5.3625(2) Å, and V=385.55(3) Å^3. Structure solution and Rietveld refinement revealed a polymorph of *dia*-Hg(**Im**)$_2$, based on two-dimensional (2D) sheets of composition Hg(**Im**)$_2$, with a square-grid (*sql*) topology (**Fig. 3a,b**). In contrast to reported *dia*-Hg(**Im**)$_2$, where Hg^{2+} adopts a roughly tetrahedral coordination with N-Hg-N angles from 98.3°-117.7° and Hg-N bonds from 2.18 Å-2.32 Å, the geometry of Hg^{2+} in *sql*-Hg(**Im**)$_2$ is highly distorted, best described as "see-saw" (**Fig. 3c**).
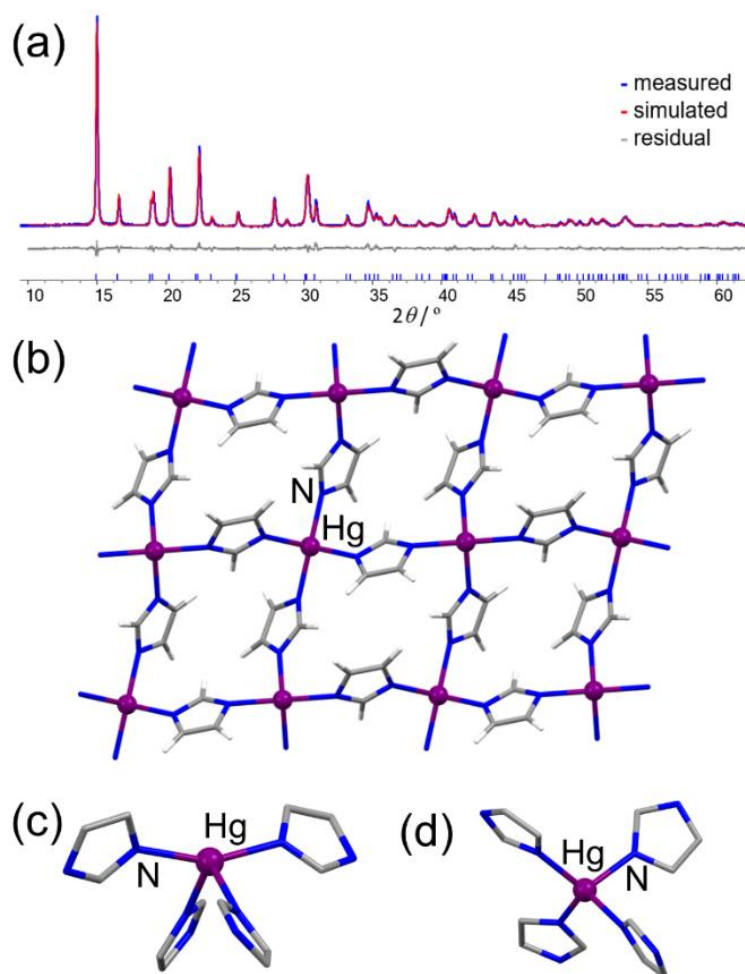
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Fig. 3. (a) Final Rietveld refinement fit for the structure of *sql*-Hg(**Im**)$_2$: experimental PXRD pattern is shown in blue, calculated pattern in red, and difference curve in grey. (b) view of a single layer of *sql*-Hg(**Im**)$_2$ along the crystallographic *c*-axis. Comparison of the coordination geometries of the metal node in: (c) *sql*-Hg(**Im**)$_2$ and (d) *dia*-Hg(**Im**)$_2$, with hydrogen atoms omitted for clarity.

The environment of each Hg^{2+} is defined by two shorter (2.18(2) Å) Hg-N bonds at an angle of 156.1(6)$^{\circ}$, and a pair of longer ones (2.31(2) Å), at an angle of 104.6(7)$^{\circ}$ (**Fig. 3d**). In contrast to other reported *sql*-topology ZIFs Ni(**Im**)$_2$ (CSD ALIDUU)[31] and zinc benzimidazolate (CSD KOLYAM),[32] where neighboring layers arrange in an offset way, the sheets in *sql*-Hg(**Im**)$_2$ stack directly on top of each other (see ESI). The coordination of Hg^{2+} in *sql*-Hg(**Im**)$_2$ is consistent with its ^{199}Hg solid-state nuclear magnetic resonance (ssNMR) spectroscopy, revealing a powder pattern[33] indicative of axial symmetry, very different from the one seen in *dia*-Cd(**Im**)$_2$ by ^{113}Cd ssNMR (see ESI).

We were surprised that all explored mechanochemical and solution-based experiments gave *sql*-Hg(**Im**)$_2$, without any evidence of *dia*-Hg(**Im**)$_2$ or the hexagonal phase reported by Fernández-Bertrán.[29] In contrast, the *dia*-Cd(**Im**)$_2$ phase reported by Masciocchi *et al.* was readily reproduced (see ESI). In an attempt to reproduce any of the reported Hg(**Im**)$_2$ phases, we explored a milder synthetic route, by aging[34] a 1:2 stoichiometric mixture of HgO and H**Im** at 100% relative humidity (RH). Real-time PXRD monitoring[35] (**Fig. 4a**) revealed X-ray reflections of *dia*-Hg(**Im**)$_2$

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(**Fig. 2e,c**) and Rietveld analysis of the *in situ* data revealed that content of *dia*-Hg(**Im**)$_2$ increases for ca. 90 minutes, after which it diminishes along with the appearance of *sql*-Hg(**Im**)$_2$ (**Fig. 4b**). After 140 min, the PXRD pattern exhibits only *sql*-Hg(**Im**)$_2$.
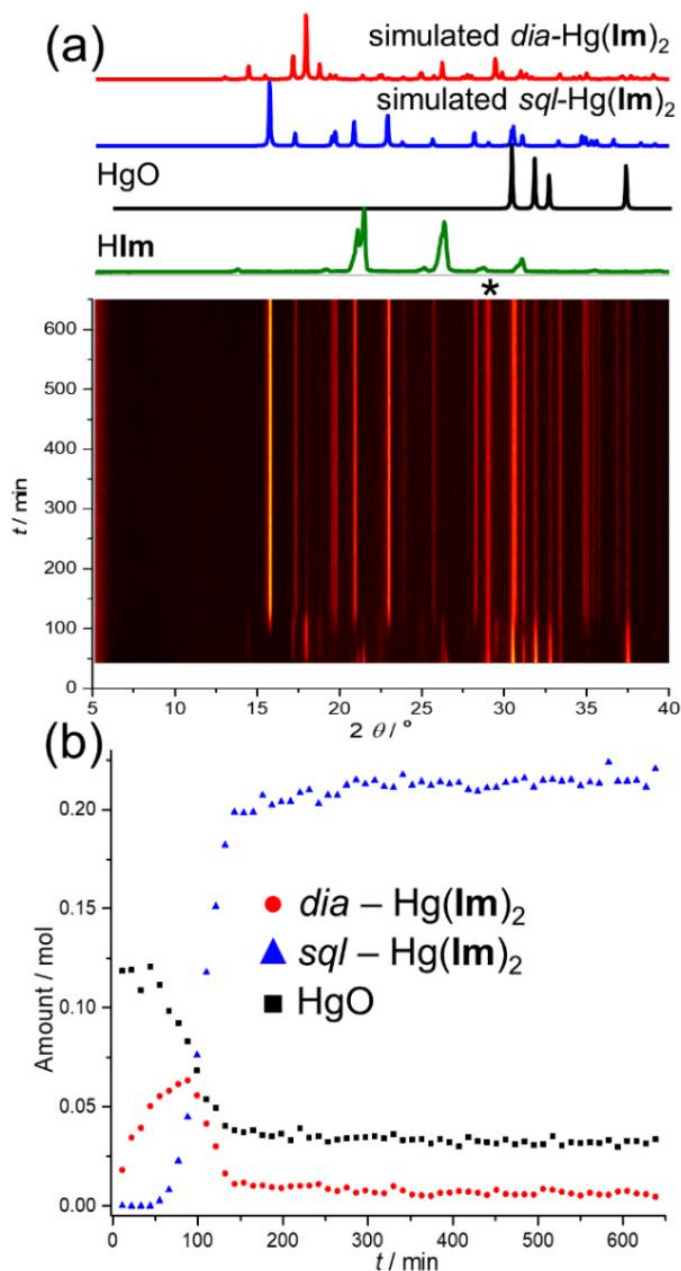

Fig. 4. Real-time monitoring of the aging reaction of HgO and H**Im** by PXRD: (a) time-resolved diffractogram, with diffraction patterns of selected phases shown on top, and Bragg reflection of CeO$_2$ standard labeled with '*'; (b) reaction profile based on Rietveld fitting, demonstrating changes in amount of HgO, *dia*- and *sql*-Hg(**Im**)$_2$. Quantitative kinetics analysis was hindered by preferred orientation in the static reaction mixture.

Initial, short-lived appearance of *dia*-Hg(**Im**)$_2$ in aging led us to explore the milling reaction of HgO and H**Im** at short reaction times. Indeed, PXRD analysis after 30 seconds LAG with MeOH

revealed the appearance of *dia*-Hg(**Im**)$_2$ along with unreacted HgO and H**Im** (**Fig. 2d**). After 1 minute, the reaction mixture exhibits only reflections of *sql*-Hg(**Im**)$_2$.

Calculated densities of *dia*- and *sql*-Hg(**Im**)$_2$ are remarkably similar, preventing the deduction of relative stabilities. However, the *dia*-Hg(**Im**)$_2$→*sql*-Hg(**Im**)$_2$ transformation in aging and milling indicates that *sql*-form should be the thermodynamically more stable phase.[24] This was validated by periodic density functional theory (DFT) calculations, performed in periodic DFT code CRYSTAL17[36] using the hybrid B3LYP[37] functional combined with the Grimme D3 semiempirical dispersion correction,[38] which showed that the *sql*-form is 10.21 kJ mol^{-1} lower in energy than the *dia*-one. This contrasts Zn(**Im**)$_2$[39] and Cd(**Im**)$_2$, whose most stable forms exhibit three-dimensional (3D) *zni*- and *dia*-topologies, respectively.

Intrigued by the unexpected difference between our study and previous reports on Hg(**Im**)$_2$, we performed similar calculations for the reported *dia*-Cd(**Im**)$_2$ and the hypothetical *sql*-Cd(**Im**)$_2$ structure obtained by DFT optimization of a model obtained by replacing all Hg atoms in *sql*-Hg(**Im**)$_2$ with Cd. In this case, the two structures were found to have very similar energies, *sql*-Cd(**Im**)$_2$ being just 0.39 kJ mol^{-1} more stable. The improved stability of the *dia*-structure in Cd(**Im**)$_2$ is consistent with numerous experimental observations of *dia*-Cd(**Im**)$_2$.

Stabilization of the 2D *sql*-structure in Hg(**Im**)$_2$ compared to a more extensively connected and interpenetrated 3D *dia*-framework is unexpected and, we believe, associated to weak intermolecular interactions between layers. This is consistent with calculations of relative stabilities of *dia*- and *sql*-Hg(**Im**)$_2$ using the B3LYP functional uncorrected for dispersion. Under such conditions, stabilities of the two structures are inverted, with the *dia*-form becoming 7.81 kJ mol^{-1} more stable. Whereas the *sql*-Hg(**Im**)$_2$ structure reveals short contacts between neighboring layers, readily interpreted as C-H···π and π···π interactions, it also exhibits a short H···Hg contact of 3.26(3) Å, not present in the *dia*-form. Most proposed van der Waals radii for Hg range from 2.00 to 2.53 Å,[40] indicating that this contact might be up to 9% shorter than the sum of van der Waals radii of hydrogen (1.25 Å) and mercury. The unique appearance and energetic stability of *sql*-Hg(**Im**)$_2$, as opposed to its hypothetical *sql*-Cd(**Im**)$_2$ analogue, led us to perform Bader's quantum theory of atoms in molecules (QTAIM)[41] analysis on the DFT-optimized structures, searching for bond critical points (BCPs) as evidence for structure-stabilizing interactions. The *sql*-Hg(**Im**)$_2$ and Cd(**Im**)$_2$ structures display a very similar distribution of non-covalent BCPs (see ESI), with the exception of one BCP in the vicinity of the Hg atom. This critical point, unique to *sql*-Hg(**Im**)$_2$, reveals a moderate bonding interaction (0.074 *electrons Å^{-3}*) between the metal atom and the C-H bond of an imidazolate linker from an adjacent metal-organic layer. This BCP is coincident with the experimentally noted short H···Hg contact, suggesting its importance for the overall stabilization of *sql*-Hg(**Im**)$_2$. While this H···Hg contact cannot be interpreted as a conventional bond, it is clearly stabilizing, tentatively corresponding to a weak agostic bond.[42]

In summary, a re-investigation of an early report of mechanochemical MOF formation has revealed a novel, layered polymorph of a so far unique mercury(II) imidazolate framework. Experiment and theory indicate that the layered polymorph is thermodynamically more stable than the previously reported interpenetrated *dia*-framework, evidently due to weak intermolecular forces that include previously unreported intermolecular agostic-like C-H···Hg contacts. Such stabilization of a layered structure makes a striking contrast between Hg^{2+} and its congeners Cd^{2+} and Zn^{2+}, whose imidazolates in their most stable form favor 3D frameworks, highlighting the potential for differences in MOF formation when using a heavy element compared to its lighter congeners.

Conflicts of interest
There are no conflicts of interest to declare.

Acknowledgements

Notes
‡Mercury compounds are highly toxic, and all operations must be conducted with great care and precaution.

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