Solvent diffusion through a non-porous crystal ‘caught in the act’ and related single-crystal-to-single-crystal transformations in a cationic dinuclear Ag(I) complex with 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and BF4- as counterion

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<th>Journal:</th>
<th>CrystEngComm</th>
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<td>Manuscript ID:</td>
<td>CE-ART-07-2015-001348.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>06-Sep-2015</td>
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</tbody>
</table>
| Complete List of Authors:         | Alen, Jo; KU Leuven, Chemistry  
                                      Van Meervelt, Luc; KU Leuven, Chemistry  
                                      Dehaen, Wim; KU Leuven, Chemistry  
                                      Dobrzanska, Liliana; KU Leuven, Chemistry |
Solvent diffusion through a non-porous crystal ‘caught in the act’ and related single-crystal-to-single-crystal transformations in a cationic dinuclear Ag(I) complex with 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and BF₄⁻ as counterion

Jo Alen, Luc Van Meervelt, Wim Dehaen and Liliana Dobrzańska

The effect of a range of solvents on non-porous single-crystals of a cyclic, dinuclear silver(I) complex with 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bitmb) of the formula [Ag₂(bitmb)₃][BF₄] (1) was investigated by single-crystal X-ray diffraction studies. It allowed us to get a few snapshots of the process of solvent diffusion through the crystal, connected with a series of reversible transformations. We have isolated disolvated 2a and monosolvated 2b forms with acetonitrile, monosolvated forms 3b and 4b with acetone and ethanol respectively, as well as a monosolvated form 4c with ethanol which is an intermediate between 1 and 4b. Longer exposure of the crystals to solvent vapours leads to the formation of a polymeric 1D Ag(I) complex of general formula [Ag₄(bitmb)(BF₄)]ₙ (5).

Introduction

Single-crystal-to-single-crystal transformations (SC-SC) allow us to follow in situ structural changes triggered by different types of stimuli such as temperature, pressure, solvents, or even metal ions, which can also be replaced/captured in SC-SC fashion in the case of coordination compounds. These types of studies expand our knowledge concerning structure-properties relationships, which in turn leads to proper, rational design of materials of desired properties. The literature concerning the occurrence of SC-SC has been growing in the past couple of years, partly as the result of hardware progress. However, the majority of the reports are devoted to the alterations taking place in polymeric coordination compounds, especially metal-organic frameworks. Molecular organic crystals or discrete metal-organic complexes do not gain so much attention, being perceived as more difficult to survive the transformations, which is connected with the presence of weaker interactions between the molecules. However, this could also be turned into an advantage, as it could lead to higher molecular flexibility. Investigating the response of crystals of discrete molecules to different types of external stimuli, we have revealed for example a series of guest-induced interconversions, taking place in a crystal of a neutral, dinuclear Cu(II) complex, that involve positional and conformational changes. Recently, we also revealed conformational switching (1,3-alternate ↔ 1,2-alternate), induced by solvent, taking place in a single-crystal of homodithiacalix[4]arene. Continuing our work on SC-SC, we would like to present here solvent-induced transformations taking place in a single-crystal of [Ag₂(bitmb)₃][BF₄]. The study allows us to gain some valuable insight into the transport of solvent molecules through this seemingly non-porous crystal.

By exposing the single-crystal of the title Ag(I) complex to a range of solvents, we have isolated 3 distinct forms in SC-SC fashion. These structures illustrate well how complicated and unexpected the process of solvent uptake can be.
Experimental

Reagents and materials

The ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bitmb), was synthesised by the Sn2 substitution reaction of imidazole with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene, as reported previously.1b\textsuperscript{13} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz) δ 7.31 (s, 2H), 7.04 (s, 1H), 7.03 (t, 2H, J = 1 Hz), 6.74 (s, 2H, J = 1 Hz), 5.15 (s, 4H), 2.33 (s, 6H), 2.20 (s, 3H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 150 MHz) δ 138.6, 137.8, 136.5, 131.4, 130.0, 129.5, 118.4, 45.2, 19.9, 15.3. Anal. calcd for C\textsubscript{19}H\textsubscript{18}N\textsubscript{2}O: C, 68.43; H, 7.43; N, 18.78%.

Synthesis of [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} (1)

A solution of 0.1 mmol AgBF\textsubscript{4} in acetonitrile (10 mL) was added to a solution of 0.1 mmol bitmb in acetonitrile (25 mL). The mixture was stirred for a few minutes and left in a dark environment for slow evaporation. After three weeks, colourless crystals suitable for single-crystal X-ray diffraction studies were obtained.

Preparation of the crystals

The single-crystal-to-single-crystal transformations were achieved by immersing a single-crystal of 1 into a solvent or by leaving the single-crystal of 1 in the vapour of a particular solvent overnight or for a longer period (specified further on in the paper). Immersion of the crystal in the solution causes more rapid transformations, leading to worse quality crystals. Immersion of a crystal of 1 in acetonitrile for longer than 2 minutes causes fragmentation of the crystal. Starting from 1, we have isolated 5 new solvates, namely: [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}-2CH\textsubscript{3}CN (2a), [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}-CH\textsubscript{3}CN (2b), [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}-(CH\textsubscript{3})\textsubscript{2}CO (2c), [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}OH (2d), [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}OH (2e). It is worth mentioning that the crystals of 1 are not affected by water from the environment, as was checked after exposure to the atmosphere for 6 months.

Structure determination

The single-crystal X-ray diffraction data were collected on an Oxford Diffraction SuperNova diffractometer with Eos CCD detector, MoK\textsubscript{\alpha} radiation, \( \lambda = 0.71073 \) Å. Data frames were processed (unit cell determination, intensity data integration, correction for Lorentz and polarization effects, and empirical absorption correction) using the corresponding diffractometer’s software package.14\textsuperscript{a} Each structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods based on \( F^2 \) using SHELXL-97.\textsuperscript{14b} The programs MERCURY\textsuperscript{14c} and POV-Ray\textsuperscript{14d} were used to prepare the molecular graphics images. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions with displacement factors fixed at 1.2 times \( U_{eq} \) of the parent C atoms and 1.5 times \( U_{eq} \) for methyl groups with C-H = 0.95 (aromatic), 0.98 (methyl) and 0.99 Å (methylene). In 1 and 2a, geometrical and anisotropic displacement parameter restraints were applied to the counterions. The ethanol molecules in 2b and 2c were found to be disordered and modelled into two orientations. The H atoms (O-H) in 2b and 2c were located in a difference map and refined with restrained O-H bond lengths. The crystals’ quality of 2c and 5 resulted in poor datasets. Therefore, we did not deposit those structures with CCDC. However, as the results were significant for the paper, we discussed them in the main text. Applying the SQUEEZE instruction of PLATON confirmed the presence of the number of solvent molecules given.\textsuperscript{14e} Because the process is taking place so quickly, thermal analyses could not be performed.

A summary of the data collection and structure refinement parameters is provided in Table 1.

Results and discussion

In one of our previous reports concerning metal complexes with bitmb\textsuperscript{13}, we presented the effect of counterions on the formation of silver(I) complexes with metal to ligand ratio 1 to 1.\textsuperscript{1b} Therein we have also demonstrated that seemingly non-porous discrete metalallocyclic complexes [Ag\textsubscript{2}(bitmb)\textsubscript{2}](SbF\textsubscript{6})\textsubscript{2} and [Ag\textsubscript{2}(bitmb)\textsubscript{2}](PF\textsubscript{6})\textsubscript{2} are able to undergo reversible single-crystal-to-single-crystal transformations upon uptake/release of acetonitrile molecules. In the present study, we have investigated the effect of a range of solvents, namely acetonitrile, acetone and ethanol on single-crystals of a related, new dinuclear [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} complex (1).

Crystal structure of [Ag\textsubscript{2}(bitmb)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} (1)

The crystal structure of complex 1 is reminiscent of the structures of analogous bitmb\textsubscript{2} complexes with counterions PF\textsubscript{6}\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} (previously reported by our group) as well as SbF\textsubscript{6}\textsuperscript{−}, for which we were able to collect the full data set in meantime (see SI for the preparation, the crystallographic data and the refinement parameters). The dinuclear Ag(I) compound 1 crystallises in the triclinic centrosymmetric space group P1 with half a cationic Ag(I) complex, consisting of a silver ion located on a general position and one bitmb ligand, and two crystallographically independent counterions with half occupancy each (as they were found disordered around an inversion centre) in the asymmetric unit (Fig. 1).

It is worth noting the absence of disorder in the case of the larger counterions SbF\textsubscript{6}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−} with octahedral geometry, and its occurrence in the case of a smaller, trigonal NO\textsubscript{3}\textsuperscript{−} counterion (to follow the effect of the counterion on the size/shape of the metalallocycle, see Table S1).

The silver ions in the metalallocycle are coordinated in a linear fashion (N-Ag-N = 174.1 (1°)) to N atoms of imidazole rings originating from two distinct, bridging bitmb ligands in syn conformation. The distance between two silver ions forming a box is 7.170 Å. The mesitylene rings are oriented almost orthogonally to the plane of the metalallocycle, defined by N17-N3-N17’-N3’, with an angle of 84.77°. As a result of the
symmetry of the cationic metal complex, the mesitylene rings present in the cyclic unit are pointing opposite directions. The imidazole rings are directing to the middle of the metallocycle with angles between the planes of imidazole rings on the same ligand of 40.26°. One of the disordered counterions is trapped in the centre of the metallocycle.

In the packing arrangement, we can distinguish layers of stacked metallocyclic units in the \( ab \) plane, which are separated by counterions (Fig. 2). Simplified, they can be considered as tilted columns of metallocycles stacked along the \( b \) axis, held together by C-H\( \cdots \)F interactions (whereby F is originating from the counterion encapsulated in the ring) with distances between the silver ions of adjacent complexes of 9.441 Å, that are extended into rows along the \( a \) direction by C-H\( \cdots \)π interactions (C13-H13B\( \cdots \)(N1-C5); C\( \cdots \)centroid distance of 3.622(6) Å and C-H-centroid angle of 143°) with an adjacent Ag\( \cdots \)Ag distance of 8.974 Å.

**Fig. 1** Atomic displacement plot showing 1 (50% probability). Unlabelled atoms are related to the labelled atoms by the symmetry operations -\( x, 1-y, 1-z \) for the metallocycle and encapsulated \( \text{BF}_4^- \); and -\( x, 2-y, 2-z \) for the other counterion; the same labelling applies to 2a.

As mentioned, the counterions occupying the interstitial spaces are also disordered and interact weakly by C-H\( \cdots \)F interactions with the layers of metal complexes surrounding them. The distances between Ag\( \cdots \)Ag ions of cyclic units from adjacent layers guarded by \( \text{BF}_4^- \) ions are 5.453 Å.

**Fig. 2** Packing arrangement of 1 projected down the \( b \) axis, with parallel layers of metallocycles in the \( ab \) plane coloured red and disordered counterions in black and blue.

**Crystal structure of \([\text{Ag}_2(\text{bitmb})_2](\text{BF}_4)_2\cdot2\text{CH}_3\text{CN} \) (2a)**

Immersion of a crystal of 1 in acetonitrile for 2 minutes or leaving it in acetonitrile vapour for a week allowed us to isolate the disolvated form 2a, similar to the disolvates of the complexes with counterions \( \text{SbF}_6^- \) and \( \text{PF}_6^- \). However, the difference in geometry and the size of the counterion in 2a once again accounts for disorder, which also influences the stability of the solvate formed. If not held under a steady stream of liquid nitrogen, 2a transforms back to 1 within a couple of minutes. This was not the case for the compounds with \( \text{SbF}_6^- \) and \( \text{PF}_6^- \) counterions, whereby the disolvated forms were stable for weeks. After solvent uptake, the centrosymmetric triclinic crystal structure is maintained and its main features at first glance have not changed much (Fig. 3). The dinuclear Ag(I) complex 2a shows a similar conformation as in 1 (see Figure 4) with an Ag\( \cdots \)Ag distance of 7.167 Å and an angle N-Ag-N of 175.2(2)°. As previously, the inversion centre is located in the middle of the cyclic unit. There are two distinct counterions present, one of which is trapped in the metallocycle as before, and the other one is located in the space formed between the layers of metallocycles. However, this space has expanded to accommodate the acetonitrile molecules. The appearance of solvent influences simultaneously the unit cell parameters, mostly the \( c \) axis, causing its elongation of ca. 1.6 Å in comparison with 1 (see Table 1).

A closer look at the packing arrangement indicates that the solvent uptake is accompanied by the reorientation of the layers leading to an alignment of silver ions from adjacent layers (Fig. 3). The distance between silver ions from metallocycles separated by solvent molecules is 6.257 Å, meaning an increase of 0.8 Å compared with the corresponding distance in 1. The silver ions from adjacent molecules stacked along the \( b \) axis are slightly further apart (Ag\( \cdots \)Ag is 9.667 Å), but closer for those stacked along the \( a \) axis (Ag\( \cdots \)Ag is 8.730 Å). However, in general, the interactions between the molecules are not much affected.

**Fig. 3** Packing arrangement of 2a projected down the \( b \) axis, with layers of metallocycles in the \( ab \) plane coloured red, disordered counterions in black and blue, and acetonitrile molecules in yellow.
The solvent molecules are occupying separate voids, which can only be mapped as continuous channels with a spherical probe radius below 1.1 Å (solvant accessible surface). The acetonitrile molecules are located in close proximity of the Ag ions (N···Ag is 3.000(6) Å) and also further interact with the cationic metal complexes via C-H···N interactions involving C5 and C20 of the imidazole rings originating from cyclic units from adjacent layers and N from the solvent molecule. There are also some short C-H···F type contacts with the counterions occupying the interstitial spaces.

Fig. 4 Overlay of the metallocycles 1 (grey) and 2a (red), with the silver ions represented as balls; r.m.s. deviation is 0.1198 Å.

Crystal structure of [Ag2(bitmb)2](BF4)2·CH3CN (2b)

As mentioned before, the solvent molecules are not strongly retained in the crystal of 2a, which readily returns to the solvent-free form 1 if exposed to air for a couple of minutes. However, by leaving the crystal 2a for 1 min in air, we were able to isolate a partially solvent loaded form 2b. The same form, showing the presence of only one molecule of acetonitrile per metallocycle, could be obtained by immersing a crystal of 1 in acetonitrile for 30 seconds or leaving it overnight in acetonitrile vapour. 2b also belongs to the centrosymmetric triclinic space group P1 and shows the presence of one metallocyclic cationic complex, two counterions and one acetonitrile molecule in the asymmetric unit. The cationic Ag(I) complex itself is not centrosymmetric anymore, meaning that its conformation has changed, causing deformation of the metallocycle compared with 1 and 2a. This is evident from the orientation of the imidazole rings, especially those containing N19 and N22 (see Fig. 5). The geometry around the silver ions slightly deviates from linearity with N1-Ag1-N40 and N19-Ag2-N22 angles of 172.1(2)° and 174.0(2)° respectively. The angles between the planes of opposite imidazole rings are 17.50° and 42.22° for the pairs N1/N19 and N22/N40 respectively and the angle between the planes of the mesitylene rings and the plane of the metallocycle, defined as before, are 89.7 and 81.3°. The Ag···Ag distance in the box is 7.045 Å, which is slightly shorter than that in 1 and 2a.

One of the counterions again is trapped in the middle of the metallocycle and the other one is located between the layers of metallocycles in close proximity to Ag2 (F51···Ag2 is 3.187(3) Å). None of the counterions is disordered this time. The acetonitrile molecules are located between the layers of metallocycles in the space guarded by the silver ions (with an Ag···Ag separation of 6.752 Å; i.e. an increase of ca. 0.5 Å compared with 2a), the imidazole rings from metallocycles originating from adjacent columns of distinct layers and BF4− counterions. Each acetonitrile molecule stays in close proximity to Ag1 with an N-Ag distance of 3.193(8) Å. Comparison of the packing diagrams of 2b and 2a indicates that the solvent molecules in 2b are located in every second space between the columns of metallocycles (Fig. 6). As a result of molecular rearrangements, the Ag···Ag distance between solvent-free spaces is 4.072 Å, which is much shorter (ca. 1.4 Å) than the corresponding distance in 1. Furthermore, the pore formed in 2b is bigger than in 2a and it can be mapped as a continuous channel with a spherical probe radius below 1.22 Å (solvant accessible surface).
Crystal structures of \([\text{Ag}_n(\text{bitmb})_2][\text{BF}_4]_2\)·acetone (3b)

The immersion of 1 in acetone for 2 minutes or exposure of 1 to acetone vapour overnight resulted in the transformation of 1 to 3b, which matches well with the crystal structure 2b (the unit cell parameters are almost the same, see Table 1). The transformation is reversible, returning to 1 in just a couple of minutes. We were not able to isolate a disolvated structure corresponding to 2a. Most likely the bulky shape and size of the acetone molecules (having a molecular volume of 64 Å³ compared with 49 Å³ for acetonitrile) prohibits further rearrangements needed for the formation of the pores to accommodate the second solvent molecule (Fig. 7). The silver ions’ distance between the columns of adjacent layers increases with ca. 0.2 Å in comparison with 2b (value of 6.917 Å). The conformations of 2b and 3b stay more or less the same (r.m.s. deviation of 0.1237 Å). The oxygen atom from the acetone molecule is located at a distance of 3.211(6) Å from Ag1. Acetone interacts more intensely with the counterions located between the layers than acetonitrile in 2b, involving both methyl groups in C-H⋯F interactions. There are also other contacts formed with the metallocycles that involve the methyl groups and the O atom from the solvent molecule.

Crystal structures of \([\text{Ag}_n(\text{bitmb})_2][\text{BF}_4]_2\)·EtOH (4b)

Immersion of 1 in ethanol for 1 minute or its exposure to ethanol vapour for two nights resulted in the transformation of 1 to 4b. The transformation is reversible and, in a couple of minutes, the crystal is going back to 1. The crystal structure of 4b is isostructural with 2b and 3b. Once again we did not succeed in isolating a disolvated form, which we assume is due to the angular shape of the solvent, which is only slightly bigger than acetonitrile (molecular volume of 54 Å³) (Fig. 7).

The conformation of the metallocycle doesn’t really change (overlay with 2b – r.m.s. deviation is 0.0780 Å). The distance between the silver atoms from metallocycles located in adjacent layers is 6.629 Å, which is even slightly shorter (ca. 0.1 Å) than in 2b. The solvent molecules are disordered over two positions with the O atom staying in the vicinity of Ag1 (3.354(6) Å). They are less involved in intermolecular interactions than acetone, forming O-H⋯F hydrogen bonds with the adjacent counterion and a weak C-H⋯N hydrogen bonding with the closest metallocycle (whereby C-H is originating from a methylene group of the solvent).

Crystal structures of \([\text{Ag}_2(\text{bitmb})_2][\text{BF}_4]_2\)·EtOH (4c)

Checking the reversibility of the transformation from 4b to 1, we have identified one more form, namely 4c, which we believe is an intermediate between the former two. The crystal quality was very poor, but we succeeded to solve the crystal structure and get a satisfying model. The single-crystal went through much bigger changes than those observed for the previous forms. The symmetry of the crystal, has altered from the triclinic \(P\) to the monoclinic \(C2/c\) space group. In the asymmetric unit, there are two halves of crystallographically distinct metallocycles with the bitmb ligand and a silver ion located on general positions, two counterions encapsulated in these two cyclic units with half occupancy each (as the corresponding B atoms are located on special positions, such as an inversion centre in the Ag1 containing metallocycle, and a two-fold axis for the one with Ag2), one counterion occupying the interstitial space between the metallocycles located on a general position, and a disordered molecule of ethanol modelled into two orientations. The metallocyclic units (Ag1) correspond quite well with those present in 1 (r.m.s. deviation of 0.1437 Å, see Fig. S1). More special is the other metallocycle (Ag2), the conformation of which to our surprise differs not only by changes in the position of the imidazole rings, but also by the orientation of the mesitylene rings which are pointing in the same direction (Fig. 8).
Further comparison of these two metallocycles indicates other smaller changes such as the Ag–Ag distance or the angle between the planes of opposing imidazole rings in the cyclic unit which are 7.056 Å/50.77° for Ag1 and 7.245 Å/34.20° for Ag2. The coordination geometry of the silver ions does not differ much between these two units, with N-Ag-N' angles of 172.1(4)° and 174.8(4)° for Ag1 and Ag2, respectively.

An overlay of both metallocycles present in 4c (see Fig. 9), could indicate that the deformation of the metallocycle observed in the b forms is an effect remaining from the rotation/swinging of the mesitylene rings during the preceding step.

The ethanol molecules are occupying more or less the positions which were initially taken by one of the disordered counterions in 1 (see Fig. 10). The remaining counterion is well ordered. The Ag–Ag distances originating from the cyclic units from the adjacent layers in which molecules do no longer stack so orderly as in 1 or 2a are 5.341 Å, which is only ca. 0.1 Å shorter than in 1.

It looks like the solvent molecules are taking advantage of the free space available in the crystal caused by the disordered counterions and are pushing their way between the layers. This obviously does not take place without molecular response of the metal complexes, namely rearrangements/conformational changes leading to further uptake without damaging the single-crystals. However, we are fully aware that what we present are merely a couple of snapshots from a very complicated continuous process.

Conclusions

The presented results show that in some cases solvent diffusion through a non-porous crystal can be more complicated than could initially be expected. Having revealed only two structures of the presented system, namely the solvent-free (1) and disolvated (2a) form, one could easily draw the wrong conclusion that the process is rather simple. As the molecular structures of the Ag(I) complex in these two forms stay more or less the same, we could assume that the process is based on minor rearrangements involving the layers consisting of metallocycles in the crystal lattice. However, deeper insight into the process reveals that switching from form 1 to 2a and back actually involves a few intermediate steps including the formation of monosolvated forms. The transformations taking place engage not only a rearrangement of the molecules, but also conformational changes of the metal complexes, such as a swinging of the mesitylene rings or flapping of the imidazole rings, to facilitate the diffusion.
process. All this happens in a very short time, in a concerted fashion, in a single-crystal and it could be very easily overlooked for this system, as the solvent molecules are just traversing by the crystal and do not form stable solvates. Moreover, the size/shape of the solvent molecules is crucial in the loading process. Further studies, aimed at better understanding of guest diffusion are being undertaken, including the use of larger solvent molecules, with different H bonding capacities.

Acknowledgements

We thank the Hercules Foundation for supporting the purchase of a diffractometer through project AKUL/09/0035.

References


Table 1 Crystal data and details of the refinement parameters for the crystal structures.

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<td>1.674</td>
<td>1.671</td>
</tr>
<tr>
<td>μ MoKα mm⁻¹</td>
<td>1.101</td>
<td>1.008</td>
<td>1.066</td>
<td>1.063</td>
<td>1.071</td>
<td>1.069</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>9149</td>
<td>15189</td>
<td>17972</td>
<td>23022</td>
<td>25028</td>
<td>22696</td>
</tr>
<tr>
<td>No. unique reflections (Rint)</td>
<td>4118 (0.0245)</td>
<td>5062 (0.0442)</td>
<td>9706 (0.0462)</td>
<td>9473 (0.0343)</td>
<td>9305 (0.0347)</td>
<td>10160 (0.1185)</td>
</tr>
<tr>
<td>No. reflections with I &gt; 2σ(I)</td>
<td>3632</td>
<td>4095</td>
<td>6367</td>
<td>7202</td>
<td>7264</td>
<td>5273</td>
</tr>
<tr>
<td>No. refined parameters</td>
<td>292</td>
<td>320</td>
<td>521</td>
<td>531</td>
<td>544</td>
<td>574</td>
</tr>
<tr>
<td>R₁, wR² values /</td>
<td>0.0500, 0.1235</td>
<td>0.0575, 0.1416</td>
<td>0.0575, 0.1281</td>
<td>0.0504, 0.1197</td>
<td>0.0662, 0.1768</td>
<td>0.1182, 0.2662</td>
</tr>
<tr>
<td>R₁, wR² (all data)</td>
<td>0.0587, 0.1294</td>
<td>0.0767, 0.1574</td>
<td>0.1015, 0.1592</td>
<td>0.0745, 0.1386</td>
<td>0.0882, 0.1919</td>
<td>0.2012, 0.3345</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.092</td>
<td>1.082</td>
<td>1.020</td>
<td>1.069</td>
<td>1.092</td>
<td>1.040</td>
</tr>
</tbody>
</table>

\[ a\ R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}. \]
\[ b\ wR_2 = \left(\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}\right)^{1/2}. \]
Graphical abstract

A few snapshots from a dynamic solvent diffusion process, through a seemingly non-porous crystal of a dinuclear, cyclic Ag(I) complex, were revealed. These indicate the complexity of the process, which involves not only relocation of the molecules in the crystal lattice, but also conformational adjustments of the metallocycles in response to solvent uptake/release. The transformations are reversible and do not cause the deterioration of the single-crystals, pointing out cooperativity of the molecules enclosed in the crystal unity.
\([\text{Ag}_2\text{L}_2](\text{BF}_4)_2\) + solvent $\leftrightarrow$ \cdot acetone + solvent + 2 acetonitrile - solvent - 2 acetone - ethanol - 2 ethanol